Kohn-Sham orbital functional theory methods for the description of ground and excited states of molecules

Habilitationsschrift

zur Erlangung der Lehrbefähigung
für das Fach Theoretische Chemie

Der
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vorgelegt von
Dr. Andreas Heßelmann

Erlangen, im September 2011
“In a lecture of this length it has been impossible to give a balanced account of so large a subject and I must ask you, Mr. President, to forgive me for having said virtually nothing about experimental problems and achievements in this lively field. But it is clear to all of us that new methods of investigation, such as the measurement of scattering cross-sections and crystal lattice frequencies, will soon provide ample information on which to test our theories. It is also to be hoped that the theory of intermolecular forces will soon be powerful enough not only to explain the crystal structures of simple substances but also to predict the stable conformations of the molecules which we ourselves are made of. “

H. C. Longuett-Higgins (Spiers memorial lecture, 1965)
Preface

The works compiled in this thesis have basically been done at three locations: the University of Essen, the University of Århus (Denmark) and the University of Erlangen. It goes without saying that none or only a fraction of the research done could have been realised without the support and hospitality that I experienced at those locations. In the first place I would like to thank Prof. Andreas Görling (University of Erlangen), Prof. Georg Jansen (University of Essen), and Prof. Poul Jøgensen and Prof. Jeppe Olsen (University of Århus) for their support and invaluable advices. Secondly, I would like to thank all the co-workers who have not only contributed to the scientific publications, but who also in some places invited me to work with them at their university. These are: Martin Schütz ((at that time) University of Stuttgart), Fred Manby (University of Bristol), Trond Saue (University of Strasbourg), Tatiana Korona (University of Warsaw), Michal Pitonak (University of Praha), Christian Kollmar (University of Bonn), Martin Kaupp ((at that time) University of Würzburg), Paul Wormer and Ad van der Avoird (University of Nijmegen), Pawel Salek (University of Stockholm) and all other co-authors not mentioned.

Most (≥ 90%) of the new methods presented in this thesis were developed using the Molpro quantum chemistry program from Stuttgart/Cardiff [1]. Therefore I would like to thank Peter Knowles (University of Cardiff) for providing me an ongoing developers licence of Molpro and Andy May (University of Cardiff) for technical help regarding the Molpro program.
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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>adiabatic connection</td>
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<tr>
<td>ACPF</td>
<td>average coupled pair functional</td>
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<td>ALDA</td>
<td>adiabatic local density approximation</td>
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<td>AT</td>
<td>adenine-thymine base pair</td>
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<td>ATDEXX</td>
<td>adiabatic time-dependent exact exchange</td>
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<tr>
<td>aug-cc-pV(D,T,Q)Z</td>
<td>augmented correlation consistent double/triple/quadruple zeta basis set</td>
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<tr>
<td>B3LYP</td>
<td>Becke-Lee-Yang-Parr 3-parameter hybrid functional</td>
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<tr>
<td>BFGS</td>
<td>Broyden-Fletcher–Goldfarb–Shanno (optimisation)</td>
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<tr>
<td>BO</td>
<td>Brueckner orbital</td>
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<td>BOKS2</td>
<td>second-order Brueckner orbital Kohn-Sham method</td>
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<td>BOX</td>
<td>Brueckner orbital expectation value method</td>
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<td>BCCD</td>
<td>Brueckner coupled cluster doubles</td>
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<tr>
<td>BCCD(T)</td>
<td>Brueckner coupled cluster doubles with perturbative triples</td>
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<td>BR</td>
<td>Becke-Roussel exchange hole model</td>
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<td>BSSE</td>
<td>basis set superposition error</td>
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<td>CCSD</td>
<td>coupled cluster singles doubles</td>
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<tr>
<td>CCSD(T)</td>
<td>coupled cluster singles doubles with perturbative triples</td>
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<tr>
<td>CEDA</td>
<td>common energy denominator approximation</td>
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<td>CEPA</td>
<td>coupled electron pair approximation</td>
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<td>CI</td>
<td>configuration interaction</td>
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<td>CG</td>
<td>conjugate gradient (optimisation)</td>
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<td>CT</td>
<td>charge-transfer</td>
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<td>DF</td>
<td>density-fitting</td>
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<td>DFT</td>
<td>density functional theory</td>
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<td>DFT+D</td>
<td>density functional theory with dispersion correction</td>
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<td>DNA</td>
<td>deoxyribonucleic acid</td>
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<td>DOSD</td>
<td>dipole oscillator strength distribution</td>
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<td>dRPA</td>
<td>direct random phase approximation</td>
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<tr>
<td>EOM</td>
<td>equation-of-motion</td>
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<td>EXX</td>
<td>exact exchange (density functional theory)</td>
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GC  guanine-cytosine base pair
GGA  generalised gradient approximation
GL2  Görling-Levy second-order perturbation theory
HF  Hartree-Fock / hydrogen fluoride
HFCC  hyperfine coupling constant
HOMO  highest occupied molecular orbital
KS  Kohn-Sham
LDA  local density approximation
LHF  localised Hartree-Fock
LUMO  lowest unoccupied molecular orbital
MP2  second-order Møller-Plesset perturbation theory
MP2C  coupled second-order Møller-Plesset perturbation theory
MP3  third-order Møller-Plesset perturbation theory
OEP  optimised effective potential method
PBE  Perdew-Burke-Ernzerhof exchange-correlation functional
PP  pseudo-potential
RPA  random phase approximation
SAPT  symmetry-adapted intermolecular perturbation theory
SOSEX  second order screened exchange
TDDFT  time-dependent density functional theory
TDEXX  time-dependent exact exchange density functional theory
TLHF  transformation localised Hartree-Fock
UCHF  uncoupled Hartree-Fock
WC  Watson-Crick
WXhole  weighted exchange hole
XC  exchange-correlation
Xhole  exchange hole
xOEP  exchange-only optimised effective potential method
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Part I.

Kohn-Sham orbital functional theory methods
1. Kohn-Sham density functional theory methods

Shortly after the foundations of quantum theory were developed, Douglas Hartree introduced the first nonempirical method for treating many-electron systems [2]. This so-called Hartree self-consistent field method was based on approximating the (generally) complicated many-electron wave function by the product of one-electron wave functions (spin orbitals) that is varied in a self-consistent way so that the total energy of the system is minimised [3]. It was pointed out by Fock and Slater [4–7], however, that the Hartree wave-function ansatz violates the Pauli principle or antisymmetry condition that allows no more than one electron per spin-orbital. They therefore used antisymmetrised sums of products of spin-orbitals as wave function ansatz to fulfill this fundamental postulate of quantum mechanics. The resulting Hartree-Fock self-consistent field method [8] developed by Fock and Slater still builds the basis of quantum chemistry wave function methods to the present day. The type of electron-electron interactions described by the Hartree-Fock method are shown in figure 1.1.

The exchange interaction sketched in figure 1.1(2b) constitutes an important process that deletes the self-interaction error of the classical Coulomb interaction present in the Hartree method. In fact, the first order exchange interaction is a completely quantum mechanical effect and is sometimes also referred to as Pauli correlation. However, this correlation effect only correlates electrons with parallel spin, while electrons with opposite spin are uncorrelated in the Hartree-Fock method. Though the Hartree-Fock method usually yields about up to 99 per cent of the total energy of the electronic system, it turns out that the remaining fraction, termed as correlation energy (more precisely, Coulomb correlation in order to distinguish it from the Pauli correlation), is of crucial importance to achieve chemical accuracy, that is 1 kcal/mol for binding energies, 0.01 Å for bond distances, 10 cm$^{-1}$ for vibrational frequencies and 0.1 eV for excitation energies.

In wave function theories correlation effects are described by augmenting the single Slater determinant in Hartree-Fock theory. This is usually done by adding a sum of excited determinants to the ground-state reference determinant that improves the variational freedom of the total wave function. The most simple ab initio correlation method is second-order Möller-Plesset perturbation theory (MP2) [8] which uses the Hartree-Fock wave function as reference determinant and in addition accounts for the second order correlation effects sketched in figure 1.2.
Figure 1.1.: Possible first order interactions between two particles described by the Hartree-Fock method [9]:

1: an extra particle enters the system
2a: direct (Coulomb) interaction: the extra particle lifts a particle out of its place and creates a particle-hole pair that is immediately destroyed
2b: exchange interaction: as in 2a, but the extra particle exchanges with the particle from the system
3: extra particle moves out of the system

While MP2 is the most efficient ab initio correlation approach that scales as \(N^5\) with respect to the molecular size \(N\) (typically measured by the number of electrons), it has severe limitations in the description of static correlation effects, that is, if the electronic system is far from its ground state equilibrium [10]. This holds true also for higher order perturbation theory methods. Moreover, MP2 theory fails in situations where long-range correlation effects become important, e.g., in case of \(\pi - \pi\) interactions between aromatic rings [11].

The shortcomings of perturbation theory methods can be overcome by using, e.g., coupled-cluster [12], random-phase approximation (RPA) [9], (multi-reference) configuration interaction [8] or related coupled-pair functional methods [13]. However, in conventional implementations all these methods scale at least with the sixth power of \(N\) and therefore soon become impractical for larger chemical systems containing more than 100 electrons. The development of new computational algorithms like density-fitting [14–16] and Cholesky decomposition [17, 18], the transformation into local basis functions [19–21] or the exploitation of parallel computer architectures [22–25] has lead, however, to an increase of the feasibility of ab initio correlation methods and it can be expected that this development continues, supported by new ideas to make use of special computer hardware like graphic cards [26, 27].
1. Kohn-Sham density functional theory methods

Figure 1.2.: Possible second- and higher-order interactions between two particles described, e.g., by second order Möller-Plesset perturbation theory (MP2) [8] and the (direct) random-phase approximation (RPA) [9], respectively:
1: an extra particle enters the system
2: the extra particle interacts with a particle of the system, lifts it out of its place, thus creating a hole
3: the extra particle plus the ‘hole’ and the ‘lifted-out’ particle (particle-hole pair) travel through the system
3x: as an alternative to 3 the extra particle and the ‘lifted-out’ particle exchange places
4: the lifted-out particle creates another particle-hole pair and drops back in its hole
5: same as 3
6: the extra particle again interacts with the ‘lifted-out’ particle knocking it back into the hole, thus destroying the particle-hole pair
7: the extra particle leaves the many-body system

The movie 1-2-3-4-5 corresponds to a direct (Coulomb) correlation process while the movie 1-2-3x-4-5 corresponds to an ‘exchange’ correlation process in second order. MP2 theory accounts for the sum of the processes 1-2-3-4-5 and 1-2-3x-4-5 while RPA contains the sum of all repeated particle-hole interactions, i.e. $\sum_{n=0}^{\infty} 1-2-3-(4-5)_n$-6-7.
The underlying reason why wave function methods generally become expensive (and complicated to implement) with the increasing number of electrons \( N \) is that in these methods one has to approximate the (electronic) wave function which is a multidimensional function containing \( 4N \) variables (3N electron coordinates and their spin values). However, the electronic Hamiltonian operator is written in terms of integrals containing no more than six spatial coordinates. It can therefore be anticipated that the wave function contains more information than needed in order to compute the energy of the electronic system. In 1964, Hohenberg and Kohn have proved that the ground-state molecular energy, the wave function and all other molecular properties are uniquely determined by a (yet unknown) functional of the electronic density \( \rho(r) \), a quantity that depends solely on 3 coordinates \( r = (x, y, z)^T \) [28]. In combination with a second theorem by Hohenberg and Kohn, stating that the Hohenberg-Kohn functional is an upper bound to the exact energy for any \( N \)-representable test density [28], this new insight has lead to the development of density functional theory (DFT) methods [29] in which the explicit calculation of an electronic wave function is omitted and the energy is modelled as a functional of the electronic density \( \rho(r) \) only. It turned out, however, that the direct mathematical modelling of the energy functional \( E[\rho] \), as is done in the Thomas-Fermi model for atoms [29–31], is too inaccurate to describe molecular systems due to large errors in the approximations of the kinetic energy functional \( T[\rho] \).

In order to solve the kinetic energy problem of classical DFT, in 1965 Kohn and Sham developed a pseudoparticle model system of noninteracting electrons that move in a local external effective potential that is such that the energy and the ground-state properties of this system are identical to the true many-body interacting system [32]. This local Kohn-Sham potential is given by

\[
v_{KS}(r) = v_{\text{ext}}(r) + v_{\text{Coul}}(r) + v_{xc}(r)
\]

where \( v_{\text{ext}}(r) \) is the external potential, generally being the nuclear attraction potential, \( v_{\text{Coul}}(r) \) is the classical Coulomb potential and \( v_{xc}(r) \) is the exchange-correlation potential that is the functional derivative of the corresponding exchange-correlation functional \( v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \). The difference between the Kohn-Sham system and the true interacting system is sketched in figure 1.3.

The total energy of the system is determined by

\[
E[\rho] = \int v_{\text{ext}}(r)\rho(r)d\mathbf{r} + T_s[\rho] + J[\rho] + E_{xc}[\rho]
\]

where \( T_s[\rho] \) is the kinetic energy of the Kohn-Sham pseudoparticle system, \( J[\rho] \) is the Coulomb energy which is a known functional of the density and \( E_{xc}[\rho] \) is the exchange-correlation energy. The big advantage of the Kohn-Sham approach is now, that \( T[\rho] - T_s[\rho] \) is small, i.e., \( T_s[\rho] \) accounts for most of the kinetic energy contributions of the many-body system, the remaining fractions of the exact kinetic energy are contained in \( E_{xc}[\rho] \). The quantity \( T_s[\rho] \) is known exactly.
interacting system noninteracting KS pseudo−particles

Figure 1.3.: Interacting many-body system (left) and noninteracting Kohn-Sham pseudoparticle system moving in an external (fictious) local effective potential $v_{KS}$ (right).

since the electrons of the Kohn-Sham system do not interact with each other and is given by

$$T_s[\rho] = -\frac{1}{2} \sum_i \nabla^2 \phi_i(r)$$  \hspace{1cm} (1.3)

with $\phi_i(r)$ being the eigenfunctions (so-called Kohn-Sham orbitals) of the following Kohn-Sham eigensystem equations

$$\left( -\frac{1}{2} \nabla^2 + v_{KS}(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r)$$  \hspace{1cm} (1.4)

As can be seen, the kinetic energy $T_s[\rho]$ of the Kohn-Sham system is not explicitly given in terms of the density $\rho$, but it is an implicit density functional because the (exact) density is given in terms of the Kohn-Sham orbitals:

$$\rho(r) = \sum_i \phi_i^2(r)$$  \hspace{1cm} (1.5)

The only remaining unknown quantity in Eq. (1.2) is the exchange-correlation functional $E_{xc}[\rho]$ that comprises, apart from fractions of the kinetic energy of the true electronic system, all nonclassical electron-electron interaction contributions, see, e.g., figures 1.1 and 1.2.

In standard approaches (LDA: local density approximation [29, 33], (hyper/meta)-GGA: generalised gradient approximation) [34–36] of Kohn-Sham DFT the exchange-correlation functional is usually written in the following form

$$E_{xc}^{LDA,GGA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc} \left[ \rho(\mathbf{r}), \nabla^n \rho(\mathbf{r}), \ldots, \phi_i(\mathbf{r}), \tau(\mathbf{r}) \right]$$  \hspace{1cm} (1.6)

where $\epsilon_{xc}$ is the exchange-correlation energy density that itself is approximated as a function of the density (LDA), density derivatives (GGA if first derivatives are used, meta-GGA otherwise), occupied Kohn-Sham orbitals $\phi_i$ (hyper-GGA $\rightarrow$ if exact exchange is used also refered to as
1. Kohn-Sham density functional theory methods

hybrid-GGA), or the kinetic energy density \( \tau = 1/2 \sum_i |\nabla \phi_i|^2 \) that itself is written in terms of derivatives of Kohn-Sham orbitals (meta-GGA). Exchange-correlation functionals that are written in terms of density derivatives or occupied Kohn-Sham orbitals are also termed as semi-local functionals.

To the present day almost all DFT methods that are in use to describe molecules and solids are based on the LDA and GGA of Eq. (1.6) and this is mainly due to the following reasons:

- LDA/GGA methods are very efficient, their scaling behaviour with respect to the molecular size is \( N^3 - N^4 \) in conventional implementations and the computational cost can even further be reduced in various ways such that almost linear scaling is achieved [37, 38].

- LDA/GGA methods are more accurate than Hartree-Fock for many molecular properties and sometimes even surpass the accuracy of ab-initio perturbation theory correlation methods [39].

- LDA/GGA methods can easily be extended for describing time-dependent and magnetic properties while this often gets difficult with ab-initio correlation methods where the underlying equations to solve not only become very complicated but also computationally very demanding. Time-dependent density functional theory (TDDFT) methods based on the LDA/GGA are usually based on the adiabatic local approximation (ALDA,AGGA) in which the exchange-correlation kernel is approximated as

\[
\begin{align*}
  f_{xc}^{KS}(r, r', \omega) & = \frac{\delta E_{xc}^{KS}(\rho)}{\delta \rho(r')} = \frac{\delta F_{xc}^{KS}[\rho]}{\delta \rho(r') \delta \rho(r')} \approx f_{xc}^{ALDA,AGGA}(r) \tag{1.7}
\end{align*}
\]

i.e., the nonlocality and frequency dependence of the exact exchange-correlation kernel is omitted [41].

- LDA/GGA methods are easy to implement and are available in almost any quantum chemistry program.

There exist, however, a number of shortcomings of DFT methods based on the LDA or GGA that mostly originate from the local form of the functional of Eq. (1.6), more precisely these shortcomings arise due to the fact that the exchange-correlation kernel in Eq. (1.6) solely depends on the density and related quantities at a local point in space while it is known that the exact exchange-correlation functional has to be nonlocal [33]. The main shortcomings of standard DFT methods stemming from this simplification of the exchange-correlation functional can be summarised by the following points:
1. Kohn-Sham density functional theory methods

(i) The hydrogen atom, the most simple chemical system, is not described exactly since the Coulomb self-interaction of the single electron is not corrected [39].

(ii) The long-range behaviour of the exchange-correlation potential is wrong, leading to the incorrect description of a number of molecular properties, e.g.:

→ dipole polarisabilities are often overestimated [42, 43]
→ higher-lying excited states and Rydberg excitations are not well described [43–45]
→ the description of anions is problematic [46, 47]

(iii) Band gaps in extended systems are much smaller than experimental band gaps [48, 49].

(iv) Van-der-Waals or weak nonbonded interactions can not properly be described due to missing long-range correlation effects [50, 51].

(v) Static correlation (in spite of the localised exchange-correlation hole, see above) is poorly described, i.e., still common DFT methods can not correctly describe bond dissociation [52, 53].

(vi) Systems with multi-reference character are problematic [39, 54–57].

(vii) Time-dependent extensions to the LDA/GGA use adiabatic and local exchange-correlation kernels that in a time-dependent DFT framework are unable to describe long-range (charge-transfer) excitations [58–60]. Moreover, the hyperpolarisabilities of long conjugated molecular chains are strongly overestimated by TDDFT methods with adiabatic and local kernels [61, 62].

This habilitation thesis compiles published works (part III) that try to analyse and give solutions to many of the above mentioned shortcomings of standard DFT. These mainly can be categorised as orbital functional methods that combine wave function theory methods with standard DFT approaches. The following sections briefly describe these methods that were developed and a few results will be presented that will demonstrate their feasibility. For a more complete description the original publications given in part III may be refered to.
2. Exact-exchange density functional methods

Publications: 11.1, 11.2, 11.3, 11.4, 11.5 and 14.2

2.1. Numerically stable optimised effective potential method for molecules

A serious shortcoming of common DFT methods based on the LDA/GGA is the presence of Coulomb self-interaction which stems from the incomplete cancellation of Coulomb energy contributions with approximate exchange energy terms. While this, e.g., leads to an incorrect description already for the simplest chemical system, the hydrogen atom \[39\], the self-interaction error also strongly influences the Kohn-Sham orbitals and eigenvalues in general. As these are, e.g., the input data for time-dependent DFT calculations, this also means that excited states described by LDA/GGA methods can have large errors due to a wrong underlying single-particle spectrum of the Kohn-Sham system \[43\].

A natural solution to this problem exists if one extends standard DFT methods such that the functional may also depend on the occupied Kohn-Sham orbitals. In Hartree-Fock (HF) theory the exchange energy term (see figure 1.1) exactly cancels the Coulomb self-interaction (for the occupied states) and thus is adopted in exact exchange DFT methods \[63\]. The exact exchange energy functional in terms of Kohn-Sham orbitals \(\phi_i\) is given by

\[
E_{x}^{KS}[\rho] = -\frac{1}{2} \sum_{ij}^{occ} \int d\mathbf{r} d\mathbf{r}' \phi_i(\mathbf{r})\phi_j(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}')\phi_j(\mathbf{r}')
\]

The resulting total energy expression is then minimised under the constraint that the orbitals \(\phi_i\) are the solutions of a non-interacting electronic system in a local effective potential. While now the derivation of the exact exchange energy functional is straightforward, there exists the problem to derive the functional derivative, i.e. \(\delta E_{x}^{KS}[\rho]/\delta \rho\) required for solving the Kohn-Sham equations (1.4). The method for obtaining the functional derivative for orbital dependent functionals is the optimised effective potential (OEP) method that was developed even before the Kohn-Sham approach was invented, see a brief history of the OEP method in figure 2.1.

While the OEP method is a general method to implement orbital-dependent functionals,
2. Exact-exchange density functional methods

- J. C. Slater (1951): derivation of a local potential which averages the Hartree-Fock potential and suggestion of deriving a local potential which minimises the total energy [64]
- J. D. Talman and W. F. Shadwick (1976): first exact exchange OEP method for atoms developed as an approximation to HF [66]
- J. B. Krieger, Yan Li and G. J. Iafrate (1992): first accurate approximation to xOEP which is also applicable to molecules [67]
- A. Görling et al. (1994, 1999): outline and implementation of basis set xOEP methods for solids and molecules [68, 69]

Figure 2.1.: History of the optimised effective potential method.

mostly exchange-only OEP methods (xOEP) are termed as OEP method. There exist several equivalent approaches to derive the OEP:

- Direct energy minimisation of the functional

\[ \frac{\delta \langle \Phi_{KS}^{\text{KS}} | \hat{H} | \Phi_{KS}^{\text{KS}} \rangle}{\delta v_{KS}} = 0 \]

with \( \Phi_{KS} \) the Kohn-Sham determinant, \( \hat{H} \) the Hamilton operator and \( v_{KS} \) the local Kohn-Sham potential.

- Taking the functional derivative via the chain rule

\[ v_{x}(\mathbf{r}) = \frac{\delta E_{x}}{\delta \rho(\mathbf{r})} = \int d\mathbf{r}' d\mathbf{r}'' \sum_{\text{occ}} \delta E_{x} \frac{\delta \phi_{i}(\mathbf{r}'')}{\delta \rho_{i}(\mathbf{r}'')} \frac{\delta v_{KS}(\mathbf{r}'')}{\delta \rho(\mathbf{r})} \]

- Perturbation theory along the adiabatic connection [68].

It can be shown that all approaches lead to the following (closed-shell) exchange-only OEP equation [63]

\[ \int d\mathbf{r}' \chi_{KS}(\mathbf{r}, \mathbf{r}') v_{x}(\mathbf{r}') = 4 \sum_{\text{occ}} \sum_{\text{virt}} \phi_{i}(\mathbf{r}) \phi_{a}(\mathbf{r}) \frac{\langle \phi_{i} | \hat{v}_{NL}^{x} | \phi_{a} \rangle}{\varepsilon_{i} - \varepsilon_{a}} \tag{2.2} \]

where \( \hat{v}_{NL}^{x} \) is the nonlocal Hartree-Fock exchange potential, \( \phi_{i,a}/\varepsilon_{i,a} \) are occupied/virtual Kohn-Sham orbitals/eigenvalues and \( \chi_{KS} \) is the Kohn-Sham response function. While Eq. (2.2) can accurately be solved for atoms [67] and two-atomic molecules [70], the general solution to Eq. (2.2) for molecules and solids requires the expansion of both, the local potential \( \hat{v}_{x} \) and the response function in an auxiliary basis set. Details about this method can be found in Refs. [69, 71, 72].

Unfortunately, it turns out that OEP methods can be plagued with severe numerical problems in finite-basis set implementations. These are:
(1) The auxiliary basis set is (nearly) linearly dependent.

(2) The orbital basis set is not sufficiently converged for a given auxiliary basis set. Then matrix elements of $\mathbf{X}_{KS}$ and the right-hand side of Eq. (2.2) are corrupted and the response function will have eigenvalues with erroneously small eigenvalues.

(3) For extended auxiliary basis sets $\mathbf{X}_{KS}$ will have many eigenvalues with small magnitude which can be physically correct.

(4) The linear equation solver to solve the OEP equation $\mathbf{X}_{KS} \mathbf{c} = \mathbf{t}$ (matrix form of Eq. (2.2)) introduces numerical instabilities.

The numerical problems arising with finite basis set OEP methods are demonstrated for plane-wave basis set and gaussian basis set calculations in figures 2.2 and 2.4. In both cases it can be observed that the larger the auxiliary basis set gets relative to the size of the orbital basis, the more the exchange potential starts to oscillate and gets unphysical. This also is indicated by the energy differences shown in the right panels in figures 2.2 and 2.4 which tend to small values for larger auxiliary basis sets or smaller orbital basis sets. This can not occur in infinite basis set calculations as the constraint of a local potential in the OEP will always mean that the OEP energy will be an upper bound to the Hartree-Fock energy.

In case of plane-wave basis set calculations an easy solution to this problem exists by choosing a certain ratio between cutoff values for the orbital and auxiliary basis set. Praxis has shown that this ratio should have values between 1.5 and 2.0, such that approximately the number of plane waves of the orbital basis is twice as large as for the auxiliary basis set. A corresponding similar scheme can also be adopted for gaussian basis set calculations by decreasing the progression ratio of successive exponents in uncontracted orbital basis set as shown in figure 2.4. This, however, soon becomes impractical for large molecules as this would lead to large even tempered orbital basis sets.

Therefore a new approach has been developed \cite{11,3} to obtain balanced orbital and auxiliary basis sets to enable numerically stable OEP calculations. The following recipe shows how this new approach performs for the beryllium atom and an uncontracted cc-pVQZ basis set as a test case:

(1) Choose a (standard) orbital basis set for a given test molecule and decontract it $(N_{\text{orb}} = 12, N_{\text{orb}}$: number of orbital basis functions).

(2) Use the same set of basis functions also for the auxiliary basis set resulting in: (left: exchange-potential (black curve shows exact OEP potential), right: energy difference to Hartree-Fock)
$(N_{\text{aux}} = 12, N_{\text{aux}}$: number of auxiliary basis functions)
Figure 2.2.: Demonstration of instability of the xOPEP method in plane-wave calculation of silicon. The left diagrams show the exchange potentials for increasing (top→bottom) cutoff values for the auxiliary basis set and the right diagrams show the corresponding energy differences between xOEP and HF. The cutoff value for the orbital basis was fixed to a value of 7.5 a.u.
Figure 2.3.: Solution to numerical instability of the xOPEP method in plane-wave implementations for silicon as an example. The left diagrams show the exchange potentials for increasing (top→bottom) cutoff values for the orbital basis set and the right diagrams show the corresponding energy differences between xOEP and HF. The cutoff value for the auxiliary basis was fixed to a value of 7.5 a.u.
Figure 2.4.: Demonstration of instability of the xOPEP method in gaussian basis set calculations of the beryllium atom. The left diagrams show the exchange potentials for a decreasing progression (top→bottom) ratio for the exponents of the orbital basis set while the auxiliary basis set was fixed to an uncontracted aug-cc-pVQZ basis. The right diagram shows the energy difference between xOEP and HF. The dashed horizontal line marks the energy difference between numerical (i.e., practically exact) xOEP and HF for comparison.
(3) Augment the orbital basis set by adding functions whose exponents are the geometric means of the exponents of the initial basis. Add also one more tight and diffuse function. (diagram shows several options that result in similar energy changes) 
\(N_{\text{orb}} = 12 + 13\text{aug}, \ N_{\text{aux}} = 12\)

(4) Remove tight and diffuse functions from the auxiliary basis set. 
\(N_{\text{orb}} = 12 + 13\text{aug}, \ N_{\text{aux}} = 12 - 4\text{tight}\)

(5) Add one (or more) functions to the auxiliary basis set to improve the quality of the xOEP potential. 
\(N_{\text{orb}} = 12 + 13\text{aug}, \ N_{\text{aux}} = 12 - 4\text{tight} + 2\text{aug}\)
(6) Stepwise remove all orbital basis functions added in (3) that nearly leave the OEP-HF energy difference unchanged.

\( N_{\text{orb}} = 12 + 2\text{aug}, \; N_{\text{aux}} = 12 - 4\text{tight} + 2\text{aug} \)

As can be seen in the diagrams for step (6) above, the balancing scheme leads to an exchange potential that is very close to the exact exchange potential for beryllium. The repetition of the above given recipe for a larger orbital basis set with 18 s-type gaussian basis functions practically reproduces the exact exchange potential as is shown in figure 2.5.

The OEP method presented in 11.3 enables exact-exchange DFT calculations that are numerically stable and therefore lead to physically meaningful Kohn-Sham orbitals and eigenvalues. It has been made use of as the basis of exchange-only time-dependent density functional theory calculations [12.4, 12.5, 12.6] and also as the starting point for deriving general orbital-dependent exchange-correlation functionals [13.3, 13.5, 13.7].

In 14.2 open-shell OEP methods were tested to predict the hyperfine coupling constants (HFCC) of phosphorus and nitrogen. It turns out that with ab-inito correlation methods the HFCC very crucially depends on both, the basis set size and the level of correlation. Moreover, both, standard DFT methods and approximate exact-exchange approaches like localised Hartree-Fock (LHF) (see section 2.2), even do not correctly predict the correct sign of the hyperfine coupling constant of phosphorus. It has been found that DFT calculations employing the full exact-exchange OEP functional with an accompanying standard GGA correlation functional leads to remarkable improvements over standard DFT methods especially for the
2. Exact-exchange density functional methods

Figure 2.5.: Finite basis set exchange-only calculation OEP calculation for beryllium: the left diagram shows the exchange OEP potential (red) in comparison to the exact exchange potential (black) and the right diagrams shows the energy difference to Hartree-Fock (the dashed horizontal line marking the energy difference between Hartree-Fock and exact OEP). The cc-pVQZ orbital basis set augmented with six additional s-type basis functions was used. The numbers shown in the right diagram are the condition numbers of the overlap matrix of the occupied-virtual orbital product basis with the auxiliary basis functions.

phosphorus atom, see [14.2]. However, still the HFCC was underestimated with this approach that indicates missing dynamical correlations contributions that are apparently important to obtain this property in close agreement with the experiment.

The prerequisite for using the OEP method of [11.3] is that one uses uncontracted orbital basis sets, see [11.2] and [11.4] for an analysis of the dependence of the quality of an OEP calculation on the orbital basis set. While this constitutes no problem for small molecules with up to 50 electrons, in case of larger systems such OEP calculations become prohibitively expensive. Moreover, the large uncontracted basis functions soon lead to small eigenvalues in the overlap matrix of the basis functions that can lead to convergence problems in the self-consistent Kohn-Sham calculation. Practical alternatives to full exchange OEP methods solving these problems are described in the next section.

### 2.2. Efficient approximate exact-exchange methods

There exist alternative methods to full OEP calculations for molecules to realise exact-exchange DFT calculations and that do not suffer from numerical instabilities [73–75]. These all employ the exact exchange functional of Eq. (2.1) but take the functional derivative only approximately. In the Local Hartree-Fock [73] or the equivalent Common Energy Denominator Approximation method [74] one replaces the orbital energy-differences in the OEP Eq. (2.2) by a constant value that eliminates the unoccupied orbitals in the equations. This leads to a decomposition of the
exchange potential into two contributions, the Slater potential and the response potential:

\[ v_x(r) = v_x^{\text{Slater}}(r) + v_x^{\text{resp}}(r) \]  

(2.3)

with

\[ v_x^{\text{Slater}}(r) = -2 \sum_{ij} \frac{\phi_i(r) \phi_j(r)}{\rho(r)} \int dr' \frac{\hat{\phi}_i(r) \phi_j(r)}{|r - r'|} \]  

(2.4)

\[ v_x^{\text{resp}}(r) = 2 \sum_{ij} \frac{\phi_i(r) \phi_j(r)}{\rho(r)} \langle \phi_i | \hat{v}_x - \hat{v}_x^{\text{NL}} | \phi_j \rangle \]  

(2.5)

As can be seen, the response potential depends on the total local exchange potential so that an iterative solution to Eqns. (2.4) and (2.5) has to be employed. The LHF method allows to calculate the (approximate) exchange potential directly on a numerical quadrature grid and can easily implemented in existing DFT programs. It turns out, however, that the calculation of the Slater potential of Eq. (2.4), which can nominally be computed with \( N_{\text{grid}} \times N_{\text{occ}}^2 \) floating point operations (with \( N_{\text{grid}} \): number of grid points and \( N_{\text{occ}} \): number of occupied orbitals) is very expensive in praxis. This is so, because the computation of the electrostatic potentials \( \int dr' \phi_i(r) \phi_j(r)/|r - r'| \) requires first the calculation of the corresponding electrostatic potentials in the atomic orbital basis \( \varphi_\mu \), i.e., \( \int dr' \varphi_\mu(r) \varphi_\nu(r)/|r - r'| \) which requires \( N_{\text{grid}} \times N_{\text{bas}}^2 \) operations, where \( N_{\text{bas}} \) is the number of atomic orbital basis functions which usually is much larger than \( N_{\text{occ}} \). Moreover, the computation of electrostatic potentials on the quadrature grid has a large prefactor and thus standard LHF calculations are much more expensive than standard DFT calculations.

In Ref. [73] the computational efficiency of the LHF method was improved by employing the resolution of the identity in the orbital basis set to approximate the Slater potential. This, however, as in basis set OEP calculations, requires large basis sets since otherwise the Slater potential becomes inaccurate especially in the asymptotic range. In [11.1] an efficient LHF method is presented which is based on employing density-fitting to compute the electrostatic potentials \( \int dr' \phi_i(r) \phi_j(r)/|r - r'| \) and which can be used in conjunction with small contracted basis sets so that it enables the calculation of the (approximate) exact exchange potential for large molecules. Figure 2.4 shows the total timings for the calculation of the Slater potential with this new approach compared to the conventional implementation for four molecules. It can be observed that the computational efficiency is greatly enhanced with the use of density-fitting. Moreover, the Poisson fitting furthermore speeds up the calculations since it only requires the calculation of the auxiliary basis functions instead of corresponding electrostatic potential integrals on the quadrature grid, see [11.1] for details.

Since the Slater potential of Eq. (2.4) is expressible as the electrostatic potential of the exchange hole density

\[ \rho_x(r, r') = 2 \sum_{i,j} \frac{\phi_i(r) \phi_j(r) \phi_i(r') \phi_j(r')}{\rho(r)} \]  

(2.6)
Figure 2.6.: Total timings for the calculation of the Slater potential (Eq. (2.4)) using the standard approach and density fitting employing Coulomb-fitting and Poisson-fitting. A 2.0 GHz AMD Opteron processor was used in the calculations.

Figure 2.7.: Energy differences of approximate exact-exchange methods to Hartree-Fock theory for a range of molecules. See [11.1] for details.
one can derive approximate expressions for the Slater potential from approximations to the exchange hole. One such model is the Becke-Roussel (BR) model [76] that was derived from the well-known form of the exchange hole of a hydrogenic atom. In 11.1 the BR model has been used to calculate the Slater potential and it has been studied how well this model performs in comparison to the standard LHF method for molecular energies and properties. Figure 2.7 shows the energy differences of this approach (termed as LHF(BR)) to Hartree-Fock energies compared to LHF and transformation LHF (TLHF), the latter being a one-step transformation method of the nonlocal Hartree-Fock exchange to the localised Hartree-Fock potential and subsequently solving the Kohn-Sham equations self-consistently with the exchange potential kept fixed. It can be observed that the LHF energies always underestimate the HF energies on magnitude as it should be due to the additional constraint of a local potential enforced in the LHF method. In contrast to this the more approximate TLHF and LHF(BR) methods in most cases overestimate the HF energies, but the deviations to Hartree-Fock are rather small. Moreover, the LHF(BR) energies are of similar accuracy as the TLHF energies which demonstrates the usefulness of the BR approximation to the Slater potential. As the BR Slater potential is a function solely of the density, its gradient and the kinetic energy density, it can much more easily computed than the exact Slater potential and thus a LHF(BR) calculation again speeds up the LHF method so that it enables the description of large molecules with exact-exchange DFT methods. A variant of the LHF(BR) method was used, e.g., in 12.6 in a hybrid exact-exchange/GGA method to calculate molecular excitation energies.

2.3. Efficient exact exchange Kohn-Sham method for solids

For the treatment of extended and infinite systems it is advantageous to use plane-waves with pseudopotentials instead of local basis functions to describe the Kohn-Sham orbitals and potential [77]. In conventional DFT calculations this leads to highly efficient implementations as all occurring integrals required can be computed on the fly with the aid of the fast Fourier transformation. Exact-exchange DFT (EXX, identical to xOEP) calculations for solids have certain advantages over Hartree-Fock calculations, even without accounting for electron correlation. These are:

- exchange-only OEP potentials are discontinuous functions with respect to the electron number as the exact xc potential; they therefore yield improved bandgaps in bulk semiconductors compared to the LDA/GGA approaches [48]
- compared to the treatment of exact exchange with a nonlocal exchange operator (i.e. Hartree-Fock theory) the locality of the exchange potential significantly simplifies bandstructure calculations, since it is independent of the Bloch wave vector
- EXX(GGA) models (i.e. EXX method including GGA correlations) accurately reproduce cohesive energies of semiconductors [48]
2. Exact-exchange density functional methods

However, standard plane-wave implementations of the EXX method are much more computationally expensive than using standard LDA/GGA methods. Here, the exact exchange potential is determined in reciprocal space and can be written as \([48, 78]\) (compare Eq. (2.2))

\[
v_x(G) = \sum_{G' \neq 0} [t(G') + t^*(-G')] \tilde{X}^{-1}_0(G, G')
\]  

(2.7)

with

\[
t(G) = \frac{2}{\Omega} \sum_{v \neq k} \langle v k | \hat{\phi}_x | c k \rangle \langle v k | e^{-iG r} | c k \rangle
\]  

(2.8)

where \(\hat{\phi}_x\) is the nonlocal exact exchange potential and \(v\) and \(c\) stand for valence- and conduction bands, respectively. \(\tilde{X}^{-1}_0\) is the inverse of the static response matrix excluding the \(G = 0\) component which only involves constant potential changes. It is given by:

\[
X_0(G, G') = \frac{4}{\Omega} \sum_{v \neq k} \langle v k | e^{-iG r} | c k \rangle \langle v k | e^{-iG' r} | c k \rangle
\]  

(2.9)

The rough scaling behaviour for the computation of \(t(G)\) is given by \(n_k^2 n_e^2 n_c n\), for \(X_0(G, G')\) by \(n_k^2 n_e n_c n^2\) and for \(\tilde{X}^{-1}_0(G, G')\) by \(n^3\) where \(n_k\): number of k-points, \(n_v\): number of valence bands, \(n_c\): number of conduction bands and \(n\): number of basis functions.

As described in section 2.1, one way to solve the OEP is to minimise the total energy with respect to potential changes. In the plane-wave formalism the EXX energy gradient is given by

\[
\frac{\delta E_{\text{tot}}[v_{\text{loc}}]}{\delta v_{\text{loc}}} = \sum_{ik} \int dr' \int dr'' \frac{\delta E_{\text{tot}}}{\delta \phi_{ik}(r')} \frac{\delta \phi_{ik}(r'')}{\delta v_{\text{loc}}(r'')} \frac{\phi_{ik}(r) \phi_{jk}(r) \langle j | k - v_{\text{KS}} + v_{\text{ext}} + v_{NL}^n | i \rangle}{\varepsilon_{ik} - \varepsilon_{jk}}
\]  

(2.10)

It turns out that this gradient can be calculated without requiring conduction bands and thus avoiding the full diagonalisation of the Kohn-Sham Hamiltonian matrix. For this one rewrites Eq. (2.10) in terms of the Kohn-Sham Green’s function \(G_i\) to obtain

\[
\frac{\delta E_{\text{tot}}[v_{\text{loc}}]}{\delta v_{\text{loc}}} = \sum_{ik} \frac{\phi_{ik}(r) \phi_{jk}(r') \langle j | k - v_{\text{KS}} + v_{\text{ext}} + v_{NL}^n | i \rangle}{\varepsilon_{ik} - \varepsilon_{jk}} + \sum_{ik} \phi_{ik}(r) \int dr' G_i(r, r') |v_{\text{diff}}| i \rangle
\]  

(2.11)

\[
= \sum_{ik} \phi_{ik}(r) \int dr' G_i(r, r') |v_{\text{diff}}| i \rangle
\]  

(2.12)

where \(v_{\text{diff}}\) is given by

\[
v_{\text{diff}} = -v_{\text{loc}}^{n-1} + v_j^n + v_{\text{PP}}^n + (v_{NL}^n)^n
\]  

(2.13)

\((n\) denoting the current iteration\) and \(G_i(r, r')\) is the Green’s function of the noninteracting Kohn-Sham system. Since

\[
G_i |x_i\rangle = \frac{1}{\varepsilon_i - H} |x_i\rangle = |i\rangle
\]  

(2.14)
one can obtain the following linear equation systems for solving for the $\psi_{ik}(r)$:

\[
(\varepsilon_{ik} - H_k)\psi_{ik} = v_{\text{diff}}\phi_{ik}
\]

\[
\Leftrightarrow (\varepsilon_{ik} - \left[ -\frac{1}{2} \nabla^2 + v_{\text{KS}} \right])\psi_{ik} = v_{\text{diff}}\phi_{ik}
\]

The solution of this equation system is computationally very cheap in the plane wave formalism since the matrix-vector product $H_k\psi_{ik}$ of the Hamiltonian $H_k$ and a test vector $\psi_{ik}$ can be decomposed into

- $-\frac{1}{2}\nabla^2\psi_{ik}$: the matrix elements of the kinetic energy operator in reciprocal space are simply:

\[
\langle G | -\frac{1}{2} \nabla^2 | G' \rangle = \frac{1}{2} |G|^2 \delta_{G,G'}
\]

$\rightarrow$ scaling: $\sim n$

- $v_{\text{loc}}\psi_{ik}$: in real space this is just a vector-vector product

$\rightarrow$ scaling: $\sim n_{\text{grid}}$ ($n_{\text{grid}}$: number of grid points)

- $v_{\text{PP}}^{nl}\psi_{ik}$: the matrix elements of the nonlocal pseudopotential operator can be written as

\[
\langle G | v_{\text{PP}}^{nl} | G' \rangle = \sum_{\text{atom},l} X_{\text{atom},l}(G) X^*_{\text{atom},l}(G')
\]

$\rightarrow$ scaling: $\sim n_{\text{atoms}} n_l n$ ($n_{\text{atoms}}$: number of atoms in unit cell, $n_l$: highest angular momentum for description of PP)

It can thus be seen that the overall cost for the calculation of the gradient with the above given scheme in a plane wave basis is given by

\[
\bar{n}_k^2 n_{\text{grid}}^2 + n_k n_v (n + n_{\text{grid}} + n_{\text{atoms}} n_l n)
\]

where the additional $n_k n_v$-loop in the first term stems from the calculation of the nonlocal exchange potential contribution to the right hand side.

It can now be seen that with increasing number of plane waves one has:

\[
n_{\text{grid}} \ll n_v n
\]

and

\[
n_v n_{\text{grid}} \ll n_v n^2
\]

and so the presented scheme for the calculation of the gradient is exceedingly cheaper than the standard EXX approach above. Moreover, as only the valence bands are needed, the memory requirements are much lower compared to the standard EXX method for solids in a plane-wave implementation.

The direct energy minimisation of the EXX energy gradient has been tested for silicon using a $2 \times 2 \times 2 \textbf{k}$-point mesh and energy and auxiliary basis set cutoffs of $E_{\text{cut}} = 12$ a.u. and $E_{\text{aux}}^{\text{cut}} = 6$ a.u., respectively. The cell parameters used were $a = b = c = 5.4309$ Å and $\alpha = \beta = \gamma = 90^\circ$. 
Figure 2.8.: Exact-exchange potential for silicon for different auxiliary basis set cutoff values.

Figure 2.9.: Convergence of the EXX energy (left) and gradient (right) with respect to the iteration cycle using a conjugate-gradient optimisation algorithm with exact line-searches in each iteration.

The exact exchange potential along the [111] direction of silicon for different auxiliary basis set cutoffs is shown in figure 2.8.

Several minimisation algorithms were tested and compared with each other. Figure 2.9 shows the convergence of the direct energy minimisation using a conjugate gradient (CG) approach and figure 2.10 shows the performance of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimisation method for different linesearch strategies.

As can be seen by comparing figures 2.9 and 2.10, the BFGS method more rapidly converges than the CG method if exact linesearches are used in each cycle, but in order to obtain a desired accuracy of the energy of $10^{-10}$ a.u. per unit cell both methods require about the same number of SCF cycles.

A disadvantage of the general unconstrained optimisation methods is that many function calls (to calculate the orbitals and energy) are needed for the linesearches. This can be avoided by ‘freezing’ the orbitals in each macro-cycle and setting

$$\frac{\delta E_{\text{tot}}[v_{\text{loc}}, \phi^N_k]}{\delta v_{\text{loc}}} = 0$$

(2.16)
2. Exact-exchange density functional methods

Figure 2.10.: Convergence of the EXX energy (left) and gradient (right) with respect to the iteration cycle using a reduced Hessian Broyden-Fletcher–Goldfarb–Shanno optimisation algorithm using exact and inexact (fulfilling weak and strong Wolfe-Powell conditions) linesearches in each iteration step. In contrast to the CG optimisation (figure 2.9) the higher $G$-components of the local potential were updated only in each macro-cycle of the SCF.

where $N$ denotes a macro-cycle in the SCF. This leads to the same linear equation system (in reciprocal space) as in the standard EXX method:

$$\bar{\chi}_0 v_x = t$$

which, however, can efficiently be solved for $v_x$ using the scheme above. It amounts to the minimisation of the function:

$$f(v_x) = \frac{1}{2} v_x^T \bar{\chi}_0 v_x - v_x^T t$$

which has the derivative

$$f'(v_x) = \bar{\chi}_0 v_x - t$$

i.e., effectively no linesearches are required anymore. A fast convergence of the local potential can then be achieved using, e.g., the direct inversion of the iterative subspace (DIIS) method. Relative CPU times of various contributions measured with respect to the total computation time for the solution of the EXX equations (given for two different energy/auxiliary cutoffs) are shown in figure 2.11.
2. Exact-exchange density functional methods

\[ E_{\text{cut}} = 12.0, \ E_{\text{cut}}^{\text{aux}} = 6.0 \ (150 \text{ plane waves}) \]

\[ E_{\text{cut}} = 120.0, \ E_{\text{cut}}^{\text{aux}} = 60.0 \ (4600 \text{ plane waves}) \]

Figure 2.11.: Relative CPU times of various contributions measured with respect to total computation time for the solution of the EXX equations for different cutoff values for the auxiliary and orbital basis set. (note that \( \chi_{x} \supset \chi_{x}(k) \supset \psi_{ik} \supset H\phi_{i} = H\phi_{i}(\text{kin}) + H\phi_{i}(v_{loc}) + H\phi_{i}(v_{nl}^{PP}) \))
3. Intermolecular interactions from density functional methods


Basically there exist two approaches to determine intermolecular interaction energies using quantum chemistry methods: the supermolecular approach and intermolecular perturbation theory [79]. In the supermolecular method the interaction energy between two noncovalently bonded systems $A$ and $B$ is simply calculated by

$$E_{\text{int}}(AB) = E(AB) - E(A) - E(B)$$  \hspace{1cm} (3.1)

where $E(AB)$ is the total energy of the supermolecule and $E(A)$ and $E(B)$ are the monomer energies. While this method is very simple and principally could be used in conjunction with any quantum chemistry method, in praxis special care has to be exercised. Firstly, the total energies usually are orders of magnitude larger than the resulting interaction energies and thus the energy calculations have to be well converged using tighter convergence thresholds than in conventional calculations. Secondly, the method used to determine the dimer and monomer energies should be size-consistent, otherwise large errors can be expected for the calculations of large systems. The standard approaches to calculate intermolecular interaction energies via Eq. (3.1) are therefore perturbation theory or coupled-cluster theory methods. A further problem of the ansatz of Eq. (3.1) is that in the dimer calculation basis functions located on one monomer to some extent also will be used to describe the electronic structure of the other monomer and vice versa. This so-called basis-set superposition error (BSSE) can only be reduced by using midbond functions or full dimer-centered basis sets also in the monomer calculations (Boys-Bernardi counterpoise correction [80]). A principle problem of Eq. (3.1) is, however, that it yields only one single number (the interaction energy) but no decomposition of it that would be useful to characterise the intermolecular interaction.

A completely different approach to calculate intermolecular interaction energies is intermolecular perturbation theory [79, 81]. In this method one usually starts from an unperturbed wave
function constructed from the product of the monomer wave functions and calculates the intermolecular interaction contributions to a given order in the intermolecular fluctuation potential directly. Certain symmetry-forcing procedures have to be applied, since the zeroth-order product wave function is not antisymmetric with respect to the exchange of electrons between the monomers. While a number of such symmetry-forcing procedures were developed \[82, 83\], the only practical approach that is accurate enough for large chemical systems is the symmetrised Rayleigh-Schödinger approach \[84, 85\] while more strong symmetry-forcing procedures become very complicated for systems with more than four electrons \[82\]. Thus, while all these methods can be termed as symmetry-adapted perturbation theories (SAPT), it has become common to use the acronym SAPT explicitly to refer to the symmetrised Rayleigh-Schödinger approach which enforces the correct symmetry only in the energy terms but not to given orders in the wave function expansion.

In SAPT the total interaction energy between two monomers $A$ and $B$ usually is calculated by the sum

$$E_{\text{int}}(AB) = E_{\text{elst}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(3)} + E_{\text{exch}}^{(1+2)} + \Delta^{(3-\infty)}$$

(3.2)

In Eq. (3.2) $E_{\text{elst}}^{(1)}$ is the electrostatic interaction energy, $E_{\text{ind}}^{(2)}$ is the induction energy (containing also charge-transfer terms), $E_{\text{disp}}^{(3)}$ is the dispersion energy, $E_{\text{exch}}^{(1+2)}$ comprises first- and second-order exchange energies that stem from tunnelings of electrons from one monomer to the other, and $\Delta^{(3-\infty)}$ denotes terms of third and higher orders in the intermolecular fluctuation potential. As the perturbation expansion is usually truncated at second order, the higher order terms that can become important in, e.g., hydrogen-bridged systems, usually are approximated on a supermolecular Hartree-Fock level that has been shown to work fairly well in a broad number of cases. The advantages of using Eq. (3.2) instead of Eq. (3.1) are:

- The interaction energy is directly calculated by a sum of physically meaningful terms that can be used to interpret the interaction on the basis of chemical intuition.
- By definition, SAPT is free from the BSSE and in fact each term in Eq. (3.2) could be calculated with an own basis set.
- It can be shown that each term in the SAPT expansion can be calculated solely in terms of monomer properties so that principally no full dimer calculation is required.
- Moreover, each term in Eq. (3.2) can be calculated with a different quantum-chemistry method (to account for the intramonomer correlation contributions).

Historically, the first SAPT implementations used a double perturbation theory ansatz (many-body SAPT approach) to account for the intramonomer correlation effects \[81\]. This means that the individual interaction contributions are calculated using Møller-Plesset perturbation theory, usually truncated at second order in the intramonomer fluctuation potentials. This approach, however, is extremely expensive for the second-order dispersion and exchange-dispersion
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contributions that then possess a computational scaling behaviour of $N^7$ with respect to the molecular size $N$ (note that in fact a perturbation expansion of the monomers to second order will yield interaction energy terms that are contained in fourth-order supermolecular perturbation theory calculations).

Independently from each other, Jansen and I [86–90] and Szalewicz and co-workers [91,92] developed a new SAPT method that uses a DFT description of the monomers, termed as DFT-SAPT (correspondingly, Szalewicz and co-workers use the term SAPT(DFT) that is, however, identical to our method with exception of the treatment of second-order exchange-dispersion). In this method the \textit{intra}monomer correlation effects are described by Kohn-Sham monomer densities, density matrices and static and frequency-dependent density (-matrix) response functions, the latter calculated using time-dependent DFT. The advantage of (standard) DFT-SAPT is, that it is cheaper than the corresponding many-body SAPT method [81] that uses a second-order intramonomer perturbation expansion while, as has been demonstrated in many works by us [90,93] and others [94, 95], yielding interaction energies that are close to highly accurate supermolecular CCSD(T) (coupled cluster singles doubles with perturbative triples) energies. This finding can be attributed to the fact that DFT-SAPT is potentially exact for the polarisation terms in Eq. (3.2), i.e., it would principally yield exact polarisation contributions provided that the exact exchange-correlation potentials and kernels were used in the monomer calculation. While this is not true for the exchange terms, since the Kohn-Sham orbitals yield the exact density but not the exact density-matrix [33], a corresponding point can at least be made for the asymptotic density matrix [91].

In [10.2] the DFT-SAPT method has been used to determine the intermolecular potential of the CO-dimer in order to calculate the rovibrational spectrum. It is known [97] that for this simple system not even the interaction potential from the supermolecular CCSD(T) method is accurate enough to reproduce the rovibrational spectrum qualitatively correctly. Figure 3.1 shows the DFT-SAPT interaction potential for (CO)$_2$ and a comparison of the global and first local minima of the DFT-SAPT and CCSD(T) potentials. It can be seen that the locations of both minima are very close to each other in both cases, however, in case of the DFT-SAPT method the global minimum is deeper by 15 wave numbers compared to CCSD(T). It turned out that this difference appears to be quite important to qualitatively correctly describe the spectrum since in the CCSD(T) case the order of the lowest and second lowest stack is wrong while this is corrected with the DFT-SAPT potential, see figure 3.2. It can be observed in figure 3.2 that the DFT-SAPT potential correctly reproduces the order of the lowest stacks, but it overestimates the value of the energy difference between the stacks. In order to obtain a potential that gives a better quantitative information, a hybrid energy surface has been calculated from the CCSD(T) and DFT-SAPT surface that for the first time yielded the correct splitting features of the CO dimer rovibrational spectrum, see figure 3.2. We have also calculated the rovibrational levels of the isotopically substituted $^{13}$CO dimer with this hybrid potential and obtained not only a qualitative but also highly accurate quantitative agreement.
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\[
E_{\text{int}} \text{ [cm}^{-1}\text{]} \quad R \text{ [\text{a}_0]} \quad \Theta_A \quad \Theta_B \quad \phi
\]

<table>
<thead>
<tr>
<th>Method</th>
<th>(E_{\text{int}})</th>
<th>(R)</th>
<th>(\Theta_A)</th>
<th>(\Theta_B)</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-SAPT, global</td>
<td>-151</td>
<td>8.10</td>
<td>135.5</td>
<td>44.5</td>
<td>180</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-136</td>
<td>8.20</td>
<td>134.2</td>
<td>45.8</td>
<td>180</td>
</tr>
<tr>
<td>DFT-SAPT, 1st local</td>
<td>-127</td>
<td>6.92</td>
<td>59.5</td>
<td>120.5</td>
<td>180</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-124</td>
<td>6.95</td>
<td>59.6</td>
<td>120.4</td>
<td>180</td>
</tr>
</tbody>
</table>

Figure 3.1.: Interaction energy potential of the CO dimer

Figure 3.2.: Rotational stacks of the CO dimer, see [10.2] for details. The experimental stacks are taken from Ref. [96].
3. Intermolecular interactions from density functional methods

with experimental data, see \[10.2\].

Despite the higher efficiency of DFT-SAPT compared to the many-body SAPT method, still the computation of the dispersion and exchange-dispersion interaction contribution requires algorithms that scale as $N^6$ with respect to the molecular size and thus are much more computationally expensive than standard supermolecular DFT calculations. We have therefore developed a new method that uses density-fitting \([14–16]\) to decompose four-index quantities occurring in the DFT-SAPT program into contractions of three- and two-index objects, see \(10.1\). As an example, a classical four-index two-electron electron repulsion integral (in chemist’s notation) can be decomposed by density-fitting (using the Coulomb norm) in the following way:

\[
(ij|kl) = \sum_{PQ} (ij|P) J_{PQ}^{-1} (Q|kl) \tag{3.3}
\]

with \((ij|P) = \int drr' \phi_i(r) \phi_j(r') g_P(r) g_P(r') \frac{1}{r-r'}\), $J_{PQ} = \int drr' g_P(r) g_Q(r') \frac{1}{r-r'}$ and $g_P$ is a Gaussian auxiliary basis function. Though Eq. (3.3) itself offers no advantage over the standard computation of the integral \((ij|kl)\) if the total scaling for its computation is measured (both require an $N^5$ transformation step), density-fitting leads to a high reduction of the prefactor for calculating such four-index objects while at the same time having a much reduced disk storage and memory requirement. Furthermore, the full exploitation of density-fitting in DFT-SAPT leads to a reduction of the scaling behaviour of the method by one order of magnitude, such that DFT-SAPT calculations can be done with an $N^5$ scaling algorithm, see \(10.1\). A comparison of the CPU times between the conventional DFT-SAPT program and the density-fitting DFT-SAPT program for the ethyne dimer is shown in figure 3.3. It can be seen that already for this small system the speedup due to density-fitting is impressive, especially for the dispersion and exchange-dispersion interaction energy where the density-fitting program is about 9 times faster than the conventional program.

We have used the density-fitting DFT-SAPT program to analyse the nature of intermolecular interaction in DNA base pairs \(10.3\) and tetraramers \(10.4\). In case of the base pairs two different fundamental types of interaction occur: a triple hydrogen-bond within each base pair step, the so-called Watson-Crick (WC) structures, and a stacked $\pi - \pi$-type interaction between the aromatic rings of the DNA bases, see figure 3.4 for an example for the adenine-thymine base pair.

The diagrams in figure 3.4 show the DFT-SAPT interaction energy decomposition for the WC and stacked structures. As expected, in case of the WC structure the electrostatic interaction energy dominates while for the stacked structure the dispersion interaction energy yields the largest contribution to the total interaction energy. However, in both cases the electrostatic interaction energy is more than compensated by the first order repulsion interaction and thus the total first order interaction energy is actually positive for both structures. Thus it can be argued that the true origin of interaction in the DNA bases is the dispersion interaction which is the largest attractive interaction energy contribution in second order. For example, in the left diagram of figure 3.4 it can be observed that the dispersion interaction is almost
3. Intermolecular interactions from density functional methods

![Graph showing CPU times for different SAPT interaction energy contributions using the conventional program and the density-fitting program.](image)

**Figure 3.3.** $\text{C}_2\text{H}_2$ dimer, T-shaped structure, aug-cc-pVTZ basis set: CPU times for different SAPT interaction energy contributions using the conventional program and the density-fitting program. The cc-pVQZ JKFit auxiliary basis set was used in the density-fitting case. Calculations were done on a 2GHz AMD-Opteron processor in 32 bit mode. The fitting error of the total interaction energy is 0.09%.

as large as the total interaction energy and thus there would be almost no stabilisation of the hydrogen-bonded adenine-thymine base pair without dispersion interactions. This shows that empirical force-field methods to describe the structure of DNA should accurately try to take dispersion forces into account.

DNA base tetramers were calculated using DFT-SAPT by considering each step in the averaged crystal structure of B-DNA as one monomer \[10.4\]. The individual interaction contributions and the total interaction energies are shown in figure 3.5. Note that here $E_{\text{ind}}-\text{tot} = E^{(2)}_{\text{ind}} + E^{(2)}_{\text{exch-ind}} + \delta(\text{HF})$ and $E_{\text{disp}}-\text{tot} = E^{(2)}_{\text{disp}} + E^{(2)}_{\text{exch-disp}}$. It becomes apparent from figure 3.5 that there is no good correlation between the total interaction energy and any of the individual interaction contributions. The best correlation between $E_{\text{int}}$ and an interaction energy contribution is found for $E^{(2)}_{\text{elst}}$, but the Pearson correlation coefficient is only $r_{xy} = 0.756$ and thus way too small to be quantitatively exploited. This shows that force-field approaches to describe the structure of DNA that only take electrostatic interaction into account can not be reliable. A notable correlation, however, is observed between $E_{\text{disp}}-\text{tot}$ and $E_{\text{ind}}-\text{tot}$ that is good enough to model the induction interactions in the tetramers from a scaled dispersion contribution with an error of $\pm 2\text{kJ/mol}$. This is an important result that can be exploited to derive empirical nonpolarisable force-field models of the DNA.

Another application that we have done using the DFT-SAPT program was the study of endohedral fullerene complexes \[10.7,10.9\]. The possibility of filling a fullerene cage with guest atoms or molecules was postulated soon after the Buckmister fullerene ($\text{C}_{60}$) was discovered and
Figure 3.4.: DFT-SAPT interaction energy contributions for the Watson-Crick (left) and stacked (right) structure of the adenine-thymine base pair, see [10.3] for details.

Figure 3.5.: Stacking energy contributions for the ten unique steps of two DNA base pairs in average B-DNA from DFT-SAPT, see [10.4] for details.
a number of experimental and theoretical works have been published about this topic thereafter [98–104]. One of the main applications that is considered in this context is to use fullerenes as a device to store hydrogen. Though a number of different theoretical works have been published about this subject in the past, these all predicted a large number of H$_2$ molecules that can be stored within one C$_{60}$ molecule despite the lack of experimental reports about at least stable (H$_2$)$_2$@C$_{60}$ structures. Moreover, most of the theoretical investigations of endohedral fullerene complexes were done using methods that can not be considered as accurate enough to study the interaction between fullerenes and molecules, e.g., they were done using semi-empirical or standard density-functional theory methods [103, 105, 106]. Our investigations of the (H$_2$)$_2$@C$_{60}$ complex using DFT-SAPT revealed that it is unlikely that it is possible to obtain a thermodynamically stable structure. This can best be demonstrated by considering only the dimer complex H$_2$@C$_{60}$ which we have found to be stabilised with an interaction energy of $-19.4$ kJ/mol if the hydrogen molecule is located in centre of the fullerene. As one can see in figure 3.6, the stabilisation of the H$_2$@C$_{60}$ is mainly due to dispersion, while other attractive interaction contributions are close to zero if the H$_2$ molecule is in the centre. Compared to this, there is a very strong repulsive interaction contribution already for the minimum structure and this strongly increases when the H$_2$ molecule is displaced from the centre. This causes that already at about a distance of 1Å the endohedral complex gets thermodynamically unstable so that there is only a volume of about 4.2Å$^3$ available to form a stable complex for the dimer.
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Figure 3.7.: Percentual absolute deviations of SAPT, SAPT+D and DFT+D interaction energies to extrapolated CCSD(T) interaction energies for the extended S22+ data base from Grimme et al. [107], see 10.4 for details.

compared to the total volume of \( \sim 180\text{Å}^3 \) of the \( \text{C}_{60} \) molecule. By studying the potential energy surface of the \( \text{H}_2 \) dimer we could therefore conclude that it is not possible to derive a stable trimer structure with two \( \text{H}_2 \) molecules inside the fullerene cage [10.7]. Thus the only realistic, if any, way to make use of the \( \text{C}_{60} \) allotrope to store hydrogen would be to physisorb it exohedrally for which we have found, however, only a very weak interaction compared to the endohedral case using DFT-SAPT [10.7].

While density-fitting DFT-SAPT calculations, as demonstrated above, are possible for systems as large as DNA base tetramers or endohedral \( \text{C}_{60} \) complexes and even larger ones by using, however, smaller basis sets, the application of the method to even larger systems or for the production of full potential energy surfaces for such systems is limited. The main reason for this are the still expensive dispersion and exchange-dispersion terms that scale as \( N^4 \) and \( N^5 \) with the molecular size while all other contributions in DFT-SAPT have a lower scaling behaviour of \( N^3 \) and thus are not more costly than standard DFT calculations. Therefore, in [10.10] it is investigated how the DFT-SAPT method performs if the sum \( E^{(2)}_{\text{disp}} + E^{(2)}_{\text{exch-disp}} \) is replaced by an empirical damped dispersion contribution which sums up atom-atom contributions using atomic dispersion coefficients and van-der-Waals radii. Such empirical force-field terms are currently also in use in DFT+Dispersion (DFT+D) methods in order to correct DFT for accounting for long-range electron correlations [51]. Figure 3.7 shows the performance of this hybrid SAPT/Force-field approach, termed as SAPT+D, for a number of 110 different structures from the S22+ data base from Grimme et al. [107]. As can be seen, the SAPT+D method yields quite accurate interaction energies for the group of complexes that are mainly stabilised by dispersion and also for the mixed type complexes in which electrostatic and dispersion interactions both contribute with an equal weight. For the mixed type complexes the SAPT+D method even outperforms the standard SAPT and DFT+D method, see figure 3.7. However, for the hydrogen-bridged complexes the performance of SAPT+D decreases. A pos-
Intermolecular interactions from density functional methods

A possible reason for this are the non-optimised dispersion coefficients used in the calculations that were taken from Ref. [108] and have been optimised for use in corresponding DFT+D methods. A possible improvement of this behaviour could be obtained by employing damped dispersion interactions determined by the weighted exchange-hole method, see section 3.3 and [10.11].

3.2. Combination of second-order Møller-Plesset perturbation theory with time-dependent density-functional theory

The currently most popular ab-initio correlation method for studying intermolecular interaction energies is second-order Møller-Plesset perturbation theory (MP2) [8]. The reason for this stems from the fact that it is not only formally but also practically the most efficient approach, current implementations often are even faster than corresponding Hartree-Fock calculations in the same basis set [109, 110]. Unfortunately, however, MP2 gives a very unbalanced description of intermolecular interactions: it yields highly accurate interaction energies for hydrogen-bridged systems but often strongly overestimates the interaction energies of dispersion dominated complexes [11, 111]. The underlying reason for this is indicated by the diagrams in figure 3.8 that shows isotropic dispersion coefficients for uncoupled (UCHF) and coupled time-dependent Hartree-Fock (TDHF) compared to accurate values from dipole oscillator strength distributions. While for the small systems shown in the left diagram the UCHF dispersion coefficients are still quite accurate, in case of the larger systems the UCHF dispersion coefficients strongly overestimate the reference values, see right diagram. It is known now, that MP2 describes the dispersion interaction on an uncoupled Hartree-Fock level [112, 113] and thus, as the isotropic C₆ coefficients are the prefactors of the leading order dispersion interaction energy term −C₆/R₆ of the asymptotic multipole expansion [79], from figure 3.8 one can deduce that MP2 can strongly overestimate dispersion interactions.

Figure 3.9 shows the magnitudes of the uncoupled and coupled dispersion energies for the S22 database of intermolecular complexes developed by Pavel Hobza et al. [114]. It can well be observed that the uncoupled dispersion interaction energies strongly deviate from the coupled ones for the dispersion dominated complexes, while for the mixed-type and especially hydrogen-bridged complexes the coupled and uncoupled dispersion interaction energies are close to each other. Due to this finding the following correction scheme to supermolecular MP2 interaction energies is proposed [10.5, 10.8]:

\[ E_{\text{int}}^{\text{MP2C}} = E_{\text{int}}^{\text{MP2}} - E_{\text{disp}}^{(2)}(\text{UCHF}) + E_{\text{disp}}^{(2)}(\text{TDDFT}) \]  

(3.4)

where \( E_{\text{int}}^{\text{MP2}} \) is the supermolecular MP2 interaction energy, \( E_{\text{disp}}^{(2)}(\text{UCHF}) \) is the dispersion energy on the uncoupled Hartree-Fock level and \( E_{\text{disp}}^{(2)}(\text{TDDFT}) \) is the dispersion energy calculated using (exchange-only) time-dependent DFT. The acronym ’MP2C’ introduced in Eq. (3.4)
3. Intermolecular interactions from density functional methods

Figure 3.8.: Isotropic $C_6$ dispersion coefficients from uncoupled Hartree-Fock (UCHF), time-dependent Hartree-Fock (TDHF) and dipole-oscillator strenght distributions (accurate). The left diagram shows the dispersion coefficients for some atoms and smaller molecules and the diagram on the right shows the dispersion coefficients for benzene (Bz) and the DNA bases adenine (A), thymine (T), cytosine (C) and guanine (G).

stands for MP2 ‘coupled’. More details about it can be obtained from the original works [10.5] and [10.8]. It should be noted that the MP2C method can be related to the DFT-SAPT method as it also combines supermolecular and perturbative interaction energy terms. The DFT-SAPT interaction energy can be written as

$$
E_{\text{DFT-SAPT}}^{\text{int}} = E_{\text{HF}}^{\text{int}} + \left[ E_{\text{elst}}^{(1)}(\text{DFT}) - E_{\text{elst}}^{(1)}(\text{HF}) \right] + \\
\left[ E_{\text{ex}}^{(1)}(\text{DFT}) - E_{\text{ex}}^{(1)}(\text{HF}) \right] + \\
\left[ E_{\text{ind}}^{(2)}(\text{DFT}) - E_{\text{ind}}^{(2)}(\text{HF}) \right] + \\
\left[ E_{\text{ex-ind}}^{(2)}(\text{DFT}) - E_{\text{ex-ind}}^{(2)}(\text{HF}) \right] + E_{\text{disp}}^{(2)}(\text{DFT}) + E_{\text{ex-disp}}^{(2)}(\text{DFT})
$$

(3.5)

and the interaction energy of the MP2C method as

$$
E_{\text{int}}^{\text{MP2C}} = E_{\text{int}}^{\text{MP2}} + \left[ E_{\text{disp}}^{(2)}(\text{DFT}) - E_{\text{disp}}^{(2)}(\text{UHF}) \right]
$$

(3.6)

In Eqns. (3.5) and (3.6) the red marked terms are supermolecular interaction energy terms, the blue marked terms are correction contributions to the supermolecular energies and the green marked terms (only occurring in Eq. (3.5)) denote contributions that are not contained in the supermolecular energies. Note that in [10.9] an extension to Eq. (3.6) has been derived to account for three-body dispersion interactions not contained in supermolecular MP2 interaction energies. While in [10.5] the MP2C method has been introduced and tested for a number of small dimer systems, in [10.8] an efficient implementation of the method is presented which
Figure 3.9.: Coupled and uncoupled dispersion interaction energies for the S22 database of intermolecular complexes. The dashed horizontal line separate the different systems into the hydrogen-bridged (left), dispersion-dominated (middle), and mixed-type complexes (right).

Figure 3.10.: Basis set extrapolated intermolecular interaction energies for the S22 systems from MP2, MP2C and CCSD(T).

makes it not much more costly than conventional supermolecular density-fitted MP2 calculations. Furthermore, the approach has been tested for a broader range of systems in [10.8]. In figure 3.10 the interaction energies of the basis set extrapolated MP2C method are compared to supermolecular MP2 and CCSD(T) interaction energies. It can clearly be seen that the MP2C method strongly improves the MP2 method for the dispersion dominated and also mixed-type group, while for the hydrogen-bridged systems, where the MP2 interaction energies are very close to the CCSD(T) values, the difference between the MP2 and MP2C interaction energies is very small.
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One of the most crucial technical problems to be dealt with when describing intermolecular interactions using ab-initio correlation methods is the basis set error. For accurate calculations one requires both, diffuse basis functions in order to converge the intermolecular correlation energy, and high angular momenta functions in order to describe the interelectronic cusp accurately. The latter problem can efficiently be solved using so-called explicitly correlated wave functions which contain terms that are explicitly dependent on the electron-electron distances \[115\]. E.g., in the F12 methods one uses the geminals \(-1/\gamma \exp(-\gamma r_{12})\) in addition to a restricted conventional expansion in terms of excited Slater determinants in the wave function \[116\]. The corresponding F12-MP2 method as implemented in the Molpro quantum chemistry program \[1, 116\] uses resolution of the identity approximations to all occurring integrals so that an F12-MP2 calculation is only by a constant factor of 5-10 more expensive than a conventional (density-fitted) MP2 calculation if the same basis set is employed in both cases. In \[10.8\] it has been analysed that the correction term \(E^{(2)}_{\text{disp}}(\text{TDDFT}) - E^{(2)}_{\text{disp}}(\text{UCHF})\) in Eq. (3.4) is rapidly converged with respect to the basis set size similar to the corresponding \(\Delta\text{(CCSD(T))}\) term used in extrapolation techniques to supermolecular CCSD(T) calculations. Thus, in order to reduce the basis set error of the total MP2C approach, the following scheme is proposed:

\[
E^{\text{F12-MP2C}}_{\text{int}} = E^{\text{F12-MP2}}_{\text{int}} + \left[ E^{(2)}_{\text{disp}}(\text{TDDFT}) - E^{(2)}_{\text{disp}}(\text{UCHF}) \right]_{\text{aug-V(D,T)Z}}
\]

(3.7)

where \(E^{\text{F12-MP2}}_{\text{int}}\) is the MP2 interaction energy calculated with the F12 method and the correction term \(E^{(2)}_{\text{disp}}(\text{TDDFT}) - E^{(2)}_{\text{disp}}(\text{UCHF})\) is calculated with a small (aug-cc-pVDZ) or moderately sized basis set (aug-cc-pVTZ).

Figure 3.11.: Basis set convergence for the systems from the S22 database of the F12-MP2C method compared to the standard MP2C method using various basis sets.
3. Intermolecular interactions from density functional methods

Figure 3.11 displays the basis set convergence of the F12-MP2C method of Eq. (3.7) compared to the conventional MP2C method using various basis sets. As can be seen, using the smallest aug-cc-pVDZ basis set, the F12-MP2C interaction energies are already as good as the MP2C interaction energies calculated with the aug-cc-pVQZ basis set. Using the aug-cc-pVTZ basis set the basis set error of the F12-MP2C interaction energies does not exceed ±0.1 kcal/mol.

3.3. Long-range correlation energies from the weighted exchange-hole

The dispersion interaction energy can be written explicitly in terms of the densities and the exchange-holes of the monomers as is shown in 10.6. While this could be achieved using a series of approximations to the response function, it has been demonstrated in 10.6 that resulting polarisabilities and dispersion coefficients were in a reasonable agreement with ab-initio or dipole-oscillator strength distribution reference results.

In 10.11 the method presented in 10.6 has been augmented by using a more reasonable approximation to the response function that is given as

\[
\chi(r_1, r_2, \omega) \approx -\rho(r_1) \left[ 2 \sum_i \frac{1}{2} \overline{\lambda}_i(\omega) \phi^2_i(r_1) \right] \delta(r_1 - r_2) - 2 \sum_{ij} \frac{1}{2} \overline{\lambda}_{ij}(\omega) \phi^2_i(r_1) \phi^2_j(r_2) \right] (3.8)
\]

where \( \overline{\lambda}_i(\omega) \) are weight factors which depend on occupied orbital energies, see 10.11 for details. In Eq. (3.8) the first term in parenthesis is a local contribution to the response function while the second term has the form of the exchange-hole, but with weight factors \( \overline{\lambda}_i(\omega) \) that favour energetically higher lying occupied states compared to lower lying ones. The total form of Eq. (3.8) to the response function is therefore termed as weighted exchange-hole approximation 10.11. The crucial point of the use of Eq. (3.8) is now, that in contrast to the exact orbital-expanded response function only occupied orbitals contribute, so that a rapid convergence of derived properties with respect to the basis set size is achieved.

In 10.11 the weighted exchange-hole form of Eq. (3.8) has been used to calculate long-range correlation energies by using localised polarisabilities derived therefrom using the localisation method by Wheatley and Lillestolen [117, 118]. The use of a damping scheme to enable the combination with a standard hybrid density functional method to account for the short-range correlation effects has lead to a method that quite accurately reproduces intermolecular interaction energies for a range of systems. Figure 3.12 shows the performance of the method, termed as WXhole, for the systems from the S22 database. While not as accurate as the MP2C method presented in section 3.2, the diagrams in figure 3.12 nevertheless show that the WXhole approach gives a more balanced description of different types of intermolecular complexes than MP2 while being much more computationally efficient.
The WXhole method presented in [10.11] is a general purpose quantum chemistry approach that corrects the deficiencies of standard DFT methods in the long-range electron correlation regime. It is less empirical than common damped dispersion correction schemes that are in use to date and can be applied to large systems. It will be investigated in a future work how well this method performs for other properties, e.g., thermodynamic properties like reaction energies.
4. Time-dependent density functional theory methods

Publications: 12.1, 12.2, 12.3, 12.4, 12.5

4.1. Blindness of the exact density-density response function to certain types of electronic excitations

Generally, excitation energies of molecular systems are obtained from the poles of the density-density response function of the system that can be written as

\[
\chi(r, r', \omega) = \sum_n \left[ \frac{\langle \Psi_0 | \hat{\rho}(r) | \Psi_n \rangle \langle \Psi_n | \hat{\rho}(r') | \Psi_0 \rangle}{E_0 - E_n + \omega + i\eta} + \frac{\langle \Psi_n | \hat{\rho}(r) | \Psi_0 \rangle \langle \Psi_0 | \hat{\rho}(r') | \Psi_n \rangle}{E_0 - E_n - \omega - i\eta} \right] \tag{4.1}
\]

where \(\Psi_{0,n}/E_{0,n}\) denote the ground- and excited-state wave functions/energies of the system. However, in 12.3 it is shown that there exist excitations for which the matrix elements \(\langle \Psi_0 | \hat{\rho}(r) | \Psi_n \rangle\) equal zero for all values of \(r\) and thus these do not contribute to the sum over states expression of Eq. (4.1). As a consequence the corresponding excited states can not be determined from the density-density response function. Examples for such excitations are the \(2p \rightarrow 3p\) excitation from the \(^1S\) ground state into the \(^1P\) excited state of the neon atom or the \(\pi \rightarrow \pi^*\) excitation from the \(\sigma_g^+\) ground state to the \(\sigma_u^-\) excited state of the nitrogen molecule, see 12.3.

In praxis this means that any method that determines excitation energies from the poles of \(\chi(r, r', \omega)\) are unable to calculate these excitation energies exactly. For example, it can be shown 12.3 that time-dependent DFT (TDDFT) methods, which generally aim at solving Casida’s equation, simply approximate excitation energies, for which \(\langle \Psi_0 | \hat{\rho}(r) | \Psi_n \rangle = 0\) holds true, by the corresponding single-particle energy differences of the Kohn-Sham system. Therefore, while TDDFT in the linear response regime can principally yield the exact excitation energies of the many-body system, provided that the exact exchange-correlation potential and and kernel is employed, this is only true for excited states \(n\) that have nonzero matrix elements \(\langle \Psi_0 | \hat{\rho}(r) | \Psi_n \rangle\). Note that this limitation has no effect on response properties like polarisabilities since these in any case are only described by nonzero contributions in the sum-over-states expression.
Note also that the time-dependent Hartree-Fock method will not be affected by the problem discussed in this section since it is based on determining the response of the density matrix that is nonlocal in space.

4.2. Exact-exchange time-dependent density functional theory methods

While in the TDDFT framework already the correct description of the asymptotic form of the exchange-correlation potential leads to improvements for certain types of excitations, namely Rydberg excitations [43], and response properties [42, 93], as is demonstrated for static and frequency-dependent polarisabilities of closed-shell atoms in [12.1], the commonly employed adiabatic local density approximation of the exchange-correlation kernel causes severe problems. Most importantly, common TDDFT methods using adabatic and local kernels are unable to treat charge-transfer (CT) excitation energies [58–60]. Moreover, hyperpolarisabilities of long conjugated molecular chains are strongly overestimated by standard TDDFT methods due to the lack of a field-counteracting term that compensates an external field-induced potential [52, 61, 62].

In [12.2] it is demonstrated that an exact-exchange treatment, in contrast to standard TDDFT methods, is able to qualitatively correctly describe charge transfer excitation energies in the HeH$^+$ system. The striking aspect of this finding was that this improvement is not induced by the underlying exact exchange kernel, which is both local and adiabatic for a two-electron system, but by the orbital energy differences of the Kohn-Sham system. Generally, a charge-transfer excitation from a donor system to an acceptor system asymptotically is given by the difference of the ionisation potential of the donor $I_d$ and the electron affinity $A_a$ of the acceptor plus a distance-dependent Coulombic term:

$$\omega_{CT} = I_d - A_a - \frac{1}{R}$$

with $R$ denoting the distance of donor and acceptor, see also the sketch in figure 4.1. In contrast to this, any LDA or GGA functional will yield $\omega_{CT} = \varepsilon_a - \varepsilon_d$, i.e., asymptotically standard TDDFT excitation energies approach a constant value given by the orbital-energy difference between the donor and acceptor system [119]. While now in exact Kohn-Sham theory the orbital energy of the highest occupied orbital (HOMO) is strictly equal to the vertical ionisation energy, i.e., $\varepsilon_d = -I_d$ [29], the orbital energy of the lowest unoccupied Kohn-Sham orbital (LUMO) does not correspond to the electron affinity since in contrast to Hartree-Fock theory all electrons 'feel' the effective field of $N-1$ electrons. As a consequence, while standard TDDFT methods fail to describe the distance dependence of $-1/R$ for the CT excited state qualitatively correctly, they also quantitatively yield completely wrong CT energies.

While a number of schemes have been developed to correct this deficiency of TDDFT methods [58, 119, 120], the most rigorous and natural approach is to treat exchange interactions exactly.
4. Time-dependent density functional theory methods

ω
CT
−I εd
−I
a
εa
acceptoracceptordonor
−
−
ε =−I
− a
ε  −1
a
d
a
a
a
=−A
−
ε  −1

Figure 4.1.: Asymptotic behaviour of the charge-transfer excitation.

on the TDDFT level. However, in contrast to two-electron systems discussed above, in general the exact-exchange kernel of DFT derived by Görling [121–123] is both frequency-dependent and nonlocal and is given by the equation:

\[ f_x(r_1, r_2, \omega) = \int d r_3 r_4 \chi_0(r_1, r_3, \omega) h_x(r_3, r_4, \omega) \chi_0^{-1}(r_4, r_2, \omega) \] (4.3)

where \( \chi_0 \) is the Kohn-Sham response function and \( h_x \) is an inner kernel term that itself is nonadiabatic and nonlocal. The solution to Eq. (4.3) gets numerically highly unstable due to the occurrences of the inverses of the Kohn-Sham response function, see section 2.1. Therefore a new exact-exchange TDDFT method, termed as TDEXX, has been developed that omits the numerical problematic inversion of \( \chi_0 \) by rewriting the response equation such that it yields the response of the local potential instead of the response to the density, see 12.4,12.5,12.6. While we have implemented and tested this method for the exchange-only case, it is generally applicable to any orbital-dependent functional.

It is found that the TDEXX method, in contrast to standard TDDFT methods, accurately describes charge-transfer excited states. Figure 4.2 shows the distance dependence of the charge-transfer excitation from the \( \pi \)-state of acetylene to the \( \sigma_u \)-state of the hydrogen molecule as one example. It can be seen that the standard TDDFT method employing the PBE functional largely underestimates the CT energy while already the adiabatic TDEXX method (ATDEXX, neglecting the frequency-dependent terms of the kernel) leads to a strong improvement and also shows some distance dependence in contrast to TDDFT using the PBE functional and its derivatives. The full nonadiabatic TDEXX or the so-called half-adiabatic TDEXX \((\omega = \omega^{\text{adiab}})\) methods are quite close to the equation-of-motion CCSD (EOM-CCSD) reference curve, the former slightly under- and the latter slightly overestimating it, as can be observed in figure 4.2.

Another problematic case for standard TDDFT methods is the description of Rydberg excitations. Figure 4.3 shows that TDDFT using the PBE potential and kernel strongly underestimates the CC3 (coupled-cluster with iterative triples approximation [124]) reference Rydberg excitations. In contrast to this already the orbital energy differences from the EXX method
\[ \text{C}_2\text{H}_2 (\pi) \rightarrow \text{H}_2 (\sigma_u) \]

Figure 4.2.: Distance dependence of the charge-transfer excitation from the $\pi$-state of acetylene to the $\sigma_u$-state of the hydrogen molecule.

Figure 4.3.: Rydberg excitation energies of the neon atom. In case of CC3 the d-aug-cc-pV6Z basis set has been used while in all other cases an uncontracted [22s17p] orbital basis set has been employed.
Figure 4.4.: Mean absolute errors of the Rydberg and valence-valence excitation energies from several methods to experimental excitation energies. The methods TDEXX and PBE refer to standard time-dependent EXX and PBE while LPBE0AC refers to calculations employing the LPBE0AC xc-potential and the ATDEXX-ALDA(0.5) xc-kernel. Considered are 11 and 4 lowest Rydberg excitations in ethylene and acetaldehyde and the lowest respectively 4 lowest valence excitations in ethylene/acetaldehyde and pyridine. See [12.6] for details.

(EXX(\Delta \varepsilon)) are rather close to the CC3 reference results. The exact exchange kernel has only a marginal effect on the Rydberg excitations for this example, as can be seen in figure 4.3.

In summary the new TDEXX method presented in [12.4,12.5,12.6] leads to improvements of standard TDDFT both for the description of charge-transfer and Rydberg excited states and can be implemented using the efficient scheme described in [12.6]. However, typical valence-valence excitation energies are generally worse with TDEXX than with common TDDFT methods which is due to the missing description of electron correlation, see figure 4.4. In [12.6] a number of schemes have therefore been investigated to account for electron correlation effects. It is found that hybrid approaches that mix the EXX/TDEXX exchange potential and kernel with GGA exchange-correlation potentials and kernels work quite well, see, e.g., figure 4.4, and probably represent the best compromise to achieve a balanced description of both charge-transfer excitations and Rydberg and valence-valence excitations using TDDFT methods.
5. Orbital-dependent correlation functionals


5.1. Brueckner-orbital based correlation functionals

In 2002 Lindgren et al. published a paper [125] that analyses a perturbation theory scheme which, by minimising the energy expectation value to all orders, yields the Brueckner determinant as the zeroth order wave function, i.e., the determinant that has maximum overlap with the exact wave function. They then derive several generalisations to the standard Kohn-Sham scheme using either a nonlocal exchange and local correlation potential (Hartree-Fock Kohn-Sham scheme) or a full nonlocal exchange-correlation potential (Brueckner Kohn-Sham scheme). In this context we have shown a few years ago that the Bruecker reference determinant from a Brueckner coupled-cluster doubles wave function already well describes the correlation effects of first- and second-order molecular properties [126, 127]. Because of this it can be anticipated that Brueckner orbitals are close to (exact) Kohn-Sham orbitals and that it might therefore be advantageous to develop density functionals that are derived through the Brueckner condition, i.e., using the maximum overlap criterion to obtain correlation potentials that yield Brueckner orbitals. Corresponding methods have been developed and are presented in [13.1, 13.2].

In section 2.1 it has been argued that the optimised effective potential method (OEP) is a general approach that can be applied to any orbital-dependent functional. It will now briefly be shown that the generalisation of the OEP method to many-body perturbation theory expressions of the (exchange-)correlation energy leads to Kohn-Sham orbitals that are approaching Brueckner orbitals in infinite order of perturbation theory (while for a truncated perturbation expansion they will resemble Brueckner orbitals to that given order). Following Lindgren et al. [125] the exact energy can be approximated as an orbital functional by

$$E_N = \langle \Psi | \hat{H} | \Psi \rangle \approx \frac{\langle \Phi | \Omega_n^\dagger \hat{H} \Omega_n | \Phi \rangle}{\langle \Phi | \Omega_n^\dagger \Omega_n | \Phi \rangle} = E_n[\Phi]$$

where $\Omega_n = 1 + \omega_1 + \omega_2 + \cdots + \omega_n$ produces $n$-th order excitations, i.e., if $n \to \infty$ one may expect the result of the expectation value on the right hand-side to become identical to the exact
energy of the many-particle system. The energy $E_n[\Phi]$ is then minimised under the constraint that the determinant wave function $\Phi$ stems from a local potential $v_s$, i.e. one seeks the local potential which fulfills the stationary condition

$$\frac{\delta E_n[\Phi[v_s]]}{\delta v_s} = 0$$

(5.2)

which is the OEP condition. Again, if $n \to \infty$ the result shall be associated with the “exact OEP” limit and should give the exact energy of the many-particle system. However, even if this procedure yields in the $n \to \infty$ limit the exact energy of the many-particle system, the resulting optimised potential $v_s$ will not be identical to the Kohn-Sham potential $v_{KS}$. This is so, because the determinant which minimises $E_n[\Phi]$ “without” the constraint of a local potential is the (approximate if the order $n$ is truncated) Brueckner determinant, i.e., the determinant which is closest to the exact wave function subject to the overlap criterion. Now note that even for a two-electron system the density $\rho_{\Phi}$ of the Brueckner determinant differs from the exact density $\rho_\Psi$. Thus, if using the additional constraint that $\Phi$ should stem from a local potential $v_s$, it is obvious that during the optimisation the local potential tries to reproduce Brueckner orbitals, i.e. those orbitals which minimise $E_n[\Phi]$ without the constraint. As a consequence, the potential $v_s$ will give the best local approximation to the nonlocal Brueckner potential and thus will differ from the Kohn-Sham potential. In summary: the correlated OEP method is not an exact DFT approach because, while it may give the exact energy of the many-particle system, it does not yield the exact Kohn-Sham potential and Kohn-Sham orbitals. In a sense this is a generalisation of the exchange-only case since the exchange-only OEP determinant also will not exactly reproduce the density from the Hartree-Fock determinant, but the densities will only be identical to first order [128]. In order to derive exact Kohn-Sham schemes the OEP method would have to be modified such that the density condition, that is the identity of the densities of the many-particle system and the Kohn-Sham system, is enforced in all orders. This is done, e.g., in Görling-Levy perturbation theory [68] or in the ab-initio DFT method by Bartlett et al. [129].

In 13.1 a Brueckner Kohn-Sham method is presented that in contrast to the scheme proposed by Lindgren et al. uses a local exchange- and correlation-potential derived by the OEP method. This is done by extending the standard OEP equations with additional nonlocal correlation potential terms obtained from the single amplitude equations of the Brueckner coupled-cluster method (BCCD). Figure 5.1 shows that the nonlocal Brueckner correlation potential in the BCCD method is given by the sum of three terms: a first-order interaction term arising due to the fact that Brueckner orbitals no longer fulfill Brillouins theorem (this term is usually small), a direct correlation contribution meaning that the operator, when acting on an occupied orbital, directly excites it into an unoccupied state, leaving the other occupied orbitals frozen, and a relaxation correlation contribution which affects the other occupied orbitals when an occupied orbital $i$ is excited to an unoccupied orbital $a$, see figure 5.1.

While the method presented in 13.1 has been shown to yield orbitals which yield quite
accurate first-order electric properties and HOMO energies which are close to experimental vertical ionisation energies, the approach is much more costly than a standard DFT calculation as it requires, in addition to the calculation of the Brueckner correlation potential, the solution of the Brueckner coupled-cluster doubles equation to obtain the doubles amplitudes, scaling as $N^6$ with respect to the molecular size $N$. Moreover, the method from uses the standard OEP approach to determine the local correlation potential and therefore relies very much on the accurate representation of occupied-virtual orbital products in an auxiliary basis set, see section 2.1. Therefore, an alternative and more efficient Brueckner Kohn-Sham method, termed as BOKS2 method, has been developed which approximates the doubles amplitudes at second order of perturbation theory and which uses an approximate OEP scheme that is a generalisation of the local Hartree-Fock method (see section 2.1) for orbital-dependent correlation functionals With this the method yields very smooth correlation potentials that are unaffected by any numerical instabilities as in the OEP method used in. Figure 5.2 shows the total BOKS2 correlation potential and its components for the CO molecule. In figure 5.2 $v_{\text{corr}}$ is the direct correlation potential according to the second diagram in figure 5.1 and $v_{\text{rel}}$ is the relaxation potential according to the third diagram in figure 5.1 and is, as can be seen, a repulsive contribution to the total correlation potential. The potential termed as $v_{\text{res}}$ is a response contribution arising due to density variations of the correlation potential and has, as can be seen in figure 5.1, a strong peak on the oxygen atom site. The total BOKS2 correlation potential is given by the sum $v_{\text{rel}} = v_{\text{corr}} + v_{\text{rel}} + v_{\text{res}}$ and is mostly repulsive in the region plotted in figure 5.1 (note that an inner core shell structure is missing in the correlation potential since the calculations were done with the core kept frozen). The decomposition of the correlation potential done in this way not only reveals a new way to interpret electron correlation effects, but might also help to develop new approximate correlation potentials and functionals.

In table 5.1 some molecular properties obtained with the BOKS2 method, more precisely with the Brueckner reference determinant of the BOKS2 method, are shown in comparison to Hartree-Fock (HF), second-order Møller-Plesset perturbation theory (MP2), the Brueckner orbital expectation value approach (BOX, see Ref. [126]), and Brueckner coupled-cluster doubles with perturbative triples (BCCD(T)), the latter serving as the reference in the table. As can be seen, the BOKS2 method yields molecular properties that are overall in a better agreement
with the high-level BCCD(T) results than those from the corresponding MP2 method while the computational scaling behaviour of these two methods of $N^5$ is the same. It can also be observed in table 5.1 that the molecular properties from the BOKS2 method are in a good agreement with those from the BOX method. This means that apparently the Brueckner orbitals from the second-order perturbation theory functional will be close to Brueckner orbitals from the Brueckner coupled-cluster doubles wave function.

The replacement of single excitations using orbital transformations, as is done in Brueckner correlation functionals, can principally also be adopted to derive orbital-optimised correlation functionals. As is shown in [13.4], in approximate correlation functionals there exists a difference between Brueckner orbitals obtained from the projective condition $\langle \Phi^a_i | \hat{H} | \Psi \rangle = 0$, which is identical to the Brueckner singles equation with $\Phi$ denoting the Brueckner determinant and $\Psi$ the full wave function, and orbitals obtained by directly minimising the energy expression with respect to orbital variations. In [13.4] we have investigated such orbital-optimised methods for a number of coupled-pair functionals. In addition to the orbital optimisation in this approach, we also optimised the excitation amplitudes so that the corresponding functionals are fully optimised with respect to all wave function parameters. This has the advantage that first-order molecular properties, e.g., molecular dipole moments, are directly accessible through the use of the Hellmann-Feynman theorem while in coupled-cluster theories the calculation of molecular properties requires a second calculation in addition to the wave function calculation in order to obtain the relaxed density matrix. In [13.4] it is shown that orbital-optimised coupled-pair
5. Orbital-dependent correlation functionals

Table 5.1.: Dipole ($\mu$), quadrupole ($Q$) and radial density ($r^2$) moments. The reference Brueckner coupled-cluster doubles with perturbative triples (BCCD(T)) results are marked in blue and the corresponding closest values to the reference values for a given molecule and property are marked in red. All calculated properties are referred to a centre-of-mass coordinate system and the main symmetry axis of the molecules has been chosen as the $z$-axis. All values are in a.u.

<table>
<thead>
<tr>
<th>System</th>
<th>Property</th>
<th>HF</th>
<th>MP2</th>
<th>BCCD(T)</th>
<th>BOX</th>
<th>BOKS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>$\mu_z$</td>
<td>-0.756</td>
<td>-0.710</td>
<td>-0.707</td>
<td>-0.717</td>
<td>-0.713</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>1.735</td>
<td>1.735</td>
<td>1.713</td>
<td>1.729</td>
<td>1.737</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>10.956</td>
<td>11.387</td>
<td>11.312</td>
<td>11.230</td>
<td>11.297</td>
</tr>
<tr>
<td>HCl</td>
<td>$\mu_z$</td>
<td>-0.466</td>
<td>-0.438</td>
<td>-0.441</td>
<td>-0.431</td>
<td>-0.437</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>2.794</td>
<td>2.734</td>
<td>2.722</td>
<td>2.679</td>
<td>2.734</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$\mu_z$</td>
<td>0.779</td>
<td>0.731</td>
<td>0.727</td>
<td>0.741</td>
<td>0.729</td>
</tr>
<tr>
<td></td>
<td>$Q_{xx}$</td>
<td>-1.797</td>
<td>-1.841</td>
<td>-1.808</td>
<td>-1.823</td>
<td>-1.827</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>-0.102</td>
<td>-0.109</td>
<td>-0.106</td>
<td>-0.105</td>
<td>-0.117</td>
</tr>
<tr>
<td>CO</td>
<td>$\mu_z$</td>
<td>-0.104</td>
<td>0.108</td>
<td>0.042</td>
<td>0.052</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
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<td>-1.492</td>
<td>-1.464</td>
<td>-1.469</td>
<td>-1.516</td>
</tr>
<tr>
<td>ethyne</td>
<td>$Q_{zz}$</td>
<td>5.450</td>
<td>4.848</td>
<td>4.861</td>
<td>5.013</td>
<td>5.013</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>25.817</td>
<td>25.676</td>
<td>25.659</td>
<td>25.306</td>
<td>25.533</td>
</tr>
</tbody>
</table>

functionals (restricted to double excitations in the functional) yield total energies and molecular properties that are very close to corresponding CCSD values.

5.2. Random phase approximation with exact Kohn-Sham exchange

In 1951 Callen and Welton derived a theorem that relates the internal fluctuations within a many-particle system to the response to some small applied external perturbation (that is that small that the system is not excited from its ground state) [130]. This fluctuation-dissipation theorem can be written as

$$
\langle \Psi_0 | (O - \langle O \rangle)^2 | \Psi_0 \rangle = -\text{Im} \int_0^\infty \frac{d\omega}{\pi} \int d\mathbf{r} \ O(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}, \omega) O(\mathbf{r})
$$

(5.3)
5. Orbital-dependent correlation functionals

Randomly moving particles (Brownian motion).

Small applied external perturbation: another particle pulled through the system.

response to internal fluctuations = response to small external perturbation

Figure 5.3.: Fluctuation-dissipation theorem

where $\Psi_0$ is the ground state wave function, $\chi$ is the density-density response function and $O$ is a one-particle observable. As can be seen, the left-hand side of Eq. (5.3) is the mean square fluctuation of the one-particle observable and the right-hand side corresponds to the dissipative (frictional) part of the response function. An interpretation of the fluctuation-dissipation theorem is given in figure 5.3: the left panel in the figure shows randomly moving particles of the many-body system and the right panel shows an extra particle which is pulled through the system and moves the particles of the system apart from each other. Since now the fundamental interactions between the particles are the same for the unperturbed and the perturbed system, the fluctuation-dissipation theorem states that both cases are related to each other through Eq. (5.3).

While the fluctuation-dissipation theorem conventionally is used in statistical physics for predicting the behaviour of non-equilibrium thermodynamical systems, Langreth and Perdew generalised this theorem to obtain an expression for the correlated part of the pair density $P^c_\alpha(r_1, r_2)$ which can directly be used to calculate the correlation energy of the many-body system [131, 132]:

$$P^c_\alpha(r_1, r_2) = -\text{Im} \int_0^\infty \frac{d\omega}{\pi} \left( \chi_\alpha(r_1, r_2, \omega) - \chi_0(r_1, r_2, \omega) \right)$$

$$\Rightarrow E_{\text{corr}} = \frac{1}{2} \int_0^1 d\alpha \int dr_1 dr_2 \frac{P^c_\alpha(r_1, r_2)}{r_{12}}$$

where $\chi_\alpha$ is the coupled response function at coupling strength $\alpha$ which switches on and off the electron-electron interaction and $\chi_0$ is the uncoupled response function. The intriguing aspect of Eqns. (5.4) and (5.5) is now, that they enable the calculation of the exact correlation energy in terms of the coupled and uncoupled response functions of the system, that is, if the
response function of the many-body system is known, then one can obtain the exact correlation energy of the system via Eqns. (5.4) and (5.5). In the context of DFT $\chi_0$ refers to the response function of the noninteracting Kohn-Sham system and is explicitly given in terms of the Kohn-Sham orbitals and eigenvalues. The coupled response function at coupling strength $\alpha$ (with $0 \leq \alpha \leq 1$) then is usually calculated by the Dyson-type equation (written in short-hand notation):

$$\chi_{\alpha} = \chi_0 + \alpha \chi_0 W \chi_0 + \alpha^2 \chi_0 W \chi_0 W \chi_0 + \ldots$$  \hspace{1cm} (5.6)

where $W$ is the electron-electron interaction operator. The exact form of $W$, however, is not known and therefore has to be approximated in praxis. The most simple approximation that can be applied is to approximate $W$ by the Coulomb interaction operator:

$$W(r_1, r_2, \omega) \approx \frac{1}{r_{12}}$$  \hspace{1cm} (5.7)

and this approximation is termed as random phase approximation (RPA) or direct random phase approximation. In terms of correlation processes it amounts to accounting only for repeated particle-hole type interactions and neglecting (higher order) exchange interactions as the second-order exchange process illustrated in figure 1.2. The direct RPA, however, usually strongly overestimates electron correlation effects due to the neglect of exchange interactions, the most striking example for this being the hydrogen atom which has a nonzero correlation energy yielded by RPA [53]. In order to go beyond the standard RPA approach we therefore have developed a new RPA method [13.3] that also takes electron exchange effects into account through the use of the exact exchange DFT kernel $f_x(r_1, r_2, \omega)$, see section 4.2. This means the electron-electron interaction operator in this method, termed as EXX-RPA, is approximated by

$$W(r_1, r_2, \omega) \approx \frac{1}{r_{12}} + f_x(r_1, r_2, \omega)$$  \hspace{1cm} (5.8)

The difference of the EXX-RPA total energies obtained by the insertion of Eq. (5.8) into Eq. (5.4) to CCSD(T) energies for a number of small organic molecules is shown in figure 5.4 in comparison to energy differences yielded by the MP2, CCSD and B3LYP method. As can be seen, the EXX-RPA energies are much closer to the accurate reference energies than those from the standard B3LYP DFT method and they closely resemble the CCSD energies. Using a set of 14 chemical reactions of some small organic molecules it has been studied whether this accuracy of the total energies also transfers to energy differences. The result is shown in figure 5.5 which shows the average errors for the corresponding chemical reactions of several methods to CCSD(T) reference reaction energies. Indeed, the reaction energies from the EXX-RPA method are in a much better agreement with the CCSD(T) values than are the MP2 or B3LYP reaction energies and the average error is clearly below 5 kcal/mol. However, as expected, the average error of the CCSD method is still significantly smaller since the CCSD method describes electron correlation on an even higher level than EXX-RPA.
Figure 5.4.: Energy differences of various methods to CCSD(T) energies. The aug-cc-pVTZ basis set has been used.

Figure 5.5.: Root-mean-squared average errors of the reaction energies of 14 chemical reaction displayed on the left for several methods to CCSD(T) reference results.
One of the most difficult cases for correlation methods is the description of static correlation effects that occur when a molecule is dissociated into its fragments. For example, it is known that a high level of correlation is required in single-reference methods to properly describe the dissociation of a triple bond as in the nitrogen molecule. For example, the CCSD energy diverges for distances beyond 3.5 a₀ of the nitrogen atoms in N₂ [133]. Standard DFT methods conventionally better describe static correlation effects than Hartree-Fock theory, but still have large errors in the dissociation limit [52, 53]. In [13.5] we have shown that the restricted EXX-RPA method is able to correctly describe the bond dissociation limit of the H₂ molecule in contrast to the standard RPA method without exchange [53] and common DFT methods [52]. In case of other systems that are far from their ground-state equilibrium the EXX-RPA method sometimes has instabilities that are due to the fact that the exchange kernel used is not the exact functional derivative of the corresponding exchange potential used, see [12.4] for an explanation. In order to correct this deficiency the exchange contributions therefore are damped in the dissociation limit using

\[ \bar{K}_x = d[\varepsilon]K_xd[\varepsilon] \]  

(5.9)

where \( K_x \) is the exchange kernel matrix and \( d[\varepsilon] \) is a diagonal matrix that in its diagonal has the elements \( d_{ia} = \text{erf}(c\varepsilon_{ia}) \) with \( \varepsilon_{ia} \) being the orbital energy difference between an occupied orbital \( i \) and an unoccupied orbital \( a \) and \( c \) is a constant that has been set to a value of \( c = 5 \). In the dissociation limit it will now happen that the HOMO-LUMO energy difference goes to zero and as a consequence the entries in the modified exchange kernel matrix of Eq. (5.9) will vanish. Using the modification of Eq. (5.9) to the exchange kernel the dissociation curves for the HF and N₂ molecule were calculated using EXX-RPA, see figure 5.6. As can be seen, in both cases the EXX-RPA curves asymptotically approach the sums of the fragment energies marked by the dashed horizontal lines in the diagrams. They, however, also exhibit some unphysical bump in the mid range region. This feature already occurs in the direct RPA (dRPA) potential curve for N₂ (see also Ref. [134]) and possibly is related to a not rapidly enough decreasing HOMO-LUMO gap for an increasing atom-atom distance.

Figure 5.7 shows the atomisation energies for some small molecules obtained by the PBE functional, EXX-RPA and the CCSD(T) method as a reference. While it can be observed that the PBE functional already performs quite well, the EXX-RPA method in many cases even improves upon the PBE results.

Despite the general good performance of the EXX-RPA method for a number of different properties, as demonstrated above, the study of intermolecular interaction energies using the EXX-RPA method revealed that the approach is not significantly better than MP2 as has been found by studying a number of small dimer systems. While EXX-RPA and other exchange-RPA variants, see [13.6,13.7], are more complete than MP2 in a perturbation theory sense, since they are exact to second-order of perturbation theory and sum up certain higher order correlation energy terms, this finding was somewhat surprising. An analysis of several exchange-RPA methods in third order of perturbation theory showed that some of these methods have large
Figure 5.6.: Dissociation curves for the HF molecule (left panel) and the N$_2$ molecule (right panel). The reference in the left diagram is the coupled electron pair approximation method (CEPA) and in the right diagram the multi-reference average coupled pair functional (MR-ACPF). The sums of the fragment energies are displayed by dashed horizontal lines. The aug-cc-pVTZ basis set has been used.

Figure 5.7.: Atomisation energies for a subset of molecules from the HEAT database [135]. The CCSD(T) reference values are taken from Ref. [136]. The energies were not corrected by the vibrational zero-point energies. All values were extrapolated to the complete basis set limit.
errors in third order. This could be revealed by comparing the corresponding correlation energy contributions to MP3 correlation energies [13.6]. Therefore in [13.6] a simple correction scheme is proposed to make (exchange-)RPA methods also exact to third order using:

$$E_{c}^{\text{total}}(M[3]) = E_{c}^{\text{total}}(M) - E_{c}^{(3)}(M) + E_{c}^{(3)}(\text{exact})$$  \hspace{1cm} (5.10)

The results presented in [13.6] demonstrated that dramatic improvements both for total energies and energy differences as reaction energies or intermolecular interaction energies for various RPA methods including exchange effects are obtained by using the scheme of Eq. (5.10).
6. Summary

The main theme of the works compiled in this thesis is the development of new density functional theory methods to describe the ground and excited states of molecular systems. While a number of different approaches were used to correct the deficiencies of the standard models of the exchange-correlation functional, they all can be summarised as orbital-dependent methods. This means that the yet unknown exchange-correlation functional is approximated in terms of the Kohn-Sham orbitals, either occupied or also unoccupied. Practical methods to implement such orbital-dependent functionals have been developed for ground \([11.1,11.3]\) and excited states \([12.4,12.6]\). The exact-exchange optimised effective potential method from \([11.3]\) has been extended to the open-shell case. It has been shown that this method, combined with a standard GGA correlation functional to account for the dynamic correlation effects, outperforms any standard density functional for the description of the hyperfine coupling constant of phosphorus, a property that, if standard wave function methods are employed, requires a high level of electron correlation and large basis sets to be obtained in close agreement with the experiment \([14.2]\).

A main field of research that was devoted to was the description of intermolecular interaction energies. A new density-fitting implementation of the DFT-SAPT method \([10.1]\) that combines DFT with intermolecular perturbation theory enabled the study of molecular systems as large as DNA base pairs and tetramers \([10.3,10.4]\) or endohedral fullerene complexes \([10.7,10.9]\) with this method. By this it was not only possible to obtain accurate information about the total stabilisation in these systems, but it also revealed the character of the interaction in the respective systems in terms of individual intermolecular interaction energy terms. Since the interaction energy terms from SAPT are comparable to terms that are commonly used in intermolecular force fields, the SAPT interaction energy decomposition also offers new and less empirical ways for calibrating nonbonded terms in force fields. Another new method that has been developed uses a combination of supermolecular second-order Møller-Plesset perturbation theory (MP2) with a dispersion energy correction term determined by time-dependent density functional response theory \([10.5,10.8]\). It has been shown for a number of systems that this approach strongly improves standard MP2 interaction energies for dispersion dominated complexes, while for hydrogen bridged complexes its performance is practically the same as with MP2, thus yielding a very balanced description for different types of intermolecular bound systems.

In order to be able to study intermolecular interaction energies for even larger systems, two
6. Summary

Methods were developed which contain a damped asymptotic dispersion interaction energy contribution [10.10, 10.11]. The SAPT+D (SAPT 'plus' dispersion) method has been shown to yield accuracies comparable to common DFT+D methods while not having the problem of double counting of correlation effects in the mid- and short-range region as in DFT+D [10.10]. The second method, termed WXhole (weighted exchange hole method), is a new DFT+D approach that uses frequency dependent localised polarisabilities from a direct approximation to the response function and is thus less empirical than standard DFT+D methods which should make it more reliable as a general purpose quantum chemistry method [10.11].

A new time-dependent DFT method that can be used in conjunction with orbital-dependent density functionals has been shown to practically solve the charge-transfer problem of standard TDDFT methods already if restricted to the exchange-only case [12.2, 12.4, 12.5]. In [12.6] we have analysed the performance of this method also for the description of Rydberg and valence excitations and it turned out that especially for the latter it is essential to account for correlation effects in order to reproduce experimental excitation energies to within a few tenth of an electron volt. While the combination of an asymptotically corrected exchange-correlation potential with a hybrid exact-exchange−GGA kernel was found to lead to significant improvements for valence-valence excitations compared to the exchange-only approach, further work is required in order to derive a more rigorous combination of exchange and correlation on the TDDFT level.

The probably most accurate orbital-dependent functional methods to date are functionals that are derived from many-body perturbation theory [13.2], the random-phase approximation [13.3, 13.5, 13.7], or coupled-cluster theory and related coupled-pair functionals [13.1, 13.4]. The new developed EXX-RPA method, which combines the random-phase approximation with exact Kohn-Sham exchange, not only yields much more accurate correlation energies and reaction energies compared to standard DFT methods [13.3], but it also is able to correctly describe the asymptotic limit of bond dissociation of single [13.5] and even triple bonds, see section 5.2. The latter was a significant finding since the breaking of triple bonds constitutes a highly difficult case even for high level single-reference wave function methods and usually requires a multi-configurational description of the reference state. In [13.6] a method has been presented that even improves upon the accuracy of RPA methods based on a correction scheme in third order of perturbation theory. The current active research focusses on the development of an efficient implementation of the EXX-RPA method that possesses a scaling behaviour of $\mathcal{N}^5$ with the molecular size $\mathcal{N}$ which makes it not more costly than standard second-order perturbation theory methods.

Most of the methods that have been developed were implemented in the developers version of the Molpro quantum chemistry program [1] and therefore will also be available to the public sooner or later. Their general accessibility hopefully will be useful to other researchers who study the electronic structure of molecular systems. Moreover, the implementation of the methods in a program that has as great a number of features as Molpro certainly will help to combine the methods from this thesis with other modules of the program to extend their
applicability and/or to make them more efficient. In order to take up the statement of Longuett-Higgins from the year 1965 that "...the theory of intermolecular forces will soon be powerful enough not only to explain the crystal structures of simple substances but also to predict the stable conformations of the molecules which we ourselves are made of..." one can possibly now proclaim that modern quantum chemistry methods have emerged as invaluable tools that not only lead to an accurate qualitative understanding of chemical systems but can also predict many molecular properties with a high quantitative accuracy competing with experimental measurements.
Bibliography


Part II.

Academic career
7. Curriculum vitae


1998–1999 Diploma thesis at the institute of theoretical chemistry at the Heinrich-Heine University of Düsseldorf under the supervision of Prof. Wolfgang Domcke about the subject: “Korrelationskorrekturen zur ersten Ordnung intermolekularer Störungstheorie”.

10/1999–2002 Promotion at the institute of theoretical chemistry at the Heinrich-Heine University of Düsseldorf.

1/2003–12/2003 Continuance of the promotion at the institute of organic chemistry at the University of Duisburg-Essen under the supervision of Prof. Georg Jansen.

12/2003 Viva voce and attainment of Ph.D. degree in chemistry at the University of Duisburg-Essen about the subject: “Die Berechnung von intermolekularen Wechselwirkungsbeiträgen mit Dichtefunktional- und Brueckner-Coupled-Cluster-Methoden”

1/2004–12/2004 Postdoctoral research at the institute of organic chemistry at the University of Duisburg-Essen.

1/2005–12/2005 Postdoctoral research at the University of Århus (Denmark) at the department of theoretical chemistry in the group of Prof. Poul Jørgensen and Prof. Jeppe Olsen.

since 1/2006 Habilitation at the University of Erlangen-Nürnberg at the department of theoretical chemistry in the group of Prof. Andreas Görling.
8. List of scientific publications and talks

8.1. List of publications

(note: publications labeled (a)-(g) were made during the Ph.D. thesis [93] and are not contained in this thesis)


8. List of scientific publications and talks


### 8.2. List of talks

**February 2003** Mariapfarr/Österreich, Arbeitstagung für Theoretische Chemie: "Intermolecular interaction contributions from Brueckner Coupled Cluster theory"

**September 2003** Mühlheim, MPI für Kohlenforschung: "A combined Kohn-Sham and intermolecular perturbation theory approach"

**December 2003** Bochum, Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum: "A combined Kohn-Sham and intermolecular perturbation theory approach"

**May 2004** Stuttgart, Insitut für Theoretische Chemie, Universität Stuttgart: "Analysis of CH-π and π-π interactions in Benzene$_2$ and Ethyne$_2$ by using the intermolecular DFT-SAPT approach"

**July 2004** Århus/Dänemark, Kemisk Insititut (Teoretisk Kemi): "DFT-SAPT: a combined density functional and perturbation theory approach for intermolecular interactions"

**September 2004** Strasbourg/Frankreich, Laboratoire de Chimie Quantique et Modélisation Moléculaire, Université Louis Pasteur: "A zoo of orbitals"

**December 2006** Bristol/UK, School of Chemistry, Bristol University: "Orbital-dependent correlation functionals"

**August 2007** Amsterdam/Niederlande: DFT2007, 12th International conference on the Applications of Density Functional Theory: "Numerically stable optimised effective potential method for molecules and solids"
September 2008 Ramsau/Österreich, 44. Symposium für Theoretische Chemie: "Excitation energies from time-dependent density-functional theory using a frequency dependent exact exchange kernel"

February 2010 Stuttgart, Insitut für Theoretische Chemie, Universität Stuttgart: "Mr. Potential and Dr. Kernel: towards new approximations for the exchange-correlation functional"

June 2010 Telluride, Telluride Science Research Center, CO/USA: “A comparison between energy decompositions of the interaction energy using intermolecular perturbation theory and intermolecular force fields’

June 2010 Lausanne, CECAM (Centre Européen de Calcul Atomique et Moléculaire): van der Waals forces in DFT, RPA and beyond, “Accurate intermolecular interaction energies from a combination of MP2 and TDDFT response theory”

August 2010 Telluride, Telluride Science Research Center, CO/USA: “Combination of wave function, density functional theory and force field methods for the description of intermolecular interactions’

September 2010 Münster, 46. Symposium für Theoretische Chemie: “Assessment of a new orbital-dependent exchange-correlation functional based on the random phase approximation with exact Kohn-Sham exchange”
9. Lehre 2004-2011 (Teaching)


Die Vorlesungen “Wissenschaftliche Programmierung in Fortran” (WS07-08/SS08) und Quantenchemie 2 (SS09/SS10/SS11) mit zugehörigen Übungen wurden in weiten Teilen selber erarbeitet (die Quantenchemie 2 Vorlesung wird seit dem SS10 in zwei Teilen angeboten wobei der erste Teil von Prof. A. Görling gehalten wird).

Für das gemeinsame Seminar des Lehrstuhles für Theoretische Chemie und des Computer-Chemie-Centrum wurde in Absprache mit Prof. Andreas Görling und Dr. Wolfgang Hieringer in Teilen die Organisation und Diskussionsleitung übernommen sowie die Betreuung von externen Gästen.

Regelmäßige Lehrveranstaltungen
(sofern nicht anders angegeben wurden die Lehrtätigkeiten an der Universität Erlangen durchgeführt)

2000-2004 Übungen zur Theoretischen Chemie an der Universität Düsseldorf.


SS 2006/07/08 Übungen zur Theoretischen Chemie 2.

SS 2006/07 Übungen zur Theoretischen Chemie 1 für Chemiker und Molecular Scientists.

WS 2006-07 Übungen zur Theoretischen Chemie 2 für Molecular Scientists.

SS 2007 Übungen zur Theoretischen Chemie 3 für Molecular Scientists.

WS 2007-08, SS 2008 Programmierkurs Fortran90.
SS 2008  Praktikum Theoretische und Computerchemie für Fortgeschrittene.

WS 2008/09  Übungen zur Theoretischen Chemie 2.

SS 2009/10/11  Vorlesung und Übungen zur Quantenchemie 2.

WS 2010-11  Übungen zur Quantenchemie 1.

Sonstige Lehrveranstaltungen


• Gelegentliche Vorlesungsvertretungen in den Vorlesungen zur Theoretische Chemie.

Supervision of scientific thesis
(Co-supervision with Prof. A. Görling)


Part III.

Scientific publications
10. Intermolecular interactions

10.1. DFT-SAPT with density fitting

**Journal:** Journal of Chemical Physics

**Author(s):** A. Heßelmann, G. Jansen, M. Schütz

**Year:** 2005

**Volume:** 122

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**Key words:**
- symmetry-adapted perturbation theory
- ethyne dimer
- benzene dimer
- density fitting
Density-functional theory-symmetry-adapted intermolecular perturbation theory with density fitting: A new efficient method to study intermolecular interaction energies

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The previously developed DFT-SAPT approach, which combines symmetry-adapted intermolecular perturbation theory (SAPT) with a density-functional theory (DFT) representation of the monomers, has been implemented by using density fitting of two-electron objects. This approach, termed DF-DFT-SAPT, scales with the fifth power of the molecular size and with the third power upon increase of the basis set size for a given dimer, thus drastically reducing the cost of the conventional DFT-SAPT method. The accuracy of the density fitting approximation has been tested for the ethyne dimer. It has been found that the errors in the interaction energies due to density fitting are below $10^{-7}$ kcal/mol with suitable auxiliary basis sets and thus one or two orders of magnitude smaller than the errors due to the use of a limited atomic orbital basis set. An investigation of three prominent structures of the benzene dimer, namely, the T shaped, parallel displaced, and sandwich geometries, employing basis sets of up to augmented quadruple-$\zeta$ quality shows that DF-DFT-SAPT outperforms second-order Møller-Plesset theory (MP2) and gives total interaction energies which are close to the best estimates inferred from combining the results of MP2 and coupled-cluster theory with single, double, and perturbative triple excitations. © 2005 American Institute of Physics.

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I. INTRODUCTION

During recent years we have witnessed substantial progress in the field of first-principle calculations of intermolecular interaction energies.\textsuperscript{1} Through permanent improvement of quantum chemical algorithms and the incessant increase of computer power it has become possible to fulfill the simultaneous needs of large basis sets and high-level electron correlation treatment—at least for dimers of small molecules. In this case one can perform coupled cluster calculations with single and double excitations and perturbative inclusion of triple excitations [CCSD(T)], which is widely considered to be the most accurate practicable method at hand. A recent example is the calculation of a complete potential energy surface of the CO dimer with CCSD(T), yielding a corresponding theoretical vibrational spectrum in fairly good, though not fully quantitative, agreement with experiment.\textsuperscript{2} Yet, the CO dimer is also known to be a case where the lack of certain fifth-order electron correlation terms in CCSD(T) leads to formally incorrect behavior of the interaction energy at large distances,\textsuperscript{3,4} and one may wonder whether this will prevent CCSD(T) from resolving the remaining discrepancies of a few wave numbers from experiment in the complete basis set limit.

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For dimers consisting of larger molecules CCSD(T) presently cannot directly be applied in conjunction with large basis sets. In these cases one often resorts to second-order Møller-Plesset perturbation theory (MP2). Though MP2 formally is able to account for the long-range part of the dispersion energy it does this merely on a level which corresponds to an uncoupled Hartree-Fock representation of the underlying dynamical polarizabilities. In case of the benzene dimer this leads to an overestimation of the dispersion energy and, in turn, to a dramatic overestimation of the interaction energy.\textsuperscript{6–8} The benzene dimer demonstrates also that current density-functional theory (DFT) in general does not properly describe dispersion interactions;\textsuperscript{9} one of the two well-established minimum structures is not bound with the popular PW91 exchange-correlation functional (xc functional), while with the BLYP and B3LYP xc functionals even neither of them is bound.\textsuperscript{10} It should be noted, however, that this is not a failure of DFT itself but rather a flaw of the currently widespread models of the xc functionals, which, despite gradient or second derivative corrections, are too local to account for the long-range part of the dispersion energy.\textsuperscript{9,11}

All of the methods mentioned so far employ the supermolecular ansatz in which the interaction energy is calculated as the difference of the total energies of the dimer and the monomers. Yet, perturbation theory has been applied to the problem of intermolecular interactions since the early
days of quantum mechanics, and it continues to provide the rational framework for their understanding, modeling, and computation.\textsuperscript{12} In particular, the advent of many-body symmetry-adapted perturbation theory (MB-SAPT) (Ref. 13) in which the important intramonomer correlation effects on the various contributions to the interaction energy are treated through Möller-Plesset perturbation theory has resulted in a viable computational tool.\textsuperscript{14} The quality of MB-SAPT interaction energies compares to CCSD(T) in many cases.\textsuperscript{15,16} Unfortunately, this is also the case for its scaling behavior: both methods contain terms which formally scale like $N^3$, where $N$ is a measure of the size of the molecular system. To be more precise, CCSD(T) contains terms scaling like $n_{\text{occ,dimer}}^3 n_{\text{virt,dimer}}^4$ and $n_{\text{occ,dimer}}^4 n_{\text{virt,dimer}}^3$ in the triple excitation contribution, where $n_{\text{occ,dimer}}$ and $n_{\text{virt,dimer}}$ are the number of occupied and virtual orbitals of the dimer, respectively, while MB-SAPT in its second-order correlation correction to the dispersion energy contains terms scaling like $n_{\text{occ,monomer}}^3 n_{\text{virt,monomer}}^4$ and $n_{\text{occ,monomer}}^4 n_{\text{virt,monomer}}^3$. Please note that for homomolecular dimers $n_{\text{occ,monomer}} = n_{\text{occ,dimer}}/2$, but $n_{\text{virt,monomer}} > n_{\text{virt,dimer}}$ if the same dimer-centered basis set is used to describe both, the dimer and the monomers, as it is usually the case. For a given dimer thus both methods, CCSD(T) and MB-SAPT roughly scale with the fourth power of the number of basis functions.

Since the treatment of intramonomer electron correlation is relatively costly in MB-SAPT it has been proposed to combine SAPT with a much less expensive description of the monomers through DFT.\textsuperscript{17,18} While the theoretical foundations of the approach presented in Ref. 18 were unsatisfactory in the sense that none of the interaction energy contributions except the first-order electrostatic Coulomb interaction can ever be calculated with exactness from it, in Ref. 17 this problem was pointed out and an improved combined DFT-SAPT method was delineated. In this approach the second-order induction energy is determined from a solution of the coupled-perturbed Kohn-Sham (CPKS) equations, while the second-order dispersion energy is obtained from solution of the frequency-dependent coupled-perturbed Kohn-Sham equations (most often briefly called time-dependent density-functional theory, TDDFT). Provided that the exact xc potential and the exact frequency-dependent xc kernel of Kohn-Sham DFT were known and employed, these first- and second-order contributions could be calculated exactly in the complete basis set limit, a feature of DFT-SAPT which has been termed “potentially exact” in Ref. 17. Unfortunately, the intermonomer electron exchange corrections to these energy contributions do not share the feature of potential exactness and can only be approximated with DFT-SAPT. Furthermore, in general one cannot work with exact xc potentials and kernels.

From a systematic comparison of the first- and second-order contributions of DFT-SAPT with those of MB-SAPT it was found, however, that the approximations underlying DFT-SAPT work very well—provided that a well-balanced asymptotically corrected model of the xc potential is employed.\textsuperscript{19–21} In the case of the helium dimer it was even possible to carry out DFT-SAPT calculations with an essentially exact xc potential used in combination with the adiabatic local density approximation (ALDA) for the xc kernel to calculate the second-order contributions.\textsuperscript{22} Making use of an estimate of third and higher orders of the intermolecular perturbation based on full configuration interaction results the accuracy was remarkable: the best theoretical estimates of about 11.0 K for the interaction energy were reproduced within 1% deviation. The deviation increases to 5% when the third- and higher-order contributions were estimated at the Hartree-Fock level, as one usually is forced to, while CCSD(T) differs by 3% from the best theoretical estimates.

The helium dimer has also been studied with the so-called SAPT(KS) approach,\textsuperscript{23} i.e., the approach proposed in Ref. 18 which employs an uncoupled approximation of the induction and dispersion energies, thus destroying their potential exactness.\textsuperscript{17} With SAPT(KS) the magnitude of the dispersion energy was overestimated by more than 1 K for all of the investigated xc potentials, leading to errors of 10% and more in the interaction energy.

The first application of DFT-SAPT on a larger scale is a recent study\textsuperscript{24} on the potential energy surface of the carbon monoxide dimer, computed at 2500 dimer geometries. As for the helium dimer, CCSD(T) and DFT-SAPT employing an asymptotically corrected xc potential were found to be of comparable accuracy: the energy difference between the two lowest rovibrational levels with zero total angular momentum deviates by $+5.4 \text{ cm}^{-1}$ from the experimental result of 0.88 cm$^{-1}$ with the DFT-SAPT surface and by $-2.9 \text{ cm}^{-1}$ with the CCSD(T) surface.

DFT-SAPT contains terms scaling like $n_{\text{occ}}^3 n_{\text{virt}}^3$, leading to a nominal $N^6$ scaling with system size (from now on $n_{\text{occ}}$ and $n_{\text{virt}}$ will always refer to monomer orbitals in the dimer centered basis set). For a given dimer DFT-SAPT scales like $N^4$ ($N$ is number of basis functions per atom) with the basis set size, due to the need to compute two-electron integrals in the MO basis. While this is a step forward with respect to the nominal scaling properties of MB-SAPT and CCSD(T) for applications to large dimer systems the scaling properties need to be improved further. This can be achieved through the density fitting (DF) approach, alternatively called “resolution-of-the-identity” (RI) approach, in which certain intermediate quantities of a calculation are approximated through expansion in an auxiliary basis set.\textsuperscript{25–28} This approach has been successfully implemented into a large variety of quantum chemical methods.\textsuperscript{25–29} Recently, it has also been proposed to use density fitting to extract dispersion energies from TDDFT calculations.\textsuperscript{30} With this approach computation of the dispersion energy scales with $N^3$ (more exactly with $n_{\text{aux}}^3$, where $n_{\text{aux}}$ is the number of auxiliary basis functions)—but only if the expansion of the required frequency-dependent linear response functions (polarization propagators) in the auxiliary basis set is already available. Unfortunately, the authors of Ref. 30 do neither consider the computational effort for obtaining the response functions and that for their fitting into auxiliary functions, nor do they provide details concerning implementation, choice of auxiliary basis set, and accuracy of the fitting. The response functions, required for a fairly small number of frequencies in the order of 10, are composed of $n_{\text{occ}}^2 n_{\text{virt}}^2$ matrix elements, so that their calculation via matrix
inversion or related iterative techniques nominally scales like 
\( n_{\text{occ}}^3 n_{\text{virt}}^3 \) (where the power of 3 may be slightly improved to 2.8 using sophisticated techniques such as Strassen's algorithm). This is the same scaling as that of the equivalent route to dispersion energies used in Ref. 21, though the latter approach presumably has a larger prefactor. Furthermore, density fitting does not come for free; for example, if one has to expand all of the products between occupied and virtual orbitals into \( n_{\text{aux}} \) auxiliary functions, as for the case at hand, one needs to solve \( n_{\text{occ}} n_{\text{virt}} \) linear equation systems of dimension \( n_{\text{aux}}^3 \times n_{\text{aux}} \) for the fitting coefficients, resulting in a nominal \( N^9 \) scaling. Assembling the fitted charge distributions to quantities with two occupied and two virtual orbitals (such as they occur, for example, in the TDDFT response equations or in MP2) requires \( n_{\text{occ}}^5 n_{\text{aux}}^2 \) operations. Thus, a nominal \( N^5 \) scaling is the best one can hope for if no further tricks are played such as efficient prescreening techniques, local methods,\(^{27-29}\) and the like. Still, even for MP2 which nominally already scales like \( N^3 \) it is very much worthwhile to introduce density fitting, in particular (but not only), since scaling with the number of basis functions per atom for a given molecule may be brought down from \( N^3 \) to \( N^3 \).

In this paper the implementation of the first complete density fitting variant of DFT-SAPT is described, i.e., in which computation of all of its first- and second-order contributions makes use of density fitting. In order to assess the accuracy of the density fitting approximation for systems dominated by \( \pi-\pi \) interactions and the scaling properties of the approach, termed DF-DFT-SAPT, three structures of the ethylene dimer (Et\(_2\), in T shaped, parallel displaced, and staggered geometries) were investigated. It will be shown that DF-DFT-SAPT scales as \( N^3 \) with the system size, and as \( N^3 \) upon increase of the basis set size for a given dimer, thus enabling to treat dimers with large basis sets which to date were accessible with second-order MP2 only. To illustrate this point, we apply DF-DFT-SAPT to the benzene dimer (Bz\(_2\)), a prototype system for the investigation of \( \pi-\pi \) interactions and, as already mentioned, a well-known example for the failure of MP2 to accurately account for dispersion energies.\(^{6-8}\) Atomic basis function sets comprising up to 1512 basis functions are used to study the interaction energies of three important dimer structures: the T shaped and parallel-displaced (PD) minima which are estimated to be more or less isosmotergetic at the CCSD(T) level (while this is not at all the case at the MP2 level), and a stacked (S) geometry.

The organization of the paper is as follows: the following section briefly describes theoretical foundations and the implementation of the density fitting approximation. Section III presents the technical details of the computations. In Sec. IV the errors and performance improvements introduced by density fitting are investigated, followed by a discussion of the interaction energy contributions for Et\(_2\) and Bz\(_2\) and a comparison to supermolecular and MB-SAPT interaction energies. The most important results are summarized in the last section.

### II. DENSITY-FUNCTIONAL SYMMETRY-ADAPTED PERTURBATION THEORY

Conventions: indices \( i,a \) denote occupied/virtual orbitals of monomer \( A \), and indices \( j,b \) denote occupied/virtual orbitals of monomer \( B \). Furthermore, greek letter indices \( \mu,\nu,\ldots \) denote AO basis functions, while indices \( P,Q \) denote functions of the auxiliary fitting basis. The following formulas refer to the closed-shell case using a dimer-centered basis set.

#### A. First-order terms

The Coulomb or electrostatic interaction energy of a dimer system \( AB \) is given as

\[
E_{\text{pol}}^{(1)} = \langle \Phi_0^A | \hat{V}_{AB} | \Phi_0^B \rangle, \tag{1}
\]

where \( \Phi_0^{A,B} \) denotes the exact ground state wave function of monomer \( A \), \( B \), and \( \hat{V}_{AB} \) is the intermolecular interaction potential which comprises all Coulomb interactions between the electrons and nuclei of the two monomers. This formula may be rewritten in terms of the densities of the monomers. Expanding these densities in an atomic orbital (AO) basis set the Coulomb energy can be expressed as

\[
E_{\text{pol}}^{(1)} = \text{Tr}(\mathbf{P}^A \mathbf{V}^B + \mathbf{P}^B \mathbf{V}^A + 2 \mathbf{P}^B \mathbf{J}^B) + E_{\text{nic}}, \tag{2}
\]

where \( \mathbf{P}^{A,B} \) are the one-particle density matrices, \( \mathbf{V}^{A,B} \) the electrostatic potentials, and \( \mathbf{J}^{A,B} \) the Coulomb matrices of \( A \), \( B \) in the AO basis set, respectively. \( E_{\text{nic}} \) is the intermolecular repulsion energy.

The first-order exchange energy is given as

\[
E_{\text{exch}}^{(1)} = \frac{\langle \Phi_0^A | \hat{P}_{\mathcal{P}} | \hat{P}_{\mathcal{P}} \Phi_0^B \rangle}{\langle \Phi_0^A | \hat{P}_{\mathcal{P}} | \Phi_0^B \rangle}, \tag{3}
\]

where \( \mathcal{P} = \mathcal{P}_1 + \mathcal{P}_2 + \cdots \) is the many-electron intermonomer permutation operator. \( \hat{P}_{\mathcal{P}} = -\sum_{\gamma<\alpha,\beta<\delta} \hat{P}_{\alpha\beta} \hat{P}_{\gamma\delta} \) exchanges single pairs of electrons between the monomers, \( \hat{P}_{\mathcal{P}} \) exchanges two pairs, etc. This expression may be expressed in terms of monomer many-particle density matrices. For a single-determinant wave function the many-particle density matrices are antisymmetrized products of the one-particle density matrix. One of the basic approximations in DFT-SAPT is to use the one-particle density matrix of the Kohn-Sham determinant to compute the many-particle density matrices. Evaluating Eq. (3) with Hartree-Fock determinants implicitly also corresponds to employing an antisymmetrized product approximation of the many-particle density matrices. Expressing the resulting equations given in Ref. 31 in terms of the AO basis yields:\(^{12}\)

\[
E_{\text{exch}}^{(1)} = -\text{Tr} \left( \mathbf{P}^A \mathbf{K}^B + 2 \mathbf{T}^A \mathbf{h}^B + 2 \mathbf{T}^B \mathbf{h}^A + 4 \mathbf{T}^B \mathbf{h}^A + 4 \mathbf{h}^B \right) + 8(\mathbf{T}^A + \mathbf{T}^B)(\mathbf{J}[\mathbf{T}^A] - \frac{1}{2} \mathbf{K}[\mathbf{T}^A]) + 8(\mathbf{T}^A + \mathbf{T}^B)(\mathbf{J}[\mathbf{T}^B] - \frac{1}{2} \mathbf{K}[\mathbf{T}^B]). \tag{4}
\]

The quantities \( \mathbf{J}[\mathbf{X}] \) and \( \mathbf{K}[\mathbf{X}] \) defined as
are Coulomb and exchange matrices formed from a generalized density matrix $X$. The matrices $\mathbf{K}^{A,B} = \mathbf{K}[\mathbf{P}]$ are the usual exchange matrices of monomer $A$, $B$ in the AO basis, and $B^{A,B} = \mathbf{V}^{A,B} + 2\mathbf{J}^{A,B} - \mathbf{K}^{A,B}$. The matrices $\mathbf{T}^{A,B}$, finally, comprise the expansion $-S + S^2 - S^3 + \cdots$ of the dimer overlap matrix

$$
\mathbf{S} = \begin{pmatrix}
0 & \mathbf{S}_{ij} \\
\mathbf{S}_{ji} & 0
\end{pmatrix} \text{ where } \mathbf{S}_{ij} = \langle \Phi_i | \Phi_j \rangle,
$$

via the inverse of the matrix $[S + 1]$, back transformed to AO basis by the MO coefficient matrices $\mathbf{C}^A$ and $\mathbf{C}^B$ of monomer $A$ and $B$, respectively. They are defined as

$$
\mathbf{T}_A = (\mathbf{C}^A)\dagger (S + 1)^{-1} - 1 \mathbf{C}^A,
$$

$$
\mathbf{T}_B = (\mathbf{C}^B)\dagger (S + 1)^{-1} - 1 \mathbf{C}^B.
$$

The second-order induction energy can be written in the general form

$$
E_{\text{ind}}^{(2)} = -\sum_{m \neq n} \frac{|\langle \Phi_m^A \Phi_n^B | \hat{V}^{AB} | \Phi_m^A \Phi_n^B \rangle|^2}{E_m^A - E_n^B}
$$

$$
-\sum_{m \neq n} \frac{|\langle \Phi_m^A \Phi_n^B | \hat{V}^{AB} | \Phi_m^A \Phi_n^B \rangle|^2}{E_m^B - E_n^A}
$$

$$
= E_{\text{ind}}^{(2)}(A \leftrightarrow B) + E_{\text{ind}}^{(2)}(A \rightarrow B),
$$

where $\Phi_m^A$ and $E_m^A$ are the ground state wave functions and energies of monomers $A$ and $B$ while $\Phi_n^B$ and $E_n^B$ denote the excited states and energies of the monomers. The two terms $E_{\text{ind}}^{(2)}(A \leftrightarrow B)$ and $E_{\text{ind}}^{(2)}(A \rightarrow B)$ indicate the induction energy of $A$ due to the perturbing field of $B$ and the induction energy of $B$ due to the perturbing field of $A$, respectively. In the framework of coupled-perturbed Hartree-Fock (CPHF) (Ref. 33) and Kohn-Sham30 theory the induction energy can be expressed as

$$
E_{\text{ind}}^{(2)} = -\mathbf{x}^{A} \omega^{B} - \mathbf{x}^{B} \omega^{A}
$$

with $\mathbf{x}^{A,B}$ representing the CPHF/CPKS coefficients obtained with the electric potential of the respective partner monomer, and

$$
\omega^{A,B} = [(\mathbf{C}^{B,A})\dagger \mathbf{V}^{A,B} + 2\mathbf{J}^{A,B} \mathbf{C}^{B,A})]_{\text{oc,virt}}
$$

$$
= [(\mathbf{C}^{B,A}) \mathbf{R}^{A,B} \mathbf{C}^{B,A})]_{\text{oc,virt}}.
$$

The corresponding exchange-induction energy in the so-called $S^2$ approximation can be written as

$$
E_{\text{exch-ind}}^{(2)}(S^2) = \langle \Phi_0^A \Phi_0^B | \hat{V}^{AB} - E_{\text{pol}}^{(1)} | \mathcal{P}_1 - \mathcal{P}_2 | \Phi_0^A \Phi_0^B \rangle |\Phi_0^A \Phi_0^B \rangle,
$$

where $\mathcal{P}_i = \langle \Phi_0^A \Phi_0^B | | \mathcal{P}_i | \Phi_0^A \Phi_0^B \rangle$ can be regarded as the square of the overlap ($S^2$) between the systems, and

$$
\Phi^{(1)}_{\text{ind}} = \sum_{m \neq n} \langle \Phi_m^A \Phi_n^B | \hat{V}^{AB} | \Phi_m^A \Phi_n^B \rangle \Phi_m^A \Phi_n^B
$$

$$
- \sum_{m \neq n} \langle \Phi_m^A \Phi_n^B | \hat{V}^{AB} | \Phi_m^A \Phi_n^B \rangle \Phi_m^A \Phi_n^B
$$

is the first-order induction wave function of the system. Transforming the corresponding expression as obtained in the single-determinant approximation of the ground state wave function14,34 into the AO basis22 the exchange-induction energy of monomer $A$ reads

$$
E_{\text{exch-ind}}^{(2)}(A \leftrightarrow B) = \text{Tr}(2\mathbf{X}^A \mathbf{K}^B + \mathbf{X}^A \mathbf{S} \mathbf{P}^B \mathbf{A}^B + 2\mathbf{X}^A \mathbf{J}[O])
$$

$$
- \mathbf{X}^A [\mathbf{K}] + \mathbf{P}^B \mathbf{S} \mathbf{X}^A \mathbf{B}^A - \frac{1}{2} \mathbf{P}^B \mathbf{S} \mathbf{X}^A \mathbf{B}^A \mathbf{O}^A
$$

$$
- \mathbf{P}^B \mathbf{S} \mathbf{O} \mathbf{X}^A \mathbf{B}^A - \frac{1}{2} \mathbf{S} \mathbf{O} \mathbf{X}^A \mathbf{B}^A \mathbf{K} \mathbf{O},
$$

where $\mathbf{S}$ now is the AO overlap matrix, $\mathbf{O} = \mathbf{P}^A \mathbf{S} \mathbf{P}^B$, $\mathbf{X}^{A,B}$ are the CPHF/CPKS coefficients backtransformed to the AO basis, and $\mathbf{O}^{A,B}$ is implicitly defined in Eq. (11). The corresponding $E_{\text{exch-ind}}^{(2)}(A \rightarrow B)$ term can be obtained by exchanging the indices $A$ and $B$ in the above expression.

C. Dispersion and exchange-dispersion terms

The second-order dispersion energy is given as

$$
E_{\text{disp}}^{(2)} = -\sum_{m \neq n} \frac{|\langle \Phi_m^A \Phi_n^B | \hat{V}^{AB} | \Phi_m^A \Phi_n^B \rangle|^2}{E_m^A - E_n^B}
$$

$$
= \langle \Phi_0^A \Phi_0^B | \hat{V}^{AB} | \Phi_0^{(1)} \rangle,
$$

where $\Phi^{(1)}_{\text{disp}}$ is the first-order dispersion wave function of the system. In the framework of time-dependent Hartree-Fock (TDHF) theory35 and TDDFT (Ref. 21) this, by virtue of the Casimir-Polder integral transform, can be written as

$$
E_{\text{disp}}^{(2)} = 4 \sum_{ia,jb} T_{ia,jb}(ia|jb),
$$

where the amplitudes $T_{ia,jb}$ are defined as

$$
T_{ia,jb} = \frac{1}{8} \pi a_{ia} a_{jb} \int_{0}^{\infty} \chi_{ia,i'j'}(i \omega) \chi_{jb,j'b'}(i \omega) d \omega,
$$

with $\chi_{ia,i'j'}(i \omega)$ specifying a generalized linear response function. In the uncoupled approximation the amplitudes can be written in the form

$$
T_{ia,jb} = \frac{(ia|jb)}{\epsilon_i - \epsilon_j - \epsilon_a - \epsilon_b},
$$

with $\epsilon_i$ and $\epsilon_j$ denoting occupied and virtual orbital energies of monomer $A$.
The corresponding exchange-dispersion energy is defined as
\[
E_{\text{exch-disp}}^{(2)}(S^2) = \langle \Phi_0^A \Phi_0^B | (\hat{V}^{AA} - E_{\text{pol}}^{(1)}(\hat{P}_1 - \hat{P}_2)) | \Phi_0^{(1)} \rangle,
\]
(19)

Using a single-determinant approximation for the ground state wave functions and expressing the dispersion wave function in the single-determinant framework with the help of the amplitudes defined in Eq. (17) yields in the MO basis:\textsuperscript{26}

\[
E_{\text{exch-disp}}^{(2)} = -2 \sum_{ia,jb} T_{ia,jb} \left[ -\sum_{a'b'} (i' a | j' b) S_{a' b'} S_{a b} + \sum_{l',j'} (i' a | j' b) S_{l' j'} + \sum_{l',j'} (i' a | j' b) S_{l' j'} - 2 (i' a | j' b) S_{l' j'} - \sum_{l' j'} (i' a | j' b) S_{l' j'} - \sum_{l' j'} (i' a | j' b) S_{l' j'} + \sum_{l' j'} (i' a | j' b) S_{l' j'} \right],
\]
\[
+ \sum_{j'} A \left[ -2 \omega_{j' b} S_{j' j} + \omega_{j' b} S_{j' j} \right] + \sum_{j'} B \left[ -2 \omega_{j' b} S_{j' j} + \omega_{j' b} S_{j' j} \right],
\]
(20)

where \( S \) now is the overlap matrix in MO basis (including both monomers), and \( \omega_{j' b} \) is defined in Eq. (11).

**D. High-order terms**

Contributions of third- and higher-order in the perturbing intermolecular interaction potential can easily be estimated on the uncorrelated level as

\[
\delta_{\text{HF}} = E_{\text{ind}}(\text{HF}) - E_{\text{pol}}^{(1)}(\text{HF}) - E_{\text{ind}}^{(2)}(\text{HF}) - E_{\text{ind}}^{(3)}(\text{HF}),
\]
where \( E_{\text{ind}}(\text{HF}) \) is the supermolecular counterpoise-corrected Hartree-Fock interaction energy, while the other terms are calculated as shown above, yet using the Hartree-Fock (response) density matrices.\textsuperscript{14}

**E. The density fitting approximation in DFT-SAPT**

The DF approximation for the four-index electron repulsion integrals (ERIs) in AO basis \((\mu | \nu | \rho | \sigma)\) takes the form

\[
(\mu | \nu | \rho | \sigma)_{\text{DF}} = \sum_{P} \langle \mu | P \rangle c_{\mu \nu \rho \sigma}^P,
\]
(22)

\[
c_{\mu \nu \rho \sigma}^P = \sum_{Q} [J^{-1}]_{PQ} \langle \Omega | \rho \sigma \rangle,
\]
(23)

where the \( \langle \mu | P \rangle \) are three-index ERIs between a pair of AO basis functions and a fitting function, \([J]_{PQ}\) is the Coulomb metric of the fitting functions, and the \( c_{\mu \nu \rho \sigma}^P \) are the fitting coefficients.

All components of the DFT-SAPT first- and second-order induction terms which involve ERIs have the form of Coulomb or exchange contractions with generalized “density” matrices (denoted by \( X \), as given in Eqs. (5). To simplify these terms, density fitting can be used in an analogous way as in DF-HF (Ref. 29) or in the Z-CPHF procedure of the DF-LMP2 analytical energy gradient.\textsuperscript{28} As in those cases, all generalized density matrices \( X \) occurring in DFT-SAPT can be written as the product of two coefficient matrices \( C \), transforming from AO to occupied MO basis of one of the monomers, which are contracted over the occupied index in this matrix multiply, i.e.,

\[
X = C^T \tilde{C}.
\]
(24)

For example, in the calculation of the first-order exchange contribution we have for \( X = T^A \)

\[
C = C^B,
\]
(25)

\[
\tilde{C} = ([S + 1]^{-1} - 1) C^A.
\]
(26)

Hence, after invoking the DF approximation for the ERIs \((\mu | \nu | \sigma)\) the expression for the exchange matrix \( K[X] \) can be rewritten in mixed AO/occupied MO basis as

\[
K[X]_{\mu \nu} = \frac{1}{2} \sum_P \sum_{i \rho} (\mu | P) \tilde{c}_{i \rho}^P.
\]
(27)

In Eq. (26) \((\mu | P)\) denotes the three-index ERIs with one index transformed to occupied space by the coefficient matrix \( C \), while \( \tilde{c}_{i \rho}^P \) represents the fitting coefficients of Eq. (25) transformed to occupied space by the coefficient matrix \( \tilde{C} \), i.e.,

\[
(\mu | P) = \sum_{\rho} (\mu | \rho) C_{\rho \nu},
\]
(27)

\[
\tilde{c}_{i \rho}^P = \sum_{\Omega} [J^{-1}]_{PQ} \langle \Omega | \rho \sigma \rangle\]
(28)

with

\[
(\mu | P) = \sum_{\rho} (\mu | \rho) \tilde{C}_{\rho \nu}.
\]
(29)

This form has the advantage that the number of fitting coefficients, which have to be evaluated via Eq. (28) and contracted via Eq. (26) is substantially reduced, relative to Eqs. (22) and (23), since one index just runs over the limited occupied rather than the whole AO space.
The construction of the Coulomb matrices is straightforward and proceeds via a two-index contraction involving the generalized density matrices $X$ directly, as described in Refs. 28 and 29.

For the dispersion- and exchange-dispersion components of the intermolecular interaction energy the frequency-dependent response propagator $\chi_{ia',i'a'}(i\omega)$ of Eq. (15) is needed. Following Görling et al., this quantity can be calculated as

$$\chi(i\omega) = \lambda + \lambda F (\mathbf{J} - N^T \lambda F)^{-1} N^T \lambda,$$

where the elements of the matrix $\lambda$ are given as

$$\lambda_{ia,i'a'}(\omega) = \delta_{ia,i'a'} \left( \epsilon_a - \epsilon_i \right)^2 + \omega^2.$$  

Here, $\omega$ is the imaginary part of $i\omega$, thus a real number. Furthermore, the matrix $F$ is defined as $(ia$ serves as a compound index in this matrix) $F_{ia,p} = (ia|P) + (ia|f_{\omega,p})$, with $f_{\omega,p}$ denoting the exchange-correlation kernel. $\mathbf{J}$ is the generalized metric of the auxiliary basis

$$[\mathbf{J}]_{PQ} = (P|\eta|Q),$$

where either $\eta = 1/r_{12}$ [the usual Coulomb metric in DF, $[\mathbf{J}]_{PQ} = [\mathbf{J}]_{PQ}$, as used in Eqs. (23) and (28)], or $\eta = 1/r_{12} + f_{\omega,p}$ (what Görling et al. denoted as the natural norm). Finally, the matrix $N$ is defined as

$$N_{ia,p} = (ia|\eta|P).$$

From the response propagators for monomer A and B the amplitudes specified in Eq. (30) can be computed as

$$T_{ia,jb}(i\omega) = -\frac{1}{8\pi} \int_0^\infty \overline{T_{ia,jb}(i\omega)} d\omega,$$

with

$$\overline{T_{ia,jb}(i\omega)} = \sum_{i'a',j' b'} \chi_{ia,i'a'}(i\omega) \times (i'a'|j' b') \chi_{j'b',i'b}(i\omega).$$

By using the DF approximation for the four-index integrals ($i'a' |j' b'$), i.e.,

$$(i'a'|j' b') = \sum_{PQ} c_{ia}^P [\mathbf{J}]_{PQ} c_{j'b'}^Q,$$

the explicit computation of the response propagators can be avoided. Instead, their contraction with the fitting coefficients is computed, i.e., the three-index object

$$\overline{X}_{ia,\omega}(i\omega) = \sum_{i'a'} \chi_{ia,i'a'}(i\omega) c_{i'a'}^P,$$

and the frequency-dependent quantity $\overline{T}_{ia,jb}(i\omega)$, which in our implementation is used for both the dispersion and the exchange-dispersion energies, is then obtained in an $N^5$ step as

$$\overline{T}_{ia,jb}(i\omega) = \sum_{PQ} \overline{X}_{ia,\omega}(i\omega) [\mathbf{J}]_{PQ} \overline{X}_{j'b',\omega}(i\omega).$$

The final amplitudes are obtained by numerical quadrature over $\omega$, according to Eq. (35). Around ten or less points in a Gauss-Chebyshev quadrature turn out to be sufficient to evaluate this integral (vide infra). Of course, the intermediate four-index object $T_{ia,jb}(i\omega)$ is computed on the fly and individual submatrices (for fixed $i, j$) are immediately discarded after accumulation to $T_{ia,jb}$. Furthermore, the quantity $\overline{X}(i\omega)$ is thrown away before computing it again for the next frequency point. Finally, after the integration is completed the dispersion energy is obtained from the amplitudes according to Eq. (15). Using the uncoupled amplitudes from Eq. (18) in the expression for $E_{\text{disp}}^{(2)}$ yields the uncoupled dispersion energy, where the integrals occurring in Eqs. (18) and (15) are computed via DF as

$$(ia|jb) = \sum_P (ia|P)c_j^P.$$  

Inserting Eqs. (35) and (39) along with Eq. (37) into Eq. (15) the dispersion energy can be written as

$$E_{\text{disp}}^{(2)} = 4 \sum_{PQ} T_{PQ} [\mathbf{J}]_{PQ},$$

with the overall computational cost scaling as $N^4$ with the molecular size when avoiding the explicit construction of $T_{ia,jb}(i\omega)$. The $T_{PQ}$ are conveniently calculated from two-index objects $\overline{X}_{PQ}(i\omega)$, which, in turn, are obtained by contraction of $\overline{X}_{ia,\omega}(i\omega)$ with the fitting coefficients. In case of the exchange-dispersion energy density fitting techniques can also be introduced straightforwardly. The terms involving two-electron integrals on the right-hand side of Eq. (20) have been approximated by using density fitting of the two-electron integrals [see Eq. (40)]. For example the first term in the brackets can be written as

$$\sum_{a'b'} (ia'|jb') S_{a',a} S_{b',b} = \sum_{a'b'} c_{ia'}^P S_{a' a} (P|jb') S_{b'b}.$$  

By applying the one-index transformations this yields

$$\sum_{a'} c_{ia'}^P S_{a' a} = c_{ia}^P,$$

$$\sum_{b'} (P|jb') S_{b'b} = (P|ja).$$

Eq. (41) then takes the form

$$\sum_{a'b'} (ia'|jb') S_{a'a} S_{b'b} = c_{jb}^P (P|ja).$$

Analogous transformations have been used for the other terms of Eq. (20). In contrast to the dispersion energy [cf. Eq. (41)] there is no straightforward way to come below a nominal $N^5$ scaling upon density fitting of the various terms in Eq. (20).

III. COMPUTATIONAL DETAILS

The density fitting DFT-SAPT (DF-DFT-SAPT) method has been implemented in the MOLPRO 2002.8 (Ref. 38) program package. In this section we describe the test calculations performed with the new program for the selected con-
formers of Et$_2$ and Bz$_2$, respectively. The geometries used for Bz$_2$ (depicted in Fig. 1) are the best estimate geometries for the T, PD, and S structures presented in Ref. 39. They were combined with the recommended monomer geometry of Gauss and Stanton,\textsuperscript{40} $R_{CC} = 1.3915$ Å and $R_{CH} = 1.0800$ Å.

In order to assess the accuracy of the density fitting approximation we also consider three analogous structures of the ethyne dimer: a T shaped and a PD structure, furthermore a “staggered” (S) structure in which the molecular axes are orthogonal to the line connecting the respective centers of mass and rotated by 90° with respect to each other (cf. Refs. 41 and 42). These structures are depicted in Fig. 2. They were optimized in very much the same way as done in Ref. 39 for the benzene dimer. First the geometries of the monomers were optimized with MP2 using the aug-cc-pVXZ ($X = D, T, Q$) basis sets from Kendall, Dunning, and Harrison,\textsuperscript{43} correlating the valence electrons only. The values obtained at the quadruple-$\zeta$ level are in excellent agreement with the best estimates of Martin, Lee, and Taylor:\textsuperscript{44} $R_{CC} = 1.2092$ Å (versus 1.2028 Å best estimate) and $R_{CH} = 1.0614$ Å (versus 1.0618 Å). The MP2 monomer geometries as obtained with the respective basis sets then were kept fixed during the location of the dimer stationary points with MP2 and CCSD(T), where up to quadruple-$\zeta$ basis sets have been employed in valence-only MP2 calculations and up to triple-$\zeta$ basis sets for CCSD(T). One- (for T and S) and two-dimensional (for PD) grids of 5 and $9 \times 4$ points (0.1 Å intervals), respectively, were computed on the counterpoise-corrected potential energy surfaces and fitted to polynomials from which the stationary points were inferred. Best estimates for intermolecular distances were then obtained from the CCSD(T)/aug-cc-pVTZ results corrected by the difference of the MP2/aug-cc-pVQZ and MP2/aug-cc-pVTZ values. The optimized intermonomer distance parameters were combined with the best estimate monomer geometries of Martin, Lee,
and Taylor quoted above to yield our best estimates of the dimer geometries. These were used in all subsequent calculations.

The aug-cc-pVXZ basis sets were also used as AO basis sets for the DFT-SAPT calculations. As auxiliary fitting basis set the JK-fitting basis of Weigend was employed for all terms involving the calculation of generalized Coulomb and exchange matrices (cf. Sec. II). Unless indicated otherwise the cc-pV(X + 1)Z JK-fitting basis was used in conjunction with the aug-cc-pVXZ AO basis, i.e., X incremented by one relative to the corresponding AO basis. For the intermolecular correlation terms, i.e., the dispersion and exchange-dispersion terms, on the other hand, the related MP2-fitting basis of Weigend, Köhn, and Hättig was employed, i.e., the aug-cc-pVXZ MP2-fitting basis together with the aug-cc-pVXZ AO basis set.

For the monomer DFT calculations the asymptotically corrected PBE0 exchange-correlation potential was used, denoted here as PBE0AC. In this xc potential the wrong asymptotic behavior of the corresponding PBE exchange potential has been corrected by a combination with the asymptotically correct LB94 xc potential via the gradient-regulated connection approach of Grünig et al. The PBE0AC xc potential has proven to give accurate first- and second-order electric properties for a range of small molecules as well as good interaction energy contributions when compared to standard many-body SAPT calculations.

Furthermore the same xc potential but with the nonlocal exact exchange part replaced by the local effective exact exchange potential has also been employed (termed as LPBE0AC in the following). The exact exchange potential has been obtained from the local Hartree-Fock (LHF) scheme by Della Sala and Görling. Only one transformation step has been made to generate the local exchange potential with the orbitals from a preceding PBE0AC calculation as input. In order to achieve an accurate representation of the local exchange potential the Slater potential has been calculated fully numerically. However, no special treatment of the far asymptotic region has been made because it has been found that this does not have a significant influence on the DFT-SAPT results presented here. The local effective exact exchange potential has then been included in a subsequent self-consistent LPBE0AC calculation to generate the orbitals and orbital eigenvalues needed for DFT-SAPT.

The exchange-correlation matrix elements were calculated via numerical integration. In order to obtain a reasonable description of the virtual orbitals fine integration grids have been used with about $8 \times 10^3$ points for the ethylene dimer and more than $2.4 \times 10^5$ points for the benzene dimer. In case of the benzene dimer also a coarser grid has been tested with about $8 \times 10^3$ points for Et$_2$ and $1.1 \times 10^5$ points for B$_2$ turned out to be sufficiently accurate.

For the computation of the amplitudes according to Eq. (35) a Gauss-Chebyshev integration scheme (as described in Ref. 52) was employed. 12 integration points were used by default. Test calculations with either 8 or 16 grid points showed deviations in the resulting dispersion energy of less than 0.0012 kcal/mol. For that reason, only eight integration points were used in the later calculations of B$_2$ within the aug-cc-pVQZ AO basis.

The $\delta$(HF) estimate of interaction energy contributions of third and higher order has always been calculated as in standard MB-SAPT (Ref. 14) (cf. Sec. II D).

IV. RESULTS AND DISCUSSION

A. Analysis of density fitting error

In Table I the absolute errors due to the density fitting approximation of the individual DFT-SAPT contributions are displayed for the PD structure of Et$_2$ (calculated in the aug-cc-pVTZ AO basis set). It can be seen that the DF error for all contributions is already fairly small even if the smallest double-$\zeta$ fitting basis set is used: the relative errors for $E^{(2)}_{\text{exch-disp}}$ and $\delta$(HF) are below 3% and for all other terms below 0.3%. It can be observed that the fitting error is systematically reduced by using larger fitting basis sets. By default we use the cc-pV(X + 1)Z JK-fitting basis set and the aug-cc-pVXZ MP2-fitting basis set in conjunction with the aug-cc-pVXZ AO basis, as mentioned above. In the given example (see Table I) one can see that at this level all relative errors are clearly below 1%. This does not change when also the monomer calculations are performed by using density fitting of the Coulomb and exchange matrix (the corresponding absolute errors are given in parenthesis in Table I). In fact some of the errors become even smaller when using DF for the monomers. Note that the reduction of the DF error in the $\delta$(HF) term is due to the fact that now both, $E_{\text{int}}$(HF) and the various Hartree-Fock interaction energy contributions have been calculated with the same DF approximations (cf. Eq. (21)).

Table I also shows the density fitting errors in the total interaction energies. Note that some of the errors in the individual interaction energy contributions tend to cancel each other. With the fortuitous exception of the double-$\zeta$ auxiliary basis set the total error is larger when also the monomer DFT calculations are made with the density fitting approximation, as it will usually be the case. This is a simple consequence of the fact that in this case the total interaction energy, and not just the intramonomer electron correlation contributions together with the (exchange-) dispersion contributions is subject to density fitting. Note, however, that even in this case the total error becomes as small as $10^{-3}$ kcal/mol or less than 0.1% of the total interaction energy with the suitable, i.e., the quadruple-$\zeta$ fitting basis set, thus justifying our choice of the default auxiliary basis sets as described above in all of the following calculations.

This analysis indicates that the errors due to density fitting in DFT-SAPT are well controllable and that even rather small fitting basis sets could be used when one wishes to calculate entire potential energy surfaces with DF-DFT.
10. Intermolecular interactions

**TABLE I.** Absolute errors due to the density fitting approximation of DFT-SAPT interaction energy contributions (in 10⁻³ kcal/mol) for Et₂ (PD structure) in the aug-cc-pVTZ AO basis set. For \( E_{\text{exch-disp}}^{(2)} \) the columns denote the aug-cc-pVXZ MP2-fitting basis sets of Weigend, Köhn, and Hättig (Ref. 46) while for all other contributions the cc-pVQZ JK-fitting basis sets of Weigend (Ref. 45) were employed. Values in parenthesis for DF-DFT-SAPT calculations based on DF-DFT monomer calculations.

<table>
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<tr>
<th>Contribution</th>
<th>Exact</th>
<th>VTZ</th>
<th>VQZ</th>
<th>VSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{pol}}^{(1)} )</td>
<td>−1561</td>
<td>0.003</td>
<td>0.021</td>
<td>0.014</td>
</tr>
<tr>
<td>( E_{\text{exch}}^{(1)} )</td>
<td>1752</td>
<td>4.629</td>
<td>3.707</td>
<td>1.108</td>
</tr>
<tr>
<td>( E_{\text{ind}}^{(2)} )</td>
<td>−515</td>
<td>−0.076</td>
<td>−0.072</td>
<td>−0.050</td>
</tr>
<tr>
<td>( E_{\text{exch-ind}}^{(1)} )</td>
<td>398</td>
<td>0.064</td>
<td>0.040</td>
<td>0.019</td>
</tr>
<tr>
<td>( E_{\text{exch-disp}}^{(2)} )</td>
<td>−1431</td>
<td>−2.295</td>
<td>−0.143</td>
<td>0.058</td>
</tr>
<tr>
<td>( E_{\text{disp}}^{(2)} )</td>
<td>180</td>
<td>−3.692</td>
<td>−0.434</td>
<td>−0.131</td>
</tr>
<tr>
<td>( \delta (\text{HF}) )</td>
<td>−175</td>
<td>−4.739</td>
<td>−3.828</td>
<td>−1.128</td>
</tr>
<tr>
<td>( E_{\text{int}} )</td>
<td>−1352</td>
<td>−6.162</td>
<td>−0.704</td>
<td>−0.110</td>
</tr>
</tbody>
</table>

\( n_{\text{aux}} \) denotes the aug-cc-pVXZ matrices for monomer A and B as well as the three-index ERIs needed in second order of DF-DFT-SAPT (see Sec. II E).

The values clearly show that the most time-consuming steps are the monomer DF-DFT calculations. Though the formal scaling behavior for a DF-DFT calculation with a hybrid functional is \( O(N^6) \) (Ref. 46) and thus less than for the calculation of the dispersion and exchange-dispersion energy (which is \( O(N^7) \) in DF-DFT-SAPT), the scaling for the DF-DFT monomer calculations has a large prefactor due to the high accuracy of the integration grid required in DFT-SAPT. Additionally, very tight convergence thresholds have been employed in the monomer calculations.

As the benzene dimer is three times as large as the ethyne dimer, the scaling behavior with the system size can readily be obtained from Table II. It can be seen that most of the contributions, namely, the monomer calculations as well as the first-order terms and the second-order (exchange-) induction energy have a scaling of \( N^3 \). Clearly the most expensive contributions are the second-order dispersion and exchange-dispersion energy which both scale as \( N^5 \). However, as can be seen from analysis of the values from Table II, the actual scaling for the dispersion energy is a bit lower and lies in between \( N^4 \) and \( N^5 \). The reason for this is that some steps in the calculation of the dispersion energy only have a scaling of \( N^3 \) or \( N^4 \), respectively (compare Sec. II E).

The scaling with respect to the number of functions \( N \) for a given dimer, i.e., the basis set quality is nominally \( O(N^3) \). Comparing the timings for the benzene dimer calculations with the three different basis sets, as compiled in Table II, one finds that the scaling exponents with respect to \( N \) of the individual terms are all below a value of 3. This demonstrates, that rather big basis sets can be used in DF-DFT-SAPT calculations.

The most time-consuming steps in DF-DFT-SAPT are

SAPT. It is expected that while dramatic time savings can be achieved in this way (note that some steps in DF-DFT-SAPT have a scaling of \( n_{\text{aux}}^3 \)), the DF errors of the total interaction energy are far below the errors introduced by the use of limited AO basis sets. This is confirmed by the results presented below.

**B. Timings and performance**

Averaged timings for the individual steps of a DF-DFT-SAPT calculation of the ethyne and benzene dimers are given in Table II. Here the entry “integrals” denotes the CPU times spent for the evaluation of the required Coulomb and exchange matrices for monomer A and B as well as the three-index ERIs needed in second order of DF-DFT-SAPT (see Sec. II E).

**TABLE II.** CPU times (in seconds) for AMD-Opteron 2 GHz in 32 bit mode. 15 and 10 iterations per monomer for SCF and CPKS, respectively. Eight frequencies for Casimir-Polder integral.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Dimer</th>
<th>aug-cc-pVDZ</th>
<th>aug-cc-pVTZ</th>
<th>aug-cc-pVQZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et₂</td>
<td>233</td>
<td>935</td>
<td>3519</td>
<td></td>
</tr>
<tr>
<td>Bz₂</td>
<td>4691</td>
<td>20784</td>
<td>87834</td>
<td></td>
</tr>
<tr>
<td>Integrals</td>
<td>34</td>
<td>114</td>
<td>381</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1758</td>
<td>6546</td>
<td>19958</td>
<td></td>
</tr>
<tr>
<td>( E_{\text{pol}}^{(1)} )</td>
<td>0.05</td>
<td>0.3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( E_{\text{exch}}^{(1)} )</td>
<td>9</td>
<td>22</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>( E_{\text{ind}}^{(2)} )</td>
<td>25</td>
<td>370</td>
<td>1620</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1872</td>
<td>9336</td>
<td>47478</td>
<td></td>
</tr>
<tr>
<td>( E_{\text{exch-ind}}^{(1)} )</td>
<td>11</td>
<td>49</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td></td>
<td>191</td>
<td>1381</td>
<td>8524</td>
<td></td>
</tr>
<tr>
<td>( E_{\text{exch-disp}}^{(2)} )</td>
<td>2558</td>
<td>14756</td>
<td>71792</td>
<td></td>
</tr>
<tr>
<td></td>
<td>482</td>
<td>3572</td>
<td>19129</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a} \)Including calculation of CPKS coefficients.

\( ^{b} \)Including calculation of response functions.
the computation of the dispersion and induction energies besides the monomer DF-DFT calculations. In these steps most of the time is spent for the computation of the amplitudes $T_{ia,jb}$ and the CPKS coefficients $x_{A,B}^{C,D}$, respectively. For the latter the iterative solution of the coupled-perturbed Kohn-Sham equations is required for both monomers. In our calculations a convergence threshold of $1 \times 10^{-6}$ has been employed for the sum of the squared differences of the response density matrices of two consecutive iterations. About ten iterations then were necessary for each monomer to reach convergence.

Having established that density fitting scales as desired and does not introduce appreciable errors when using suitable auxiliary basis sets we will drop the distinction between DF-DFT-SAPT and DFT-SAPT for the remainder of this section.

C. Interaction energy contributions

1. Ethyne dimer

Table III contains the interaction energy contributions for the three different structures of the ethyne dimer calculated with DFT-SAPT. The values are given for the PBE0AC/ALDA xc model, in which a hybrid xc kernel is used for the static response functions (as described in Ref. 21) in combination with a purely local ALDA xc kernel for the frequency-dependent response functions needed to calculate the (exchange-) dispersion energy.

The values show that in the cases of the PD and T structures the dominant attractive contributions are due to electrostatic and dispersion interactions, which in both cases are of similar importance. However, while the electrostatic and the much smaller induction energies are approximately quenched by their respective exchange counterparts, the dispersion interaction has a very small exchange-dispersion counterpart, so that basically the dispersion interaction may be regarded as being responsible for the stabilization in these two structures. This is also evident by comparing the dispersion interaction energies with the total interaction energies which are close to each other in each case. In case of the S structure the dispersion energy is by far the most important attractive interaction energy contribution while the electrostatic component is positive due to a repulsive quadrupole-quadrupole interaction. As a consequence the total interaction energy of the S structure is only very small.

The basis set dependency of the individual interaction energy terms is shown in Fig. 3. In all three geometries the individual components of the interaction energy are already well converged in the aug-cc-pVTZ basis set — with the exception of the dispersion and exchange-dispersion energies. The latter are the only contributions in DFT-SAPT which clearly require a more extended basis set. This could be exploited for the estimation of the higher order interaction energy contributions through the $\delta\text{(HF)}$ approximation, which requires a separate and rather costly Hartree-Fock dimer calculation. Since the $\delta\text{(HF)}$ term itself is fairly small in comparison to the total energy, it appears that an attractive practical approach for the computation of potential energy surfaces using DFT-SAPT would be to calculate in particular the $\delta\text{(HF)}$ term (and perhaps further SAPT terms apart from

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**Table III. Interaction energy contributions (in kcal/mol) for Et$_2$.** The PBE0AC and LPBE0AC models (aug-cc-pVTZ basis) denote differences to the PBE0AC and LPBE0AC models (aug-cc-pVTZ basis), respectively.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Contribution</th>
<th>PBE0AC/ALDA</th>
<th>LPBE0AC/ALDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>aug-cc-pVDZ</td>
<td>aug-cc-pVTZ</td>
</tr>
<tr>
<td>PD</td>
<td>$E^{(1)}_{\text{exch}}$</td>
<td>-1.56</td>
<td>-1.56</td>
</tr>
<tr>
<td></td>
<td>$E^{(2)}_{\text{disp}}$</td>
<td>1.74</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>$E^{(2)}_{\text{ind}}$</td>
<td>-0.49</td>
<td>-0.52</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{exch-ind}}$</td>
<td>0.38</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{disp}}$</td>
<td>-1.26</td>
<td>-1.43</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{exch-disp}}$</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>$\delta\text{(HF)}$</td>
<td>-0.17</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{at}}$</td>
<td>-1.20</td>
<td>-1.35</td>
</tr>
<tr>
<td>S</td>
<td>$E^{(1)}_{\text{exch}}$</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>$E^{(2)}_{\text{disp}}$</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>$E^{(2)}_{\text{ind}}$</td>
<td>-0.11</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{exch-ind}}$</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{disp}}$</td>
<td>-0.60</td>
<td>-0.69</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{exch-disp}}$</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>$\delta\text{(HF)}$</td>
<td>-0.02</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{at}}$</td>
<td>-0.07</td>
<td>-0.15</td>
</tr>
<tr>
<td>T</td>
<td>$E^{(1)}_{\text{exch}}$</td>
<td>-1.75</td>
<td>-1.77</td>
</tr>
<tr>
<td></td>
<td>$E^{(2)}_{\text{disp}}$</td>
<td>1.96</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>$E^{(2)}_{\text{ind}}$</td>
<td>-0.58</td>
<td>-0.60</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{exch-ind}}$</td>
<td>0.36</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{disp}}$</td>
<td>-1.23</td>
<td>-1.38</td>
</tr>
<tr>
<td></td>
<td>$E^{2}_{\text{exch-disp}}$</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>$\delta\text{(HF)}$</td>
<td>-0.27</td>
<td>-0.28</td>
</tr>
</tbody>
</table>
|           | $E_{\text{at}}$         | -1.36       | -1.51       | -1.54       | -0.10       | -0.09
the dispersion and exchange-dispersion energy) in a smaller basis set. Furthermore, since computation of the dispersion energy is one of the most time consuming steps in DFT-SAPT (see Sec. IV B), it might be worthwhile to explore if the use of bond functions would lead to a more rapid convergence of this term with respect to the basis set size.

The last two columns in Table III contain the differences to the results obtained with the PBE0AC and LPBE0AC xc models in the aug-cc-pVTZ basis set, respectively. In the PBE0AC model the hybrid xc kernel is employed for both, the static and the frequency-dependent response functions. The LPBE0AC model uses the localized version of PBE0AC (asymptotically corrected PBE xc potential) xc model. The new orbitals were then obtained by diagonalizing this Fock matrix. Note that the density (and also the density matrix) obtained from these new orbitals is the same as that of PBE0AC because no occupied-virtual mixing is allowed in this procedure. First-order intermolecular interaction energies thus do not change. The new orbitals and orbital energy eigenvalues were then used in a subsequent DFT-SAPT calculation in which an ALDA xc kernel has been used for all response calculations. A comparison of the induction and dispersion energies obtained in this way with the corresponding PBE0AC values has shown a very good agreement with only about 1% deviation for all three structures of Et$_2$ studied here (not shown in the table). Therefore, as the generation of the local effective exact exchange potential is rather costly, this method might be useful if hybrid functionals are used in conjunction with DFT-SAPT.

2. Benzene dimer

The interaction energy contributions for the benzene dimer are given in Table IV for the PBE0AC/ALDA xc model. In order to estimate the effect of the somewhat erroneous virtual orbital energies of PBE0AC coming from the nonlocal exchange mixing (see preceding section) the differences to the interaction energy contributions from the LPBE0AC xc model are given in the last column of Table IV.

The comparison of the total interaction energies for the three structures shows that, in analogy to the ethyne dimer, the PD and T structures are nearly isoenergetic. However, the dominant attractive contribution now is represented by the dispersion interaction while the electrostatic energy is merely of the size of the induction energy. This shows that the ethyne dimer only approximately serves as a prototype system for the benzene dimer. As usual the most repulsive contribution is given by the first-order exchange energy. In case of the sandwich structure the electrostatic interaction is also
attractive, due to an overcompensation of a repulsive quadrupole-quadrupole interaction through an attractive charge-penetration interaction. The high-order contributions, represented by the $\delta(\text{HF})$ values, are again only very small.

In Fig. 4 the basis set dependency of the individual interaction energy terms for the benzene dimer is shown. As in the ethyne dimer case the dispersion energy shows the strongest dependency on the basis set, while all other contributions are nearly converged in the aug-cc-pVTZ basis set. Hence, in practical calculations significant savings in computational resources could be obtained if notably the $\delta(\text{HF})$ term would be computed in a smaller basis set than the dispersion and exchange-dispersion terms (see Sec. IV.B).

The $\Delta$LPBE0AC values in the last column of Table IV show that for the PD and S structures the first-order SAPT contributions from LPBE0AC and PBE0AC are close to each other. This indicates that the orbitals from the local xc potential are in good agreement with those from the hybrid xc potential as is postulated in the LHF approach. However, as in the case of the ethyne dimer, significant deviations occur for the dispersion energy, for the same reasons as outlined above (i.e., the use of the ALDA kernel). The magnitudes of these deviations in the dispersion energies are considerably larger than for the ethyne dimer. From the closeness of the LPBE0AC and PBE0AC results observed for the ethyne dimer it can be estimated that the use of the hybrid xc kernel would modify the total interaction energies by a negative shift of about $-0.3-0.5$ kcal/mol. Note that in case of the T structure also a larger difference of $-0.13$ kcal/mol between LPBE0AC and PBE0AC is observed for the induction energy. This difference, however, is compensated for by a similar shift in the exchange-induction energies.

### D. Comparison with supermolecular and many-body SAPT calculations

#### 1. Ethyne dimer

In Table V the DFT-SAPT results are compared with interaction energies obtained from supermolecular MP2 and CCSD(T) calculations. In the case of DFT-SAPT $E_{\text{rest}}$ denotes the sum $E_{\text{disp}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(1)} + E_{\text{exch-ind}} + \delta(\text{HF})$ which comprises all terms of the SAPT expansion which do not depend on intermolecular correlation. It can be seen that this sum is nearly constant through all basis sets for all three structures of the ethyne dimer. Note that the sum of the two intermolecular correlation terms $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ exhibits about the same basis set dependency as the correlation contributions from supermolecular MP2 and CCSD(T) calculations (denoted in Table V as $\epsilon_{\text{corr}}$). Thus, in order to obtain estimates for the complete basis set limit (cbs) of the different methods we add the sum of the non-dispersion contributions ($E_{\text{rest}}$ and $E_{\text{ind}(\text{HF})}$, respectively) in the largest aug-cc-pVQZ basis set to the extrapolated value for the (intermolecular) correlation contributions obtained from the two-point extrapolation formula of Bak et al.53 However, since the CCSD(T) interaction energies could at most be computed in the aug-cc-pVTZ basis set the cbs limit has been assessed in this case by adding the difference between the CCSD(T) and MP2 interaction energies in the aug-cc-

<table>
<thead>
<tr>
<th>Structure</th>
<th>Basis</th>
<th>Contribution</th>
<th>PBE0AC/ALDA</th>
<th>LPBE0AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD</td>
<td></td>
<td></td>
<td>aug-cc-pVDZ</td>
<td>aug-cc-pVTZ</td>
</tr>
<tr>
<td>PD</td>
<td>$E_{\text{pol}}^{(1)}$</td>
<td>-2.14</td>
<td>-2.09</td>
<td>-2.09</td>
</tr>
<tr>
<td>PD</td>
<td>$E_{\text{exch}}^{(1)}$</td>
<td>7.60</td>
<td>7.56</td>
<td>7.55</td>
</tr>
<tr>
<td>PD</td>
<td>$E_{\text{ind}}^{(1)}$</td>
<td>-3.18</td>
<td>-3.30</td>
<td>-3.32</td>
</tr>
<tr>
<td>PD</td>
<td>$E_{\text{exch-ind}}^{(1)}$</td>
<td>2.97</td>
<td>3.11</td>
<td>3.12</td>
</tr>
<tr>
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<td>$E_{\text{disp}}^{(1)}$</td>
<td>-7.79</td>
<td>-8.31</td>
<td>-8.48</td>
</tr>
<tr>
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<td>$E_{\text{exch-disp}}^{(1)}$</td>
<td>1.26</td>
<td>1.33</td>
<td>1.37</td>
</tr>
<tr>
<td>PD</td>
<td>$\delta(\text{HF})$</td>
<td>-0.62</td>
<td>-0.62</td>
<td>-0.62</td>
</tr>
<tr>
<td>PD</td>
<td>$E_{\text{int}}$</td>
<td>-1.88</td>
<td>-2.31</td>
<td>-2.45</td>
</tr>
<tr>
<td>S</td>
<td>$E_{\text{pol}}^{(1)}$</td>
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<td>-0.56</td>
<td>-0.56</td>
</tr>
<tr>
<td>S</td>
<td>$E_{\text{exch}}^{(1)}$</td>
<td>5.31</td>
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<td>$E_{\text{ind}}^{(1)}$</td>
<td>-1.84</td>
<td>-1.88</td>
<td>-1.88</td>
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<td>1.69</td>
<td>1.75</td>
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</tr>
<tr>
<td>S</td>
<td>$E_{\text{disp}}^{(1)}$</td>
<td>-6.23</td>
<td>-6.59</td>
<td>-6.72</td>
</tr>
<tr>
<td>S</td>
<td>$E_{\text{exch-disp}}^{(1)}$</td>
<td>0.88</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>S</td>
<td>$\delta(\text{HF})$</td>
<td>-0.14</td>
<td>-0.15</td>
<td>-0.15</td>
</tr>
<tr>
<td>S</td>
<td>$E_{\text{int}}$</td>
<td>-0.87</td>
<td>-1.24</td>
<td>-1.35</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{pol}}^{(1)}$</td>
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<td>-2.07</td>
<td>-2.06</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{exch}}^{(1)}$</td>
<td>4.71</td>
<td>4.71</td>
<td>4.71</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{ind}}^{(1)}$</td>
<td>-1.36</td>
<td>-1.47</td>
<td>-1.56</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{exch-ind}}^{(1)}$</td>
<td>1.13</td>
<td>1.23</td>
<td>1.23</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{disp}}^{(1)}$</td>
<td>-4.60</td>
<td>-4.94</td>
<td>-5.03</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{exch-disp}}^{(1)}$</td>
<td>0.61</td>
<td>0.67</td>
<td>0.69</td>
</tr>
<tr>
<td>T</td>
<td>$\delta(\text{HF})$</td>
<td>-0.40</td>
<td>-0.41</td>
<td>-0.41</td>
</tr>
<tr>
<td>T</td>
<td>$E_{\text{int}}$</td>
<td>-1.97</td>
<td>-2.27</td>
<td>-2.44</td>
</tr>
</tbody>
</table>
As it has been observed before (see Sec. IV C) the 25% fraction of nonlocal exchange in PBE0AC leads to positive shifts of the dispersion energy when an ALDA xc kernel is used. Therefore Table V also contains the corresponding values of the correlation terms obtained with LPBE0AC and their sum with \( E_{\text{cor}} \) (PBE0AC). It can be seen that there is a nearly perfect agreement between the DFT-SAPT cbs values from PBE0AC/ALDA and CCSD(T). Contrary to this the estimates for the MP2 interaction energies are all about \(-0.1\) kcal/mol lower than their CCSD(T) counterparts. However, as stated above, the replacement of PBE0AC/ALDA with the theoretically more sound LPBE0AC model for the (exchange-) dispersion part also leads to more negative total interaction energies which are now closer to MP2 than to CCSD(T) for the PD and T structure. But in case of the S geometry, which is a structure in which the dispersion interaction constitutes the main attractive contribution to the total interaction energy (see Fig. 3), the correspondence is still better with the CCSD(T) energy than with the MP2 energy, which overestimates the correlation effect by about 17%. This already indicates that the DFT-SAPT method is substantially more accurate than MP2 in cases where the dispersion interaction is important (vide infra).

The DFT-SAPT cbs estimates displayed in Table V show that the interaction energy obtained with the aug-cc-pVTZ basis set for the PD structure is in error by about 0.08 kcal/mol, and by about 0.03 kcal/mol with the aug-cc-pVQZ basis set. These errors are one to two orders of magnitude larger than the error of about 0.001 kcal/mol due to density fitting with the default auxiliary basis sets.

2. Benzene dimer

Table VI compiles cbs estimates of the interaction energies for the benzene dimer. Here the MP2 and CCSD(T) values are taken from Ref. 39. Note that contrary to Ref. 39 we prefer to use extrapolated MP2 interaction energies as cbs estimates rather than MP2-R12 values because severe instabilities have been found for MP2-R12 interaction energies in the benzene dimer case.\(^{54}\) Again, as for the ethyne dimer, the correlation contribution of DFT-SAPT has been estimated by using both, the PBE0AC/ALDA xc model and the LPBE0AC xc model. Note, however, that we have not calculated the LPBE0AC values for the aug-cc-pVQZ basis set due to the cost of the generation of the local effective exact exchange potential. The cbs estimate for LPBE0AC has therefore been calculated as the sum of the cbs estimate for PBE0AC/ALDA and the difference between the values of LPBE0AC and PBE0AC/ALDA in the aug-cc-pVTZ basis set. This difference is fairly constant through the aug-cc-pVDZ and aug-cc-pVTZ basis set so that this approximation is anticipated to be rather good.

In the benzene dimer the dispersion component of the interaction energy is of even greater importance than in the ethyne dimer. In fact, the overall interaction energy of the benzene dimer is primarily governed by dispersion (cf. Fig. 4), and, as a consequence, a high-level correlation treatment is mandatory for a proper description of the benzene dimer. This is manifest also in the values compiled in Table VI: in comparison to CCSD(T), MP2 strongly overestimates the correlation contribution to the interaction energy. On the other hand, in analogy to the findings for the S structure of the ethyne dimer, the DFT-SAPT results from PBE0AC/ALDA and the difference between the values of LPBE0AC and PBE0AC/ALDA in the aug-cc-pVTZ basis set. This difference is fairly constant through the aug-cc-pVDZ and aug-cc-pVTZ basis set so that this approximation is anticipated to be rather good.
TABLE V. Ethyne dimer: basis set extrapolation of intermolecular correlation energies (in kcal/mol). DFT-SAPT energies calculated with the PBE0AC/ALDA xc model, unless otherwise noted.

<table>
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<th>Method</th>
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*From LPBE0AC xc model.
*bCorresponds to $E_{\text{int}}(\text{PBE0AC}) + E_{\text{disp}}^{(2)}(\text{LPBE0AC}) + E_{\text{exch-disp}}^{(2)}(\text{LPBE0AC}).

Table VII compares our DFT-SAPT results with the conventional many-body SAPT2 results from Sinnokrot and Sherrill.\(^5\) Note that the dimer geometries are slightly different in the two cases since Sinnokrot and Sherrill used optimized MP2/aug-cc-pVTZ structures for their SAPT2 calculations. For these calculations a reduced aug-cc-pVDZ basis set, denoted as aug-cc-pVDZ\(^*\), has been used, where the most diffuse $d$ function on carbon and all diffuse $s$, $p$ functions on hydrogen are omitted. It is observed that the SAPT2 and DFT-SAPT values are entirely different. In particular, the SAPT2 total interaction energies are much larger than the corresponding DFT-SAPT values. For example, for the PD structure the SAPT2 interaction energy amounts to 2.94 kcal/mol, while the corresponding DFT-SAPT value is only 0.74 kcal/mol. This discrepancy mainly stems from the differences in the dispersion energies ($-7.89$ versus $-5.34$ kcal/mol for SAPT2 and DFT-SAPT, respectively). In SAPT2 the dispersion energy is calculated at the uncoupled Hartree-Fock level ($E_{\text{disp}}^{(20)}$), which usually overestimates the dispersion energy by about 15%.\(^2\) Even larger deviations of up to 35% have been found for dimer systems where the dispersion interaction dominates the total interaction energy as is the case for Ne\(_2\) or NeHF.\(^3\) As the $E_{\text{disp}}^{(20)}$ term is the only dispersion contribution in a supermolecular MP2 calculation (apart from additional small relaxation terms) this also serves as an explanation why the MP2 method overshoots the magnitude of the total interaction energy in the benzene dimer (cf. Table VI). Since $E_{\text{disp}}^{(20)}$ will be even larger if a more extended basis set is used, it can be expected that SAPT2 exhibits the same behavior as a supermolecular MP2 calculation, i.e., a considerable overestimation of the magnitude of the benzene dimer interaction energy relative to CCSD(T), provided that a basis set of reasonable size is employed.

Yet, apart from the discrepancies in the dispersion energy between SAPT2 and DFT-SAPT, one can also observe noticeable differences in the first-order terms for the PD and S structures. A comparison of the Coulomb energies with the corresponding Hartree-Fock values collected in Table VIII, shows that even a change in the sign of the intra-monomer correlation effect of MP2 and PBE0AC does occur for the three conformers of the benzene dimer. In order to analyze this further we have carried out calculations on the electrostatic interaction energy with larger basis sets and other (higher level) correlation methods. The results of these cal-

with respect to CCSD(T) of 0.3 and 0.2 kcal/mol, respectively. In case of the T structure, however, DFT-SAPT and CCSD(T) are then in very good agreement.
10. Intermolecular interactions

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V. CONCLUSIONS

A density fitting implementation of the DFT-SAPT method has been described and its performance has been

Calculations are compiled in Table VIII. Here the basis set denoted by aug-cc-pVTZ' corresponds to an aug-cc-pVTZ basis where the most diffuse d and f functions on carbon and all diffuse s, p, d functions on hydrogen are omitted. As correlation methods beyond MP2 we used MP3 (third-order Muller-Plesset perturbation theory), BO (densities from Brueckner orbitals; Ref. 56) and AQCC (nonrelaxed average quadratic coupled cluster$^9$). The MP2(ae) and MP3(ae) Coulomb energies (all electrons correlated) were calculated with the many-body SAPT program by Jeziorski et al.$^{15}$ From Table VIII it is evident that the additional diffuse functions in the aug-cc-pVDZ basis (relative to the aug-cc-pVTZ basis) only have a slight effect on the electrostatic interaction energies. A similar behavior is expected also for the aug-cc-pVTZ and aug-cc-pVQZ basis sets. On the other hand, extending the basis set from double- to triple-$\zeta$ leads to a significant reduction of the magnitude of the Coulomb energies for all ab initio correlation methods (in particular, for the PD and S conformers the Coulomb energies become significantly less negative), while the corresponding Hartree-Fock and PBE0AC values are much less affected. Moreover, the higher-level correlation methods show appreciable differences to MP2: the MP2 Coulomb energies are more negative than the AQCC values by about $-0.1$ to $-0.2$ kcal/mol for the PD and S conformers, while the BO values, which are in good agreement with PBE0AC for the aug-cc-pVTZ' basis, are shifted upward with respect to the AQCC Coulomb energies by about 0.15 kcal/mol for these geometries. We suppose that the AQCC Coulomb energies, which are also very close to MP3 for the aug-cc-pVDZ' basis, are our best estimates. Hence, we conclude that the MP2 method yields electrostatic interaction energies which are considerably too low for the PD and S geometry while the BO and PBE0AC values are somewhat too high. However, the large differences between the AQCC-values in the double- and triple-$\zeta$ basis set indicate that they are far from convergence and may become even closer to the PBE0AC Coulomb energies for larger basis sets. For the T structure only a small intramolecular correlation effect on the Coulomb energy is found and evidently, PBE0AC is rather close to both BO and AQCC, while MP2 yields a slightly too low Coulomb energy (by about $-0.1$ kcal/mol).

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V. CONCLUSIONS

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From Table VIII it is evident that the additional diffuse functions in the aug-cc-pVDZ basis (relative to the aug-cc-pVTZ basis) only have a slight effect on the electrostatic interaction energies. A similar behavior is expected also for the aug-cc-pVTZ and aug-cc-pVQZ basis sets. On the other hand, extending the basis set from double- to triple-$\zeta$ leads to a significant reduction of the magnitude of the Coulomb energies for all ab initio correlation methods (in particular, for the PD and S conformers the Coulomb energies become significantly less negative), while the corresponding Hartree-Fock and PBE0AC values are much less affected. Moreover, the higher-level correlation methods show appreciable differences to MP2: the MP2 Coulomb energies are more negative than the AQCC values by about $-0.1$ to $-0.2$ kcal/mol for the PD and S conformers, while the BO values, which are in good agreement with PBE0AC for the aug-cc-pVTZ' basis, are shifted upward with respect to the AQCC Coulomb energies by about 0.15 kcal/mol for these geometries. We suppose that the AQCC Coulomb energies, which are also very close to MP3 for the aug-cc-pVDZ' basis, are our best estimates. Hence, we conclude that the MP2 method yields electrostatic interaction energies which are considerably too low for the PD and S geometry while the BO and PBE0AC values are somewhat too high. However, the large differences between the AQCC-values in the double- and triple-$\zeta$ basis set indicate that they are far from convergence and may become even closer to the PBE0AC Coulomb energies for larger basis sets. For the T structure only a small intramolecular correlation effect on the Coulomb energy is found and evidently, PBE0AC is rather close to both BO and AQCC, while MP2 yields a slightly too low Coulomb energy (by about $-0.1$ kcal/mol).
tested by calculating some specific structures of the ethyne and benzene dimers. It was demonstrated that large basis sets with suitable auxiliary basis sets thus being one or two orders of magnitude smaller than the errors due to the use of augmented quadruple- and triple-ζ atomic orbital basis sets, respectively.

While the formal scaling behavior of DF-DFT-SAPT, both, with respect to the basis set size and the molecular size, is the same as that of DF-MP2, it has been shown that the accuracy of total interaction energies in general is better than that of MP2 if compared with supermolecular interaction energy results from CCSD(T). This is especially the case if the dispersion energy dominates the total interaction energy. The supermolecular MP2 interaction energy describes the dispersion energy only at the uncoupled Hartree-Fock level which often considerably overestimates the dispersion interaction. As a consequence the MP2 method is not suitable to study π–π interactions because, as the partitioning of the total interaction energy of DFT-SAPT and also MB-SAPT2 has shown, the dispersion energy is by far the most attractive contribution for the three investigated structures of the benzene dimer. On the other hand the DFT-SAPT method is potentially exact with respect to the calculation of the dispersion energy, i.e., the dispersion energy could be calculated exactly if the exact xc potential and the exact xc kernel for the monomers would be known. A recent study has shown that the dispersion energy can be obtained rather accurately if the asymptotic PBE0AC xc potential is used in conjunction with a hybrid xc kernel for the calculation of the dynamic response functions. Therefore this xc potential has also been used to calculate the intermolecular interaction contributions for Et2 and Bz2. It turned out that it somewhat underestimates the magnitude of the electrostatic interaction energy for the PD and S structure of Bz2 at the triple-ζ basis set level when compared with the AQCC method. On the other hand it has been found that MP2 overestimates the magni-

### Table VII. Benzene dimer: comparison with many-body SAPT (SAPT2) interaction energies (in kcal/mol) taken from Ref. 55, obtained with an aug-cc-pVDZ basis set. $E_{\text{int}} = E_{\text{exch}}^{(2)} + E_{\text{disp}}^{(2)} + \Delta \langle \text{HF} \rangle$. $E_{\text{disp}} = E_{\text{disp}}^{(2)} + E_{\text{disp}}^{(3)}$.

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### Table VIII. Benzene dimer: Coulomb energies (in kcal/mol). All-electron correlation calculations denoted as "ae."}

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<th>Structure</th>
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</table>
tude of the Coulomb energy for these dimer structures by about the same amount, i.e., 0.1–0.2 kcal/mol.

The present implementation of the DF-DFT-SAPT method is limited to local xc kernels for the calculation of the dynamic response functions, which are needed to calculate the (exchange-) dispersion interactions. As a consequence the dispersion energies are affected by positive shifts if hybrid xc potentials are used to obtain the monomer orbitals. These shifts can be ascribed to improper energy values for the virtual orbitals which are too high due to the effect of the nonlocal exchange operator. In the conventional DFT-SAPT method this is compensated for by also employing a hybrid xc kernel, i.e., adding a corresponding amount of the TDHF exchange kernel to the ALDA kernel. For DF-DFT-SAPT we solved this problem by using fully local hybrid xc potentials which were constructed by replacing the nonlocal exact exchange potential with the local effective exchange-cc potentials which were constructed by replacing the nonlocal exact exchange potential in the Kohn-Sham monomer calculations. It has been shown that the results from corresponding LPBE0AC xc potential overestimate the CCSD(T) correlation energies for the PD and S structure of the benzene dimer by about 0.3 and 0.2 kcal/mol, respectively, while for the T structure the agreement with the CCSD(T) interaction energy is rather good. Thus, while CCSD(T) slightly favours the T structure as the most stable structure of the benzene dimer, the situation is just reversed in the case of DFT-SAPT, although the relative stabilizations are quite small in both cases.

In order to achieve further performance improvements of DFT-SAPT local methods could be employed. Work along these lines is in progress.

**ACKNOWLEDGMENTS**

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10.2. New CO-CO interaction potential tested by rovibrational calculations

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**Key words:**
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- rovibrational spectrum
- rotational stacks
- symmetry-adapted perturbation theory
- isotopically substituted $^{13}$CO dimer
New CO–CO interaction potential tested by rovibrational calculations

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A four-dimensional potential energy surface (PES) for the CO dimer consisting of rigid molecules has been calculated, using a scheme that combines density functional theory to describe the monomers and symmetry adapted perturbation theory for the interaction energy (DFT-SAPT). The potential is fitted in terms of analytic functions, and the fitted potential is used to compute the lowest rovibrational states of the dimer. The quality of the PES is comparable to that of a previously published surface [G. W. M. Vissers, P. E. S. Wormer, and A. van der Avoird, Phys. Chem. Chem. Phys., 5, 4767 (2003)], which was calculated with the coupled cluster single double and perturbative triples [CCSD(T)] method. It is shown that a weighted average of the DFT-SAPT and the CCSD(T) potential gives results that are in very good agreement with experimental data, for both \((^{12}\text{CO})_2\) and \((^{13}\text{CO})_2\). The relative weight was determined by adjusting the energy gap between the origins of the lowest two stacks of rotational levels of \((^{12}\text{CO})_2\) to the measured value. © 2005 American Institute of Physics. [DOI: 10.1063/1.1835262]

I. INTRODUCTION

The molecule carbon monoxide is abundant: it appears in the earth’s atmosphere as well as in interstellar clouds. Because of the possibility of dimer formation, the CO dimer has been the subject of several theoretical and experimental studies.1–3 It is a prototype of weakly bound van der Waals molecules. The spectra of van der Waals complexes provide accurate information on intermolecular potentials and the CO dimer is an interesting example, because the \(ab\) \(initio\) calculation of an accurate CO–CO potential energy surface turned out to be more difficult than for other systems.4–6

Work on the CO dimer dates back as far as 1979, when Vanden Bout et al. reported the observation of five lines due to \((\text{CO})_2\) in a molecular beam radiospectroscopic measurement.7 Although these lines still remain unassigned, much experimental knowledge has been gained about this system since then. Havenith et al.2 reported studies of the dimer in the midinfrared, and analyzed their results in terms of an asymmetric rigid rotor model. This analysis was later rejected by Brookes and McKellar,3,7 who described the dimer rather as consisting of two hindered rotors. Millimeter wave experiments added to the body of knowledge, to the point that there are now several stacks of accurately known rovibrational energy levels, both for the “normal” \((^{12}\text{CO})_2\) (Refs. 8–12) and for the isotopically substituted \((^{13}\text{CO})_2\).13,14

On the theoretical side of the problem, progress was considerably slower. Until recently, there were only two \(ab\) \(initio\) potential energy surfaces (PESs) available. The first, by van der Pol et al.15 is a sum of first-order Heitler-London energy and a damped multipole expansion for the electrostatic, induction and dispersion interactions. The second surface, by Meredith and Stone16 is an extension of the potential of van der Pol. They included \(C_9\) and \(C_{10}\) coefficients in the multipole expansion of the dispersion energy, and refined the electrostatic and induction energies by using distributed multipoles. Both potentials show a global minimum at or near a T-shaped structure, and local minima corresponding to slipped antiparallel structures. However, rovibrational calculations on these potentials showed that neither of them can explain the observed spectroscopic properties of the CO dimer.16,17

Two possible reasons for the inaccuracies of these potentials are the use of the multipole approximation and the neglect of electronic correlation effects on the exchange-repulsion energy. However, an attempt4 to correct these deficiencies by fourth-order Møller-Plesset and coupled cluster (CC) calculations showed that high-order correlation effects are important, and that both CCSD(T) (CC restricted to single, double, and noniterative triple excitations) and CCSDT (CC with iterative triple excitations) do not have the correct asymptotic behavior. Furthermore, it was pointed out that very large basis sets are needed for an accurate description of the CO–CO potential energy surface.5,6 Nevertheless, a CCSD(T) potential was recently published18 that gives energy levels that are in semiquantitative agreement with experiment. This surface shows two minima at slipped antipar-
allel structures: the global minimum with the C–C distance smaller than the O–O distance and a local minimum where the O-atoms are closer together. It was shown that the existence of the two slipped antiparallel structures, occurring at different intermolecular separations, can account for the experimentally observed existence of stacks of rotational levels with different rotational constants.\(^{18}\)

The supermolecular approach as employed in the CCSD(T) calculations of the CO dimer is certainly the most straightforward and therefore perhaps the most widely used way to extract intermolecular interaction energies from \textit{ab initio} electronic structure calculations. Yet, in the last decade symmetry-adapted intermolecular perturbation theory (SAPT) has emerged as a viable alternative.\(^{19}\) In SAPT the interaction energy is calculated as a sum of terms of distinct physical origin, i.e., the first-order Coulomb and the second-order induction and dispersion energies, each of these terms being accompanied by a corresponding exchange correction due to the simultaneous exchange of electrons between the monomers. All of these contributions are affected by intramonomer electron correlation. In the many-body version of SAPT (MB-SAPT) (Ref. 20) intramonomer electron correlation is described through Møller-Plesset perturbation theory of various orders, depending on the accuracy requirements for each interaction contribution. In many cases the quality of the total interaction energies is similar to that obtained from CCSD(T) calculations.\(^{21,22}\)

As an alternative to treating intramonomer electron correlation through many-body perturbation theory it has been proposed to combine SAPT with a relatively inexpensive description of the monomers through density functional theory (DFT).\(^{23,24}\) Such a combined DFT-SAPT scheme is well founded for the first-order Coulomb and the second-order induction and dispersion energy contributions, which are potentially exact if (time-dependent) coupled-perturbed Kohn–Sham DFT is utilized to calculate the monomer response densities, and provided that the exact exchange-correlation potential (xc-potential) and the exact exchange-correlation kernel (xc-kernel) are known.\(^{24}\) By contrast, the intermolecular exchange corrections to the first- and second-order contributions are not potentially exact and can only be approximated with DFT-SAPT. Yet, this does not seem to be a serious drawback for practical use of the method: from a comparison of the results of DFT-SAPT with those of MB-SAPT it was found that monomer electron correlation effects on both first-order Coulomb and exchange energies were accurately reproduced, provided that a well-balanced asymptotically correct xc-potential was employed.\(^{25,26}\) This holds also true for the second-order contributions.\(^{27,28}\)

The accuracy one can achieve with DFT-SAPT for those cases, where essentially exact xc-potentials can be utilized, has been demonstrated recently for the helium dimer: DFT-SAPT is able to reproduce the best theoretical estimates for the interaction energy within 1% if the effect of third and higher orders of the intermolecular perturbation are estimated on the correlated level.\(^{29}\) An estimate of the third- and higher-order corrections usually is available on the Hartree-Fock level only. Utilizing the uncorrelated correction the accuracy of DFT-SAPT for the interaction energy of He\(_2\) drops to 5%, but considering the relatively low computational effort of the DFT-SAPT method this is still competitive with CCSD(T), which deviates by 3% from the most reliable estimates.\(^{29}\)

In this paper, we present a PES for the CO dimer, calculated using DFT-SAPT. We present results of rovibrational calculations on this potential and show that the results are comparable to those of the CCSD(T) potential. Furthermore, we take a step toward creating a quantitatively correct potential, by combining the DFT-SAPT potential and the CCSD(T) potential into a hybrid potential with one empirical parameter. We will show that this hybrid potential gives results that are in very close agreement to the experimental data.

II. DETAILS OF THE CALCULATIONS

A. DFT-SAPT calculations

In the DFT-SAPT calculations the interaction energy was obtained as

\[
\Delta E_{\text{AB}} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \delta(\text{HF}),
\]

where \(E_{\text{pol}}^{(1)}\) and \(E_{\text{exch}}^{(1)}\) are the first-order Coulomb and exchange interaction energies, \(E_{\text{ind}}^{(2)}\) and \(E_{\text{exch-ind}}^{(2)}\) the second-order induction energy and its exchange correction, and \(E_{\text{disp}}^{(2)}\) and \(E_{\text{exch-disp}}^{(2)}\) the second-order dispersion energy and its exchange correction, respectively. The last term \(\delta(\text{HF})\) is determined from counterpoise-corrected supermolecular Hartree-Fock calculations\(^{20}\) and describes the effect of third and higher orders in the interaction potential on an uncorrelated level.

All of the intermolecular perturbation contributions up to second order were obtained with a self-written program (attached to the MOLPRO program package\(^{30}\)) which determines the second-order induction and dispersion energies along with their respective exchange corrections via a coupled (time-dependent) Kohn-Sham DFT approach, as first suggested in Ref. 24. Further methodological details on the calculation of individual interaction energy contributions may be found in Ref. 25 for the first-order terms and Ref. 27 for the second-order induction contributions. As in Ref. 29, the latter were determined from analytical instead of numerical solutions of the coupled-perturbed Kohn-Sham equations. The dispersion energies were calculated from the eigensolutions of the time-dependent DFT equations as described in Ref. 28 (cf. Ref. 31 for an equivalent route to DFT-SAPT dispersion energies) which were also used to determine its exchange correction. The PBE0\(\text{AC}\) xc-potential, introduced and defined in Ref. 25, was used to determine the Kohn–Sham orbitals, and the xc-kernel employed was of the hybrid adiabatic local density approximation type.\(^{28}\)

Further technical parameters of the calculations were kept as close as possible to the previous CCSD(T) study of the CO dimer:\(^{10}\) the Gaussian type function basis set employed consists of the augmented correlation-consistent polarized valence triple zeta aug-cc-pVTZ atomic basis sets\(^{32,33}\) to which an uncontracted \(3s3p2d1f\) set of bond functions

\(98\)
10. Intermolecular interactions

New CO–CO interaction potential

was added at the midpoint between the centers of mass of the CO molecules. The CO bond distance was fixed at 2.132 bohr and the following atom masses were used: 15.994 915 0 u for $^{16}$O, 12 u for $^{12}$C (by definition), and 13.003 354 8 u for $^{13}$C. The interaction energies first were calculated at exactly the same 1512 geometries as discussed in Ref. 18: the angles $\theta_A$ and $\theta_B$ between the vector $\mathbf{R}$ from the center of mass of monomer $A$ to that of monomer $B$ and the vectors $\mathbf{r}_A$ and $\mathbf{r}_B$ pointing from the C-atom to the O-atom in the monomers, respectively, were varied according to a six-point Gaussian-Legendre grid, while the dihedral angle $\phi$ between the planes defined by $(\mathbf{R}, \mathbf{r}_A)$ and $(\mathbf{R}, \mathbf{r}_B)$, respectively, was varied according to a six-point Gauss-Chebyshev grid. The distance $R = |\mathbf{R}|$ was varied in steps of 1 bohr for the range 5–10 bohrs, and in steps of 2.5 bohrs for the range between 10 and 25 bohrs. In a second series of calculations these geometries were extended by another 936 geometries, making up for a total of 2448 computed points on the potential energy surface. These points were restricted to the distance range between 5 and 10 bohrs and to the same six values of the dihedral angle $\phi$ as given above. The $\theta_A$ and $\theta_B$ grids, however, were refined to include the angles 10°, 62.401 384°, and 170°.

B. Analytic fit of the potential

The first step in fitting the potential, was a least squares fit of the calculated interaction energy to angular functions, for each of the 12 intermolecular distances:

$$\Delta E_{AB}(R, \theta_A, \theta_B, \phi) = \sum_{L_A L_B M} C_{L_A L_B M}(R) A_{L_A L_B M}(\theta_A, \theta_B, \phi),$$  
(2)

with $0 \leq L_A, L_B \leq 6$ and $0 \leq M \leq \min(L_A, L_B, 5)$. The angular functions $A_{L_A L_B M}$ are given by

$$A_{L_A L_B M}(\theta_A, \theta_B, \phi) = P^{L_A}_{\theta_A}(\cos \theta_A) P^{L_B}_{\theta_B}(\cos \theta_B) \cos M \phi,$$  
(3)

where the $P^{L}_{\theta}$ are Schmidt seminormalized associated Legendre functions. The resulting expansion coefficients were then subjected to a similar fit procedure as used in the fit of CCSD(T) potential. First the long-range part was fitted as in the earlier work

$$C_{L_A L_B M}(R) = c_{L_A L_B M} R^{-\nu_{L_A L_B M}} \text{ for } R \geq 15a_0.$$  
(4)

It was verified that the numbers $\nu_{L_A L_B M}$ are close to what is predicted by long-range theory. For instance, the contributions with $(L_A, L_B M) = (2, 2, 0)$, $(2, 2, 1)$, and $(2, 2, 2)$ constitute (together with a Clebsch-Gordan coupling coefficient) the important quadrupole-quadrupole interaction. The exponents $\nu_{2, 2, M}$ are, respectively, 4.92, 4.96, and 4.97, while in the multipole expansion they are 5 exactly. We also experimented with the usual long-range terms that have the exact integer exponents, but it turned out that the form chosen is easy to fit and needs fewer parameters, while giving a better fit of the expansion coefficients over a wide range of distances. Certain $(L_A L_B M)$ combinations do not appear in the long range, in those cases $c_{L_A L_B M}$ was put equal to zero.

These long-range terms were damped with a Tang-Toennies damping function $T(R; \eta_{L_A L_B M}, \alpha_{L_A L_B M})$ and subtracted from the original coefficients to give the short-range coefficients:

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<th>$R_e$ (bohrs)</th>
<th>$\theta_A$</th>
<th>$\theta_B$</th>
<th>$D_s$ (cm$^{-1}$)</th>
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<tr>
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<td>8.20</td>
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<td>45.8</td>
</tr>
<tr>
<td>Local minimum</td>
<td>6.95</td>
<td>59.6</td>
<td>120.4</td>
</tr>
</tbody>
</table>

*Reference 18.*
The short-range terms were then finally fitted to the form

\[ C_{L_A L_B}^{SR}(R) = \exp(-\alpha_{L_A L_B} R) \sum_{k=0}^{\infty} \alpha_{L_A L_B}^{k} R^{k}. \]  

(6)

The integers \( n_{L_A L_B}^{M} \) used in the Tang-Toennies damping function were taken to be the integer nearest to \( r_{L_A L_B}^{M} \). The \( \alpha_{L_A L_B}^{M} \) that appear both in the damping function and the short-range fitting functions were obtained by starting with all \( \alpha \)'s equal to unity and iterating the fitting procedure until they converged.

### C. Rovibrational calculations

The methodology for computing the rovibrational bound states of the dimer is the same as was used previously in Ref. 18. Since in the rovibrational calculations the Wigner-Eckart theorem is applied, it was more convenient to have the potential expanded in coupled angular functions. Therefore the fitted potential was first reexpanded in functions

<table>
<thead>
<tr>
<th>Stack</th>
<th>K</th>
<th>Symmetry</th>
<th>( R_{a} )</th>
<th>( \text{Origin} ) (cm(^{-1}))</th>
<th>( B ) (cm(^{-1}))</th>
<th>( D ) (cm(^{-1}))</th>
</tr>
</thead>
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<td>A'</td>
<td>8.48a₀</td>
<td>0.00</td>
<td>0.0596</td>
<td>1.6×10⁻⁶</td>
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<tr>
<td>b</td>
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<td>0.0608</td>
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<td>A'</td>
<td>7.94a₀</td>
<td>11.59</td>
<td>0.0681</td>
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</tr>
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<td>7.89a₀</td>
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<td>0.0690</td>
<td>-2.3×10⁻⁵</td>
</tr>
<tr>
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<td>6.46</td>
<td>0.0598</td>
<td>-3.0×10⁻⁴</td>
</tr>
</tbody>
</table>

TABLE II. Calculated values characterizing rotational stacks for \(^{13}\)CO dimer, from the DFT-SAPT potential energy surface. The effective intermolecular distance \( R_{\text{e}}=\text{(2μB)}^{1/2} \).
was fitted through a physically meaningful subset of the resulting values. This procedure gave \( D = 247.79 \text{ cm}^{-1} \), \( a_M = 0.6200 \text{a}_0^{-1} \), and \( R_0 = 7.0129 \text{a}_0 \). To obtain a basis in which also the effect of the continuum on the wave function could be represented, the Morse potential was extrapolated linearly for \( R > 10.05 \text{a}_0 \), leading to \( V_{\text{ext}} \).

The first 15 radial basis function and angular functions up to \( j_A, j_B = 10 \) were used in the calculations. Rovibrational states were calculated for total angular momentum up to and including \( J = 6 \), both for \( ^{12}\text{CO} \) dimer and the isotopically substituted \(^{13}\text{CO} \) dimer. Off-diagonal Coriolis terms, coupling blocks with different \( K \) values, were taken into account. The monomer rotational constants were fixed at 1.9317 \text{ cm}^{-1} \) for \(^{12}\text{CO} \) and 1.8465 \text{ cm}^{-1} \) for \(^{13}\text{CO} \), consistent with the monomer bond length of 2.132\text{a}_0 \). Since \(^{13}\text{CO} \) is of nuclear spin zero, only states with \( A^+ \) or \( A^- \) symmetry are allowed for the \(^{13}\text{CO} \) dimer. The \(^{13}\text{C} \) nucleus has a spin of 1/2, however, so this restriction does not apply to this isotopomer, and levels for all four symmetries \((A^+, B^z)\) were calculated.

When substituting \(^{12}\text{C} \) by \(^{13}\text{C} \), the centers of mass in the

![FIG. 5. Cuts through the wave function of the lowest level in the \( K = 0 \) stack on the DFT-SAPT potential: (a) \( J = 0 \) (upper left), (c) \( J = 0 \) (upper right), (e) \( J = 1 \) (lower left), and (j) \( J = 1 \) (lower right). The cuts are for \( \phi = 180^\circ \) and \( R = R_{\text{eff}} \). Contours are drawn at values \( \pm k |\phi_{\text{max}}|/10 \) for \( k = 1, \ldots, 9 \).](image)

<table>
<thead>
<tr>
<th>Stack</th>
<th>( K )</th>
<th>Symmetry</th>
<th>( R_{\text{eff}} )</th>
<th>Origin (cm(^{-1}))</th>
<th>( B ) (cm(^{-1}))</th>
<th>( D ) (cm(^{-1}))</th>
</tr>
</thead>
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<td>( a )</td>
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<td>( A^+ )</td>
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<td>0.00</td>
<td>0.058 22</td>
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</tr>
<tr>
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<td>( B^+ )</td>
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<td>2.26</td>
<td>0.057 48</td>
<td>0.9 \times 10^{-6}</td>
</tr>
<tr>
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<td>( A^+ )</td>
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<td>2.26</td>
<td>0.058 70</td>
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</tr>
<tr>
<td>( c )</td>
<td>0</td>
<td>( A^+ )</td>
<td>8.50\text{a}_0</td>
<td>6.95</td>
<td>0.072 51</td>
<td>5.7 \times 10^{-6}</td>
</tr>
<tr>
<td>( d_1 )</td>
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<td>( B^+ )</td>
<td>7.64\text{a}_0</td>
<td>9.03</td>
<td>0.071 08</td>
<td>9.6 \times 10^{-6}</td>
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<td>( A^+ )</td>
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<td>9.03</td>
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<td>( e )</td>
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<td>( B^+ )</td>
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</tr>
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<td>( f_1 )</td>
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<td>( A^+ )</td>
<td>8.27\text{a}_0</td>
<td>11.41</td>
<td>0.060 65</td>
<td>2.4 \times 10^{-4}</td>
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<td>( f_2 )</td>
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<tr>
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<td>( A^+ )</td>
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<td>11.54</td>
<td>0.061 71</td>
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<tr>
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<td>10.29</td>
<td>0.066 49</td>
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</tr>
<tr>
<td>( k_1 )</td>
<td>1</td>
<td>( A^+ )</td>
<td>8.42\text{a}_0</td>
<td>6.36</td>
<td>0.058 57</td>
<td>2.4 \times 10^{-6}</td>
</tr>
<tr>
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<td>( B^+ )</td>
<td>8.36\text{a}_0</td>
<td>6.36</td>
<td>0.059 37</td>
<td>2.6 \times 10^{-6}</td>
</tr>
</tbody>
</table>

\( ^4 \text{Fit with } J \leq 3 \text{ states only.} \)
CO molecules shift slightly. To account for this effect, the coordinates $R$, $u_A$, $u_B$, and $f$ for $^{13}$CO dimer were transformed to coordinates describing the same geometry in $^{12}$CO dimer using the formulas from Ref. 35, and the potential was again reexpanded, this time using angular functions up to $L_A, L_B \leq 7$ inclusive.

III. RESULTS

A. DFT-SAPT potential

In Fig. 1, the radial dependence of the DFT-SAPT potential is compared to that of the previous CCSD($\tilde{T}$) potential. On each point on the $R$ grid, the potential is minimized in all three angular coordinates. The DFT-SAPT potential shows the same double-well structure as the CCSD($\tilde{T}$) potential; the difference in energy between the global minimum at larger $R$ and the local minimum at smaller $R$ is more pronounced in the DFT-SAPT surface. Furthermore, the global minimum is located at a slightly shorter intermolecular distance than for the CCSD(T) potential.

The angular dependence of the DFT-SAPT potential is shown in Fig. 2. The figure is a cut through the full surface, for $\phi = 180^\circ$, and $R$ values that minimize the potential in each $(\theta_A, \theta_B)$ point. Overall, the shape is the same as that of the CCSD(T) potential. The depths of the two wells in both potentials and the corresponding geometries are compared in Table I. Due to the truncation of the expansion in Eq. (2) to $L_A, L_B \leq 6$, the fit contains small errors, especially in the valley around the local minimum. In Fig. 3, the potential along a minimum energy path through this valley is shown. It shows that the points calculated with the DFT-SAPT method smoothly go down to a minimum on the $\theta_A = \pi - \theta_B$ diagonal, and that the fit oscillates around these points. The oscillations are strong enough to cause a shallow ($\approx 2 \text{ cm}^{-1}$), unphysical minimum away from the $\theta_A = \pi - \theta_B$ axis around $\theta_A = 32^\circ$. The largest absolute error in the bound ($V < 0$) regions of the potential is $6.4 \text{ cm}^{-1}$, with an average error of $0.17 \text{ cm}^{-1}$. The largest relative error in the repulsive part of

<table>
<thead>
<tr>
<th>Stack</th>
<th>K</th>
<th>$R_{\text{eff}}$ (cm$^{-1}$)</th>
<th>$B$ (cm$^{-1}$)</th>
<th>$D$ (cm$^{-1}$)</th>
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<td>$A^+$</td>
<td>8.21a$_0$</td>
<td>0.0063 83</td>
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<td>b</td>
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<td>$A^+$</td>
<td>8.32a$_0$</td>
<td>0.0621 16</td>
</tr>
<tr>
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<td>$A^+$</td>
<td>7.76a$_0$</td>
<td>0.0713 37</td>
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<td>d</td>
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<td>$A^+$</td>
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<tr>
<td>e</td>
<td>0</td>
<td>$A^-$</td>
<td>8.15a$_0$</td>
<td>0.0644 77</td>
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<td>f</td>
<td>1</td>
<td>$A^-$</td>
<td>8.04a$_0$</td>
<td>0.0662 52</td>
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<td>$A^+$</td>
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<td>0.0692 23</td>
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<td>$A^-$</td>
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<td>0.0648 80</td>
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<tr>
<td>k</td>
<td>1</td>
<td>$A^-$</td>
<td>8.12a$_0$</td>
<td>0.0652 28</td>
</tr>
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</table>

FIG. 6. Isotopic shifts of the stack origins for the CO dimer on the DFT-SAPT potential. The squares represent the origins of $(^{12}\text{CO})_2$, and the circles those of $(^{13}\text{CO})_2$. The zero point of energy is chosen halfway between the $a$ and $e$ origins, for both isotopes.

FIG. 7. Experimental isotopic shifts of the stack origins for the CO dimer (reproduced from Fig. 1 in Ref. 13).
the potential \( V > 150 \text{ cm}^{-1} \) is \( \approx 10\% \), with an average error of 1.8\%. Although these errors may seem relatively large, they must be put in context. In the first place, the difference between the DFT-SAPT potential and the CCSD(T) potential is substantially larger than the fit errors. Since we will finally use a weighted average of the two potentials, it does not pay to spend much more attention on improving the fit. Second, the dominant source of the error shown in Fig. 3 is the truncation of the expansion in Eq. (2) to \( L_a = 6 \). Extension of this expansion would require many more CCSD(T) and DFT-SAPT calculations, while the calculated rovibrational levels are rather insensitive to the small oscillations in the potential caused by the truncation of the expansion.

Rovibrational states were calculated on this potential, and, as was the case for the CCSD(T) potential, we were able to organize these levels in different stacks of different rotational constants. Each stack was fitted separately using a simple rigid rotor expression

\[
E = E_0 + BJ(J+1) - DJ^2(J+1)^2,
\]

and the resulting parameters are summarized in Table II. In the labeling of the stacks, the experimental assignments are followed.\(^7\)\(^-\)\(^12\),\(^14\) Figure 4 shows the calculated stacks as a function of their effective intermolecular distance \( R_{\text{eff}} \). Figure 5 cuts through the wave functions of the \( K=0 \) stacks are drawn. For each stack, the cut is made for \( \phi = 180^\circ \), and \( R = R_{\text{eff}} \) of that stack. It can be seen that the \( a \) stack wave function corresponds to the isomer with the C–C distance smaller than the O–O distance. The wave functions in the \( c \) stack correspond to the other isomer with the shorter O–O distance. The \( e \) and \( j \) wave functions clearly show excitations of the geared bending motions of the two isomers. The very low excitation frequency of \( \approx 4 \text{ cm}^{-1} \) indi-

The calculated values characterizing rotational stacks for \(^{13}\)CO dimer, from the hybrid potential energy surface.

<table>
<thead>
<tr>
<th>Stack ( K )</th>
<th>Symmetry ( \alpha )</th>
<th>( R_{\text{eff}} ) (\text{cm}^{-1})</th>
<th>( B ) (\text{cm}^{-1})</th>
<th>( D ) (\text{cm}^{-1})</th>
</tr>
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<td>( A^+B^- )</td>
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<td>0.0584</td>
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<tr>
<td>( d )</td>
<td>( B^+A^- )</td>
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<tr>
<td>( j )</td>
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<td>8.22</td>
<td>0.0624</td>
</tr>
<tr>
<td>( k )</td>
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<tr>
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<td>0.0635</td>
</tr>
<tr>
<td>( o )</td>
<td>( B^+A^- )</td>
<td>8.09a0</td>
<td>6.93</td>
<td>0.0636</td>
</tr>
</tbody>
</table>

*Fit with \( J \leq 3 \) states only.
cates that the dimer is indeed very floppy. Since the artificial minima in the fit of the potential are very shallow ($\approx 2$ cm$^{-1}$), the effect on the dynamics of the dimer is negligible. Inspection of the wave functions shows no effect of these minima on the wave functions that are located in the valley around them, i.e., those corresponding to the $c$ and $j$ stacks.

Recently, a substantial amount of experimental data on the isotopically substituted $^{13}$CO dimer has become available.$^{13,14}$ To test the potential surface, we also calculated the rovibrational levels of $(^{13}$CO)$_2$. Since the total nuclear spin of $^{13}$CO is not zero, also levels of $B^-$ symmetry exist for this dimer. This results in the $K=0$ stacks having both even and odd $J$ levels, and the $K=1$ stacks splitting up in two separate stacks: one where the even $J$ levels are of $A^+$ symmetry and the odd $J$ levels are of $B^-$ symmetry, and one where the situation is reversed. The resulting data are collected in Table III. For the $f$ states, significant Coriolis mixing with $K=2$ states occurred for the rotational levels $J \geqslant 4$. This greatly influenced the rotational constants, as can be seen in Table III. Since the DFT-SAPT potential is not sufficiently accurate to predict these couplings well, these stacks were also fitted with the $J \leqslant 3$ levels only.

Following the experimental papers, we have drawn in Fig. 6 the isotope shifts of the stack origins. For both isomers, the energy zero is chosen halfway between the $a$ and $c$ stack origins. Comparing this picture with the experimental figure in Ref. 13, reproduced here as Fig. 7, it can be seen that the agreement with experiment is very bad. Nearly all $K_{eff}$ values shift in the wrong direction, and the differences are much smaller than those in the experiment. The results on the DFT-SAPT surface suggest a nearly static isotope effect where the change in rotational constants is mainly due to the shift of the centers of mass in the monomers and the average geometry of the complex is not changed. They cannot account for the opposite and much stronger effect that was found experimentally.

Calculations on $(^{13}$CO)$_2$ on the CCSD(T) potential show that it does not predict the isotope effect any better than the DFT-SAPT potential. Also on the CCSD(T) potential, the
10. Intermolecular interactions

$R_{eff}$ values of the stack origins shift only very little, and in the wrong direction.

**B. Tuning: A hybrid potential**

When comparing the calculated rotational stacks that result from the DFT-SAPT potential with those from CCSD(T) potential, the first thing one notices is that the order of the origins of $a$ and $c$ stacks is reversed. Although also in the CCSD(T) potential the global minimum is located around $\theta_A = 135^\circ, \theta_B = 45^\circ$, the zero point energy in this minimum is so large that it overcomes the difference of $\approx 11 \text{ cm}^{-1}$ with the local minimum.\(^\text{18}\) The difference in zero point energy between the two minima is due to the fact that the well at the global minimum is much narrower than at the local minimum. The DFT-SAPT potential gives the correct sign for the energy difference between the $a$ and $c$ stack origins, however, it overestimates the value of this difference. In an attempt to obtain a potential that gives better quantitative information, we constructed a hybrid energy surface as a weighted average of the two potentials,

$$V_{\text{hybrid}} = w V_{\text{CCSD(T)}} + (1-w) V_{\text{DFT-SAPT}},$$

where the weighting coefficient $w$ was chosen in such a way that the experimental value for the energy difference $\Delta E = E(c,J=0) - E(a,J=0)$ was reproduced. The resulting value for this weighting coefficient was $w = 0.7$.

The calculated rovibrational energy levels from this hybrid potential for $^{13}\text{CO}_2$ dimer are given in Table IV and a pictorial representation is shown in Fig. 8. One can see that the adjustment of the potential to reproduce the splitting between the $a$ and $c$ stacks has a positive effect on the other stacks as well. The experimentally determined stack origins are reproduced very well, the maximum error being $0.25 \text{ cm}^{-1}$. Also the computed rotational constants agree better with their experimental counterparts for most stacks.
Rovibrational levels for the isotopically substituted $^{13}$CO dimer were also calculated on the hybrid potential, and the results are summarized in Table V. This time the $g$ stacks are very strongly mixed with $K = 2$ states for $J \geq 4$. Also for the heavier isotope, the hybrid potential gives results that are much closer to the experimental data. Comparing Fig. 9 with the experimental picture in Fig. 7 shows that not only do the isotope shifts have the correct sign on the hybrid potential, also the magnitude of the shifts is in much better agreement with the experimental data. Unfortunately, the $g$ stack has not been observed for $(13\text{CO})_2$, leaving us without a check of whether the strong Coriolis coupling that the hybrid potential predicts for these stacks is real.

It is obvious from Figs. 6 and 9 that the isotopic shifts are very sensitive to the exact shape of the potential. Since the overall shape of the CCSD(T) and DFT-SAPT potentials is more or less the same, taking a linear combination of these two corresponds roughly to shifting the two deepest minima with respect to each other. Although the change in the difference between the two wells is only a few wave numbers [from $-26.5 \text{ cm}^{-1}$ on the DFT-SAPT surface and $-11 \text{ cm}^{-1}$ on the CCSD(T) surface, to $-15.5 \text{ cm}^{-1}$ on the hybrid surface], the effect on the isotopic dependence of the system is large. The reason for that can be seen when we compare the wave functions for $(^{13}\text{CO})_2$ on both surfaces. Figures 5 and 10 show cuts through the lowest $K = 0$ wave functions from the DFT-SAPT and the hybrid PES, respectively. The cuts are for $\phi = 180^\circ$ and $R = R_{\text{eff}}$. We see that on the hybrid surface, the wave functions are much more delocalized than on the DFT-SAPT surface. Whereas the wave functions on the DFT-SAPT potential are located in either of the two wells, with little or no density in the other well, the wave functions on the hybrid surface are delocalized over both wells. This reduces the difference between the wave functions of the $a/e$ and $c/j$ stacks, with the result that the resulting $R_{\text{eff}}$ values (which are different for the two wells) are also more alike. For the $^{13}$CO dimer, this effect is much smaller (see Fig. 11), since the wave functions are better localized in the two wells due to the heavier mass of the molecules. Hence, the observed behavior of the isotope effect is of a truly dynamical nature, and can only be described correctly if the relative depth of the minima is such that the wave function can tunnel through the barrier between them.

IV. CONCLUSION

The DFT-SAPT method was employed to compute a four-dimensional PES for the CO dimer. The overall shape of the potential is the same as that of a previously published CCSD(T) potential. As in the experiment, stacks of rovibrational levels could be identified and assigned in the calculated results. Though the agreement between calculations and experiment is not yet perfect, the rovibrational calculations show that the DFT-SAPT and the CCSD(T) surfaces are of comparable quality, making DFT-SAPT a viable alternative for the vastly more expensive CCSD(T) method.

In an effort to overcome the deficiencies of the two $ab\text{ initio}$ potentials, a hybrid potential was constructed by taking a weighted average of the DFT-SAPT and the CCSD(T) potential. The weighting factor was optimized only to reproduce the energy splitting between the two lowest $J = 0$ levels, but the resulting surface proved to give a huge improvement on the location of all observed stacks.

Neither the CCSD(T) nor the DFT-SAPT potential alone can explain the observed differences in the effective intermolecular separation $R_{\text{eff}}$ between $(^{12}\text{CO})_2$ and $(^{13}\text{CO})_2$. This is mainly due to the fact that the $R_{\text{eff}}$ values for the $^{13}$CO dimer are very sensitive to the relative location of the two deepest minima in the potential. The hybrid potential gives shifts that are in good agreement with the experimental values.

ACKNOWLEDGMENTS

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10. Intermolecular interactions

10.3. Interaction energy contributions of H-bonded and stacked structures of the AT and GC DNA base pairs from DFT-SAPT

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author(s): A. Heßelmann, G. Jansen, M. Schütz
year: 2006
volume: 128
pages: 11730
Key words:
- deoxyribonucleic acid
- adenine-thymine
- cytosine-guanine
- base pair
- Watson-Crick
- symmetry-adapted perturbation theory
In the past decade, we have seen a strong increase in the number of quantum chemical studies of the interaction between the purine and pyrimidine constituents of DNA.\textsuperscript{1,3} One of the goals of these studies is to provide as accurate as possible interaction energies for which, with a notable exception,\textsuperscript{6} there is hardly any experimental information available. Another important goal is to provide insight into the nature of the interactions between the nucleobases. The quantum chemical investigations carried out so far usually employed the supermolecular approach, often followed by an a posteriori rationalization of the results using notions of intermolecular perturbation theory. The interplay between the electrostatic, $E_{el}$, and the dispersion, $E_{disp}$, interaction energies has received particular attention. $E_{el}$ often is calculated from point charges or multipoles\textsuperscript{7} distributed over the monomers, thus neglecting its important penetration part.\textsuperscript{8} In supermolecular calculations, $E_{disp}$ usually is estimated from the electron correlation contribution to the interaction energy which, in fact, contains further interaction terms. A hybrid class of methods combines approximate treatments of the long-range part of $E_{disp}$ with supermolecular density functional theory (DFT)\textsuperscript{9} so as to correct for corresponding failures of the present exchange-correlation (xc) functionals.\textsuperscript{5}

To put the discussion of the interplay of the various interaction energy contributions on firm quantitative grounds, it appears most appropriate to consistently use a well-defined variant of intermolecular perturbation theory, such as symmetry-adopted perturbation theory (SAPT).\textsuperscript{9} In SAPT, the total interaction energy, $E_{tot}$, is obtained as a sum of first-order electrostatic, $E_{el}^{(1)}$, and second-order induction and dispersion contributions, $E_{ind}^{(2)}$ and $E_{disp}^{(2)}$, respectively. All of these terms do contain the corresponding penetration contributions; the second-order charge-transfer contribution is included in $E_{ind}^{(2)}$. Furthermore, these terms are accompanied by corresponding first-, $E_{exch}^{(1)}$, and second-order exchange-corrections, $E_{exch-ind}^{(2)}$ and $E_{exch-disp}^{(2)}$, respectively, describing the repulsive effects of electron exchange over the overlapping molecular charge distributions. In particular, for hydrogen bridges induction, exchange-induction and charge-transfer effects of higher than second order in the intermolecular perturbation operator become non-negligible, their combined effect can be estimated from supermolecular Hartree–Fock calculations and is denoted as $\delta^{\text{HF}}$.\textsuperscript{10}

Thanks to the combination of a DFT treatment of monomer properties with a SAPT treatment of intermonomer interactions (DFT–SAPT)\textsuperscript{10,11} and the introduction of the density-fitting approximation, SAPT calculations with extended basis sets on medium-sized systems, such as the benzene dimer, recently have become possible.\textsuperscript{12} Here we investigate the Watson–Crick (WC) and stacked (S) structures of the adenine–thymine (AT) and guanine–cytosine (GC) base pairs with DFT–SAPT.

Their gas-phase-optimized structures were taken from the work of Jurečka and Hobza.\textsuperscript{16} The aug-cc-pVXZ (X = D, T, Q) sets\textsuperscript{13} were used as atomic basis sets, and the cc-pVXZ+1\textsuperscript{14} JZ-fitting and aug-cc-pVXZ MP2-fitting sets\textsuperscript{14} were employed for the density-fitting approximation. Complete basis set (CBS) limits of DFT–SAPT interaction energies were obtained by extrapolating the augmented triple- and quadruple-$\zeta$ results for $E_{disp}$ and $E_{exch-disp}$ with the scheme of Bak et al.,\textsuperscript{15} adding all other contributions as calculated with the aug-cc-pVQZ basis set. Monomer DFT calculations were done with the LBE0/A0 xc potential.\textsuperscript{16,12,16,17} All core electrons were kept frozen in the response calculations using the ALDA xc kernel. The calculations have been done with the Molpro quantum chemistry package.\textsuperscript{18}

Table 1 displays the total interaction energies along with second-order Möller–Plesset (MP2) and coupled-cluster (CCSD(T)) results.\textsuperscript{3} Note that in order to obtain overall stabilization energies the repulsive contributions of deformation of the monomers from their gas-phase equilibrium geometries to their structure within the dimer should be added. Clearly, large basis sets are required to obtain converged results. This is most obvious for the GC(WC) pair, where the difference between the augmented double-$\zeta$ result and the CBS limit amounts to $-2.4$ kcal/mol for DFT–SAPT and $-2.9$ kcal/mol for MP2. At present, a direct CBS extrapolation is not feasible for CCSD(T); here it is assumed that the differences between MP2 and CCSD(T) as found in a double-$\zeta$ basis set constant upon increase of basis set quality so that they can be added to the CBS extrapolated MP2 energy.\textsuperscript{14} While these CCSD(T) corrections are relatively small for the WC structures ($-0.5$–$0.0$ kcal/mol), they are much more important and become repulsive for the stacked structures ($1.8$–$2.8$ kcal/mol). Similar trends were observed for the benzene dimer and can be traced back to a too attractive dispersion contribution contained in the supermolecular MP2 energy.\textsuperscript{12} DFT–SAPT, on the other hand, is known to describe the dispersion contribution in good agreement with elaborate many-body SAPT calculations.\textsuperscript{10a} With DFT–SAPT, the stacked structures of AT and GC are found to be even somewhat less bound than with CCSD(T) (by $1.4$ and $1.2$ kcal/mol, respectively). Since this is also true for the hydrogen-bonded structures, which deviate by $1.2$ (AT) and $1.6$ (GC) kcal/mol from the estimated CCSD(T) interaction energy, one finds a good agreement for the relative energies between both methods: while with MP2 the WC structure of AT is only $1.8$ kcal/mol more stable than the stacked structure, CCSD(T) and DFT–SAPT yield $4.6$ and $4.8$ kcal/mol, respectively. For the GC pair, the WC structure is favored by $10.8$ kcal/mol with MP2, while CCSD(T) and DFT–SAPT give $13.1$ and $12.7$ kcal/mol, respectively. In agreement with earlier observations,\textsuperscript{14} all methods describe GC(S) as even more stable than AT(WC).
The prevailing point of view that the WC structures are mainly stabilized by $E_{\text{el}}^{(1)}$ is supported by Figure 1 in the sense that it is the dominating attractive contribution. It is, however, overcompensated through $E_{\text{disp}}^{(2)}$ leading to overall repulsive first-order contributions of 8.3 and 5.1 kcal/mol for AT and GC, respectively. A similar observation has been made by Fonseca Guerra et al. via an energy decomposition scheme of the supermolecular DFT energy. As is clear from the figure, the interaction contributions of second and higher order in the intermolecular perturbation play a most important role for the stabilization of the WC structures.

For the stacked structures, Figure 1 shows that $E_{\text{disp}}^{(4)}$ is the most important contribution to $E_{\text{tot}}$, as expected. Yet, a closer inspection reveals also unexpected findings: while for AT $E_{\text{disp}}^{(4)}$ is roughly 2-fold larger than $E_{\text{disp}}^{(2)}$ and $E_{\text{disp}}^{(3)}$ for GC, this is not the case. Here $E_{\text{disp}}^{(4)}$ is nearly as large as $E_{\text{disp}}^{(2)}$ and $E_{\text{disp}}^{(3)}$ amounts to about 20% of $E_{\text{disp}}^{(4)}$. So, for the GC(S) pair, all three types of interaction (electrostatic, induction, and dispersion) play an equally important role. One should note, however, that this applies to the gas-phase-optimized stacked dimer structure showing two fairly close distances of 2.28 and 2.45 Å, respectively, between hydrogen atoms of strongly nonplanar amino groups of one monomer and the carbonyl group oxygen atoms of the other. Such close contacts are not found for the intrastrand stacked structures of GC in DNA. A similar proviso can be made for the AT dimer, but here the gas-phase-optimized stacked structure displays only one comparable H−O contact with a much larger distance of 2.77 Å.

Furthermore, we note that (i) the dispersion energies for the WC structures still amount to 80% (GC) and 64% (AT) of that of the stacked structures; (ii) $E_{\text{ind}}$ is quenched to a large extent by $E_{\text{el}}^{(2)}$ for the stacked structures (by 90% for AT and 80% for GC), and much less for the WC structures (by 66% for AT and 60% for GC); and (iii) $\langle \mathcal{H} \rangle$ makes a qualitatively substantial contribution to the total interaction energy of 30% (GC) to 38% (AC) for the WC and 13% (GC) to 16% (AC) for the stacked structures. Since intramonomer and higher-order intermonomer electron correlation effects are not included in this estimate, we suspect it to be responsible for most of the remaining errors in the method.

In summary, for the stacked and WC structures of AT and GC, cbs-extrapolated DFT−SAPT yields total interaction energies which deviate by an upward shift of 1.2−1.6 kcal/mol from estimated cbs CCSD(T) results. This is a very satisfactory agreement in view of the wildly differing theoretical foundations of both approaches. The rigorous determination of individual energy contributions to the total interaction energy available through DFT−SAPT furthermore allows for the detailed understanding of their interplay and should be useful for future theoretical descriptions and parametrizations of the fundamental base pair interactions in DNA.

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Supporting Information Available: Tables with interaction energy contributions. This material is available free of charge via the Internet at http://pubs.acs.org.

References


10.4. Stacking Energies for Average B-DNA Structures from DFT-SAPT

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- cytosine-guanine
- DNA base tetramer
- Watson-Crick
- symmetry-adapted perturbation theory
The σ-stacking energy between parallel layers of hydrogen-bonded base pairs is one of the important factors stabilizing the structure of DNA. It is of considerable interest to achieve a detailed qualitative and quantitative understanding of the physicochemical nature of these interactions, for example, in the notions of intermolecular perturbation theory such as the first-order electrostatic, $E_{\text{el}}^{(1)}$, second-order induction, $E_{\text{ind}}^{(2)}$, and dispersion, $E_{\text{disp}}^{(2)}$, contributions to the interaction energy $E_{\text{int}}$. These terms have been defined in the early days of quantum mechanics and continue to form the basis of our understanding of the interactions between molecules. They also form the conceptual framework of the intermolecular part of most force-fields actually in use to simulate biopolymers such as DNA. For example, in present force-fields $E_{\text{el}}^{(1)}$ usually is approximated through Coulomb interactions between partial charges located at the atoms and $E_{\text{disp}}^{(2)}$ through atom–atom potentials decaying as $1/R^6$. In particular these two contributions also play an important role in the framework of quantum chemical calculations of stacking interactions: the former in attempts to correlate $E_{\text{int}}$ from supermolecular calculations with more or less elaborate approximations to $E_{\text{el}}^{(1)}$ and $E_{\text{disp}}^{(2)}$ in methods aiming at improving density functional theory (DFT) for stacking interactions via direct addition of damped atom–atom dispersion energies.

In the present study stacking energies for all possible combinations of two base pairs arranged as in an averaged B-DNA structure were obtained directly from intermolecular perturbation theory. To this end the recently developed DFT-SAPT$^4$ combination of symmetry-adapted intermolecular perturbation theory (SAPT)$^5$ with a DFT description of the monomer properties entering SAPT has been employed. DFT-SAPT and the related SAPT/DFT$^5$ approach do not rely on any multipole approximation but rather employ the full charge densities and the frequency-dependent linear response densities of the interacting molecules to evaluate $E_{\text{el}}^{(1)}$, $E_{\text{ind}}^{(2)}$, and $E_{\text{disp}}^{(2)}$. Thus the important charge density penetration effects are fully taken into account—not only in the first-order$^2$ but also in the second-order contributions. Furthermore, the simultaneous exchange of electrons between the interacting molecules due to the antisymmetry requirement of the total waveform is taken care of in SAPT by adding the repulsive exchange corrections $E_{\text{exch}}^{(1)}$, $E_{\text{exch-\text{ind}}}^{(2)}$, and $E_{\text{exch-\text{disp}}}^{(2)}$ to the above terms. To these contributions the Hartree–Fock estimate of the third and higher order induction and exchange-induction contributions denoted as $\Delta^{(n)}(\text{HF})$ is added. In a number of previous benchmark studies including the benzene-dimer,$^4$ the acetylene–benzene complex,$^7$ and Watson–Crick (WC) and stacked structures of the guanine-cytosine (GC) and adenine-thymine (AT) dimers,$^8$ it was shown that the resulting total interaction energies are in excellent agreement with the outcome of expensive coupled-cluster calculations including up to non-iterative triple excitations (CCSD(T)). CCSD(T) is accepted to yield the most accurate $E_{\text{int}}$ for these systems to date. The present contribution thus aims at providing accurate values for both the total interaction energies and all of its contributions.

In contrast to our previous work$^9$ not only dimers but rather tetramers consisting of two stacked complementary dimers of the DNA bases were considered. While the dimer structures used previously came from ab initio gas-phase geometry optimizations$^9$ and were not representative for their arrangement in DNA, the tetramer structures in this study correspond more closely to those they assume in B-DNA. They were generated with the 3DNA program$^{11}$ using the complementary base pair ($\kappa = 0.5^\circ$, $\pi = -11.4^\circ$, $\alpha = 0.6^\circ$, $\delta = 0.00$ Å, $\delta_z = -0.15$ Å, $\delta_y = 0.09$ Å) and base-pair step parameters ($\tau = -0.1^\circ$, $\rho = 0.6^\circ$, $\omega = 36.0^\circ$, $D_{\text{x}} = -0.02$ Å, $D_{\text{y}} = 0.23$ Å, $D_{\text{z}} = 3.32$ Å) for B-DNA obtained as average values from high-resolution crystal structures. Use of these parameters provides a well-defined point of reference for later studies investigating the influence of deviations from these average values. The hydrogen atom positions were determined in second-order Møller–Plesset (MP2) geometry optimizations of the complementary AT and CG dimers, employing the TZVPP basis set$^{12}$ and constraining the positions of the C, N, and O atoms to those generated by 3DNA. Since the current version of DFT-SAPT is restricted to dimer interaction energies, each complementary dimer was considered as a supermolecule, thus treating it actually as one of the monomers in DFT-SAPT. All DFT-SAPT and accompanying supermolecular calculations were done with Molpro,$^13$ keeping core orbitals frozen. Density-fitting techniques as detailed in ref 4f were employed. The aug-cc-pVTZ basis set$^{14}$ used throughout, combined with the corresponding MP2 auxiliary basis set$^{15}$ for density-fitting of DFT-SAPT dispersion contributions and supermolecular correlation energies, while density-fitting of all other SAPT contributions was done with the cc-pVQZ JK auxiliary basis set.$^{16}$

Supermolecular $E_{\text{int}}$ were counterpoise-corrected.$^{17}$ which, by construction, is not necessary with DFT-SAPT. The exchange-correlation potential and kernel entering the DFT calculations were approximated with the LPBE0AOC$^{18}$/ALDA$^{19}$ combination justified in ref 4f.

Figure 1 compares total $E_{\text{int}}$ from DFT-SAPT to results from supermolecular electron correlation methods applicable to systems of this size, that is, MP2 and spin-component-scaled MP2$^{20}$ (SCS-MP2), also using the aug-cc-pVTZ basis set. MP2 is known to strongly overestimate the electron correlation contribution to $\tau$–$\pi$ interacting systems, while SCS-MP2 yields $E_{\text{int}}$ in much better agreement with CCSD(T).$^{20}$ The stacking energies from DFT-SAPT and the 3.5 times less time-consuming SCS-MP2 agree quite well, despite their entirely different theoretical background. Depending on the base pair step $E_{\text{int}}$ varies between −30.7 (AT-TA) and −55.0 kJ/mol (CG-GC) with DFT-SAPT and between −27.7 and −49.5 kJ/mol with SCS-MP2. SCS-MP2 underestimates the magnitude of $E_{\text{int}}$ with respect to DFT-SAPT by 0.6 (GC-AT) to 5.5 kJ/mol (CG-GC), on average by 2.5 kJ/mol. MP2, on the other hand, yields drastically larger magnitudes of $E_{\text{int}}$ that is, by 17.8 (CG-AT) to 21.7 kJ/mol (GC-CG), and on average by 20.1 kJ/mol.
Figure 2 shows the DFT-SAPT contributions to $E_{\text{ind}}$ of the first-order energies $E_{\text{el}}^{(1)}$ and $E_{\text{exch}}^{(1)}$, the sum of all induction and exchange-induction energies $E_{\text{ind}} = E_{\text{ind}}^{(1)} + E_{\text{ind}}^{(2)}$ and $E_{\text{disp}}^{(2)}$, and the second-order total dispersion energy $E_{\text{disp}} = E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}$ (cf. Supporting Information for complete data). By and large, the relative importance of the various contributions for all base-pair steps is similar to that found for $\pi$-stacked structures of the benzene dimer.\(^{26}\) In detail, $E_{\text{disp}}$ is the largest contribution, in which the repulsive $E_{\text{exch-disp}}^{(2)}$ cancels only 11 to 14% of $E_{\text{disp}}^{(2)}$. Depending on the base-pair step $E_{\text{disp}}$ varies between $-77.3$ (TA-AT) and $-94.9$ kJ/mol (CG-GC). $E_{\text{disp}}$ is the least important and most constant among all contributions. It lies between $-5.0$ (TA-AT) and $-10.6$ kJ/mol (CG-GC) and on average amounts to $-7.5$ kJ/mol. Note that $E_{\text{disp}}$ is much larger and varies much more strongly, that is, between $-24.6$ (TA-AT) and $-52.7$ kJ/mol (CG-CG). Yet, about 80 to 90% of this is compensated by the repulsive $E_{\text{exch-disp}}$. To the remainder the higher-order induction and exchange-induction estimate $\Delta(HF)$ adds between $-1.7$ (GC-GT) and $-4.2$ kJ/mol (CG-GC). The two first-order contributions, $E_{\text{el}}^{(1)}$ and $E_{\text{exch}}$, vary strongly with the base-pair step. While the electrostatic interaction energy is always negative, with values between $-4.8$ (CG-CG) and $-43.5$ kJ/mol (CG-GC), the repulsive first-order exchange energy is the decisive factor counterbalancing the dispersion contribution. It ranges from $+54.0$ (TA-AT) to $+94.0$ kJ/mol (CG-CG). The strikingly large contributions in the CG-GC step can be attributed to close contacts: three pairs of atoms have distances which are smaller by 0.2 Å than the sum of their standard van der Waals radii.\(^{26}\) In CG-GT there are such two pairs, in TA-AT one, and none in all other steps.

As becomes apparent from Figure 2 there are no quantitatively useful correlations between the total interaction energy and any of its contributions. Among all individual contributions $E_{\text{el}}^{(1)}$ still correlates best with $E_{\text{tot}}$ but the Pearson correlation coefficient $r_{xy}$ is only 0.756 and thus too small to be quantitatively exploited. The present results thus confirm the previous criticism\(^{26}\) of corresponding attempts.\(^{2a,b}\) Adding $E_{\text{exch}}$ with its partially compensating trends to $E_{\text{el}}^{(1)}$ does not help: $r_{xy}$ now drops to 0.687. There are, however, reasonable correlations between individual interaction energy components, the strongest of which is that between $E_{\text{ind}}^{(2)}$ and $E_{\text{exch-disp}}^{(2)}$ with $r_{xy} = -0.987$. As mentioned above, these two contributions cancel each other to a large extent, and their sum has about the same size as $\Delta(HF)$. The latter, however, does not correlate with $E_{\text{ind}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ ($r_{xy} = -0.949$) and $E_{\text{ind}}^{(2)}$ and $E_{\text{exch-disp}}^{(2)}$ ($r_{xy} = -0.920$). The most useful correlation for quantitative purposes, however, is that between $E_{\text{ind}}^{(2)}$ and $E_{\text{disp}}$: $r_{xy}$ here is merely 0.776, but because of the relative smallness of $E_{\text{ind}}^{(2)}$ a simple scaling of $E_{\text{disp}}$ with 1.09 reproduces the sum $E_{\text{ind}}^{(2)} + E_{\text{disp}}$ within about ±2 kJ/mol. This appears to be good enough to effectively account for the total induction contribution in a classical nonpolarizable force field for DNA simulations—at least as long as the surrounding environment (backbone, water, counterions) of the base pairs is neglected.

In summary, reliable modeling of DNA stacking requires accurate models of at least the first-order electrostatic and exchange and the second-order total dispersion contributions. The results presented here provide a well-defined basis for future developments of force-fields and quantum chemical models in this important area.

Supporting Information Available: Complete refs 11 and 13, further computational details, tables with energies and atomic coordinates, and figures of calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.
10.5. Improved supermolecular second order Møller-Plesset intermolecular interaction energies using TDDFT response theory

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- dispersion energy
- Møller-Plesset perturbation theory
- local Hartree-Fock
- adiabatic local density approximation
- rare gas dimers
- hydrogen fluoride dimer
- water dimer
The supermolecular second order Møller-Plesset (MP2) intermolecular interaction energy is corrected by employing time-dependent density functional (TDDFT) response theory. This is done by replacing the uncoupled second order dispersion contribution contained in the supermolecular MP2 energy with the coupled dispersion energy obtained from the TDDFT approach. Preliminary results for the rare gas dimers He$_2$, Ne$_2$, and Ar$_2$ and a few structures of the (HF)$_2$ and (H$_2$O)$_2$ dimers show that the conventional MP2 interaction energies are considerably improved by this procedure if compared to coupled cluster singles doubles with perturbative triples [CCSD(T)] interaction energies. However, the quality of the interaction energies obtained in this way strongly depends on the exchange-correlation potential employed in the monomer calculations: It is shown that an exact exchange-only potential surprisingly often performs better than an asymptotically corrected hybrid exchange-correlation potential. Therefore the method proposed in this work is similar to the method by Cybulski and Lytle [J. Chem. Phys., 127, 141102 (2007)] which corrects the supermolecular MP2 energies with a scaled dispersion energy from time-dependent Hartree–Fock. The results in this work are also compared to the combination of density functional theory and intermolecular perturbation theory. © 2008 American Institute of Physics. [DOI: 10.1063/1.2905808]

I. INTRODUCTION

The description of weak van der Waals interactions using quantum chemistry methods is still a demanding challenge. This on the one hand is due to the usually high level of the electron correlation method required and on the other hand because, in general, large basis sets have to be used. The latter is true because the electron correlation effects are captured best if using high angular momentum functions in the basis set and furthermore the basis set also should contain enough diffuse functions in order to properly describe the asymptotic ranges of the wave functions which is crucial for describing weak interactions between molecules. Because of these requirements it has become common to use density functional theory (DFT) methods in order to study interactions between extended molecules. This stems from the fact that firstly common DFT methods in the local density approximation (LDA) framework or in the generalized gradient approximation (GGA) framework are generally cheap electronic structure correlation methods, and secondly the basis set convergence of the interaction energies is usually faster if compared with standard ab initio correlation methods (see, e.g., Ref. 4).

However, it is well known in the community that LDA or GGA based DFT methods do not at all describe the important long-range correlation or dispersion interaction part of the total interaction between two molecules. Thus by now a large range of methods exist in order to resolve this problem. A popular, because cheap, method is to add the missing dispersion interaction to the total DFT interaction energy via a multipole expansion using empirical atom-atom dispersion coefficients. However, in these approaches the multipole expanded dispersion contribution has to be combined with a proper damping function which damps the dispersion for shorter ranges, and, moreover, since standard DFT methods are able to describe short-range correlations, this also has to be done in order to avoid the double counting of correlation effects. An interesting new DFT+ “damped dispersion” approach stems from Johnson and Becke. Here the dispersion interaction contribution is described using the fluctuating dipole moment of the exchange hole. Note, however, that a strict justification of this approach has not yet been found.

More DFT conform methods, i.e., methods which are more within the framework of standard DFT, avoid the problem of double counting by explicitly using correlation functionals which shall capture the weak van der Waals interactions. The functional developed by Lundqvist and coworkers, for example, uses an explicit nonlocal density functional expression for the correlation energy derived from the adiabatic connection formula. Another possibility is to write the correlation functional as an orbital functional so that accurate direct expressions are accessible through the use of perturbation theory. Similar to the latter ansatz are also the methods which determine the correlation energy by using the fluctuation dissipation DFT approach.
Other variants to account for the van der Waals interactions in DFT methods are generally hybrid methods. In these the DFT method is combined with conventional \textit{ab initio} correlation methods so that the latter shall capture the long-range correlation effects missing in the DFT approaches. A simple and straightforward way to realize this is to just define the total exchange-correlation (xc) energy as a weighted sum of a GGA xc energy and the (for example) second order Möller–Plesset (MP2) correlation energy functional as recently been proposed by Grimme.\textsuperscript{22} While the weight parameters are to be determined, for example, by fitting to experimental or higher level theoretical data, a drawback of this approach is the not clearly defined separation of correlation effects of the DFT and MP2 part and thus the danger of possible double counting of correlation effects. This is avoided in the so called short-range–long-range methods in which the DFT and \textit{ab initio} description of electron correlation is separated from each other by splitting the Coulomb interaction operator into a short-range and a long-range part.\textsuperscript{23–25} A clearly different method is the DFT-SAPT method\textsuperscript{26–28} which couples DFT with symmetry-adapted intermolecular perturbation theory\textsuperscript{29,30} [see also Refs. 30 and 31 and references therein for a similar approach termed SAPT(DFT) by Szalewicz \textit{et al.}]. Here the DFT method describes the intramolecular correlation effects, i.e., the correlation within each monomer, while the framework of intermolecular perturbation theory accounts for the intermolecular correlation effects. An advantage of this approach is that the intermolecular interaction energy is not indirectly calculated via the supermolecular approach but is obtained directly as a sum of physically interpretable contributions. This on the one hand enables an interpretation of the nature of the interaction and on the other hand avoids the dealing with the basis set superposition error which does not occur in intermolecular perturbation theory approaches.

While it has been shown that the DFT-SAPT method is potentially exact for some of the interaction energy contributions up to second order,\textsuperscript{26} namely, the electrostatic, induction, and dispersion interaction (which will be termed as polarization terms in the following), this is not so for the individual exchange terms. The latter appear in the total interaction energy due to the exchanges of electrons between the monomers if both monomers have a closer contact. “Potentially exact” in this case simply means that the polarization terms could be obtained exactly from the DFT-SAPT method would the exact xc potential and the exact xc kernel be employed for the ground and excited state monomer Kohn–Sham calculations, while this no longer holds for the exchange terms since these depend on (response-) density matrices of the monomers which cannot be obtained exactly even within an exact (time-dependent) Kohn–Sham framework.\textsuperscript{22} Another problem of the current standard DFT-SAPT formulation is the capturing of interaction energy terms of higher orders. In the current formulation of DFT-SAPT, this is achieved using the supermolecular Hartree–Fock method, i.e., the high order terms are described on a purely uncorrelated level. While it has been shown for a broad range of different dimer systems\textsuperscript{27,28,33,34} that this approach appears to work fairly well, it has to be noted that the third and higher order contributions can become quite large compared to the total amount of the interaction energy, especially in the case of the interaction between polar monomers.

Therefore here a new approach is proposed which avoids the discussed difficulties of the DFT-SAPT method but which makes use of the potentially exact and, if approximate xc functionals are employed, usually very accurate description of the intermolecular dispersion energy within the DFT-SAPT framework. This is achieved by combining the supermolecular MP2 energy with dispersion energies obtained from time-dependent DFT. This is possible since it is known that the supermolecular MP2 method contains the dispersion contribution on an uncoupled Hartree–Fock (UCHF) level\textsuperscript{35–37} and therefore can easily be obtained from Hartree–Fock orbitals and orbital energies as input. It is known that the uncoupled dispersion energy on the HF level can substantially differ from its coupled counterpart by 10%–20% and therefore only poorly describes the dispersion interaction.\textsuperscript{38} Moreover, even the coupled Hartree–Fock dispersion energy, which may also be identified by the term random phase or ring approximation, gives a poor description of the dispersion contribution if compared to those from an intramolecular second order many-body expansion\textsuperscript{39} as can be obtained from the many-body formulation of SAPT.\textsuperscript{29}

In this way a combination between the supermolecular MP2 energy (without its dispersion energy contribution) and dispersion energies obtained from the time-dependent DFT (TDDFT) method also improves the poor performance of the standard MP2 method in cases where the dispersion interaction dominates the total interaction between two subsystems. Prominent examples for this are interactions between rare gas dimers\textsuperscript{39} or π–π interactions which occur, for example, in stacked structures of the benzene dimer\textsuperscript{27} or DNA base pairs.\textsuperscript{34}

Note that a very similar approach has recently been developed by Cybulski and Lytle\textsuperscript{37} in which, however, a scaled dispersion contribution from coupled Hartree–Fock [time-dependent Hartree–Fock (TDHF)] is used instead of directly obtaining it from the TDDFT method. The scaling thereby is chosen such that the estimated CCSD(T) dispersion energies (see Ref. 40) are reproduced. This is done by multiplying the TDHF dispersion energies with the ratio of the $C_6$ dispersion coefficients from the CCSD(T) and the TDHF method. Cybulski and Lytle showed that this approach works fairly well for some stacked and H-bonded structures of the DNA base pairs.

In this work it will be shown that indeed the use of an exchange-only coupled correction (either from TDDFT or TDHF) to the dispersion energy contribution in supermolecular MP2 energies yields total interaction energies which are in better agreement with CCSD(T) than if a dispersion energy correction from an asymptotically corrected hybrid xc potential is used. Reasons for this finding will be discussed in Sec. III. However, for the dimer systems studied in this work, the scaling correction of the coupled Hartree–Fock dispersion energies as proposed by Cybulski and Lytle does not give better total interaction energies than if just the unscaled TDHF dispersion energy correction is used.
10. Intermolecular interactions

The method investigated in this work can be seen as a new hybrid method which combines ab initio methods with DFT in order to treat van der Waals interactions. However, while in other hybrid methods, e.g., those by Grimme or Savin, the dispersion contribution is accounted for by the respective ab initio part, here the tasks are exchanged and the dispersion interaction is described using (time-dependent) DFT. Note that a similar approach exists by Kohn et al. in which both, the long-range and the short-range correlations, are described on the DFT level.

The next section describes details about the method and the computations performed. Then in Sec. III the results of this work are presented. Finally, Sec. IV summarizes and concludes.

II. METHOD AND COMPUTATIONAL DETAILS

In the current work the total interaction energy is calculated in two steps: First a conventional supermolecular MP2 calculation is done and in a second step the dispersion energy is calculated on the UCHF and a more accurate coupled response level (see below). The calculation of the dispersion energies requires only the monomer orbitals and orbital eigenvalues as input. Then the total interaction energy of the hybrid method is obtained as described in Sec. I by the sum

$$E_{\text{int}}(M) = E_{\text{MP2}} - E_{\text{disp}}^{(2)}(\text{UCHF}) + E_{\text{disp}}^{(2)}(M),$$

in which $M$ denotes the method which is used to approximate the dispersion energy contribution (see below), $E_{\text{MP2}}$ is the interaction energy obtained from the conventional supermolecular MP2 method, $E_{\text{disp}}^{(2)}(\text{UCHF})$ is the uncoupled Hartree–Fock dispersion energy given by (in closed-shell form)

$$E_{\text{disp}}^{(2)}(\text{UCHF}) = -4 \sum_{i_a,j_b} [ \langle i^A_a | j^B_b \rangle^2 ]^2 \left( \frac{1}{\epsilon_i^A} - \frac{1}{\epsilon_j^A} + \frac{1}{\epsilon_i^B} - \frac{1}{\epsilon_j^B} \right),$$

[indices $i,j$ and $a,b$ denote occupied and virtual Hartree–Fock orbitals of monomers $A$ and $B$, respectively, $(i^A_a | j^B_b \rangle^2$ is a two-electron repulsion integral in chemist’s notation and $\epsilon_i^A$ denotes the Hartree–Fock orbital energy of orbital $i$ for monomer $A$, and $E_{\text{disp}}^{(2)}(M)$ is the dispersion interaction energy obtained with the following approximations.

**TDHF theory.** In this approximation the dispersion energy is calculated as

$$E_{\text{disp}}^{(2)}(\text{TDHF}) = -4 \sum_{i_a,j_b} \sum_{k,l,p,q} U_{a,k;p}^A U_{b,k;l}^B U_{a,q;p}^A U_{b,q;l}^B \omega_{p,q} \times (\langle i^A_a | j^B_b \rangle^2) (\langle k^A_l | p^A_k \rangle^2),$$

where $U_{a,k;p}^A$ is the $p$th eigenvector of the coupled TDHF electronic matrix of monomer $A$ and $\omega_{p,q}$ is the corresponding eigenvalue, i.e., the excitation energy.

**TDHF-AC.** The approach investigated by Cybulski and Lytle in which the TDHF dispersion energy from Eq. (3) is scaled by a factor in order to obtain accurate dispersion energies for the asymptotic range. The scaling factor used by Cybulski and Lytle is given by

$$E_{\text{disp}}^{(2)}(\text{TDHF} - AC) = E_{\text{disp}}^{(2)}(\text{TDHF}) \times C_{\text{AC}},$$

where $C_{\text{AC}}$ is the estimated $C_6$ dispersion coefficient from the CCSD(T) method and $C_{\text{TDHF}}$ is the $C_6$ dispersion coefficient from TDHF. Note that in this work the dipole-oscillator strength distribution (DOSD) dispersion coefficients from Zeiss and Meath and Kumar and Meath were used as reference values instead of estimated CCSD(T) coefficients as in Ref. 37. The corresponding values for the different systems studied in this work are given in Table I. With Eq. (4) the asymptotically corrected dispersion energy then reads

$$E_{\text{disp}}^{(2)}(\text{TDHF} - AC) = C_{\text{AC}} \times E_{\text{disp}}^{(2)}(\text{TDHF}).$$

**TDDFT.** In this approach the dispersion energy can be written in exactly the same way as in Eq. (3), however, by substituting the eigenvectors $U$ and eigenvalues $\omega$ with the corresponding quantities from a TDDFT calculation and furthermore replacing the orbitals in the two-electron integrals in Eq. (3) with the Kohn–Sham orbitals of monomers $A$ and $B$. A crucial point is now, that different choices for the xc potential and kernel may be used for the static and TDDFT calculations. In this work two different approximations were used.

- **LHF/xALDA:** The Kohn–Sham orbitals and orbital energies are calculated using an approximate exact-exchange Kohn–Sham method, namely, the localized Hartree–Fock method by Della Sala and Göring. For the xc kernel the adiabatic local density approximation (ALDA) kernel is used in its exchange-only variant, i.e., without the Vosko-Wilk-Nusair correlation contribution.

- **PBE0AC/hybALDA:** The Kohn–Sham orbitals and orbital energies are calculated using the asymptotically corrected PBE0AC xc potential, and a hybrid nonlocal-exchange/ALDA xc kernel is used for the response calculations.

For convenience in the following the above given acronyms are shortened to LHF and PBE0AC, meaning in any context that the corresponding results were obtained from fully coupled TDDFT calculations with the xc kernels as specified above.

Note that the supermolecular MP2 energy contains further intermolecular correlation contributions which may be denoted as deformation-correlation and exchange-correlation...
terms. These terms are usually very small for larger monomer distances and are not corrected using Eq. (1).

In order to test the performance of the total interaction energies as obtained with Eq. (1) (the method will be termed MP2\(E_{\text{disp}}^{\text{MP2}}(M)\) where \(M\) corresponds to the four different acronyms given in the above list), the interaction energy curves for the rare gas dimers He\(_2\), Ne\(_2\), and Ar\(_2\) were calculated since they, as will be shown below, are mainly stabilized by dispersion interactions. Moreover, in order to test the various methods for cases where already the MP2 method itself yields rather accurate interaction energies, four, respectively, six different structures of the (HF)\(_2\) and the (H\(_2\)O)\(_2\) dimer were calculated. These structures are the same as those used in Ref. 47 and can be obtained in \(xyz\)-coordinate form from Ref. 28. In the case of the hydrogen fluoride dimer, geometry I stands for the absolute minimum geometry as given in Ref. 48, geometry II, III, and IV correspond to the \(C_{2h}\) and \(C_{sv}\) transition structures and the “magic” orientation (with a \(F\)--\(F\) distance of 5.2 a.u.) as given in Ref. 49, respectively. Finally, in the case of the water dimer geometries I, II, and III correspond to a relative orientation of the (vibrationally averaged) monomers as in the absolute minimum geometry of Ref. 50, with \(O\)--\(O\) distances of 4.64, 5.58, and 6.53 a.u., respectively, while geometry IV is a \(C_{2v}\)-structure with, so to say, a lone pair from one water molecule pointing in between the hydrogen atoms of the other \((R_{O-O}=5.58\ \text{a.u.})\). Geometries V and VI denote those \(C_{sv}\) structures with two hydrogens \((R_{O-O}=6.61\ \text{a.u.})\) or two lone pairs \((R_{O-O}=5.58\ \text{a.u.})\) pointing at each other, respectively, which along with the other geometries have also been used in a study on the influence of bond functions for water dimer interaction energies.\(^{57}\)

The coupled TDHF and TDDFT dispersion contributions have been calculated using the method described in Ref. 38. The interaction energy curves from MP2\(E_{\text{disp}}^{\text{MP2}}(M)\) are compared with those from the standard supermolecular MP2 (corresponding to MP2\(E_{\text{disp}}^{\text{MP2}}(\text{UCHF})\) with the notation given above) and CCSD(T) methods as well as with total DFT-SAPT interaction energy curves. The DFT-SAPT calculations were performed too by using the combination of PBE0AC/hybrid-ALDA employed for the ground and excited state Kohn–Sham calculations, respectively. All electrons were correlated in the correlation calculations, and all supermolecular energies were counterpoise corrected in order to eliminate the basis set superposition error. The aug-cc-pVQZ atomic basis set by Kendall et al.\(^{52}\) is used for the rare gas dimers, while for the hydrogen bonded dimers the aug-cc-pVTZ basis set is employed. All calculations were performed using the MOLPRO quantum chemistry program.\(^{53}\)

### III. RESULTS

#### A. Rare gas dimers

The interaction energy curves of He\(_2\), Ne\(_2\), and Ar\(_2\) for the various methods are depicted in Figs. 1–3. It can be seen from Figs. 1 and 2 that in the case of He\(_2\) and Ne\(_2\), the MP2 method considerably underestimates the CCSD(T) interaction energies, which will be referred to as reference values in the following, in the short and well region of the interaction potential. This is a rather untypical behavior as it is much more often found that the MP2 method either gives results which are very close to CCSD(T) or that the MP2 method gives a strong overbinding compared to CCSD(T). The latter is true especially for cases where the dispersion interaction is dominating, see, e.g., Refs. 27, 34, and 54. In contrast to this for Ar\(_2\) the MP2 pair potential lies clearly below the CCSD(T) curve as can be observed from Fig. 3. The equilibrium distances and energies for the three rare gas dimers and the different methods are shown in Table II. They were obtained by using a cubic spline interpolation of the individual interaction energy potentials. From the minimum energies presented in Table II, it can be quantified that the MP2 method underestimates the CCSD(T) values by about 32% in case of He\(_2\) and Ne\(_2\), while for Ar\(_2\) it overestimates the CCSD(T) interaction energy by 18%. Moreover the MP2 equilibrium distances are \(\sim 0.18\\text{a}_0\), too large for He\(_2\) and Ne\(_2\) and \(\sim 0.1\text{a}_0\), too small for Ar\(_2\), as compared to CCSD(T).

This is clearly improved with the different

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**Fig. 1.** (Color) Interaction potentials of He\(_2\) calculated with the various methods by using the aug-cc-pVQZ basis set. All supermolecular approaches were counterpoise corrected.

**Fig. 2.** (Color) Interaction potentials of Ne\(_2\) calculated with the various methods using the aug-cc-pVQZ basis set. All supermolecular approaches were counterpoise corrected.
FIG. 3. (Color) Interaction potentials of Ar₂ calculated with the various methods using the aug-cc-pVQZ basis set. All supermolecular approaches were counterpoise corrected.

FIG. 4. Percentual contribution of the dispersion energy to the total attractive intermolecular interaction energy in second order given by the sum $E_{\text{disp}}^{1+2} = E_{\text{disp}}^{1} + E_{\text{disp}}^{2}$, plotted against the distance between the rare gas atoms. The solid vertical line marks the equilibrium distance of He₂, the dashed vertical line the equilibrium distance of Ne₂, and the dotted vertical line the equilibrium distance of Ar₂.

MP2[$E_{\text{disp}}^{2}(M)$] methods employing Eq. (1), as can be seen in Figs. 1–3. However, a notable difference between the exchange-only approaches TDHF and LHF on the one hand and the hybrid xc method PBE0AC can be observed: While the TDHF and LHF curves are very close to each other in the case of the He₂ and Ne₂ dimer, the PBE0AC curve is more attractive. However, in the case of Ar₂, the LHF and PBE0AC curves are closer to each other, while the TDHF interaction energy curve is slightly less attractive. A comparison of the pair potentials of the three correction approaches TDHF, LHF, and PBE0AC to the CCSD(T) reference curves shows that the exchange-only approaches TDHF and LHF perform better for the He₂ dimer than the PBE0AC approach, while in the case of Ne₂ TDHF and LHF are significantly too less attractive, whereas PBE0AC only slightly overbinds. In the case of the Ar₂ dimer there is a very good agreement between the LHF curve and the CCSD(T) curve, while the TDHF curve deviates somewhat more in the opposite direction, as can be seen in Fig. 3.

Figures 1–3 show also the interaction energy curves obtained with the asymptotically corrected TDHF method TDHF-AC [Eq. (5)] using the correction factor given in Eq. (4). For Ne₂ and Ar₂ this clearly leads to an improvement compared to the uncorrected TDHF values as can be seen in Figs. 2 and 3 and in Table II which contains the equilibrium distances and energies for the various methods. However, Fig. 1 and Table II show that in the case of the He₂ dimer the asymptotic correction to the dispersion energy slightly worsens the TDHF interaction energies for distances around the equilibrium. This finding is unexpected since the helium dimer is more bound by dispersion interactions than Ne₂ and Ar₂. In order to show this in Fig. 4, the ratio of the dispersion energy to the total polarization energy up to second order, i.e., $E_{\text{pol}}^{1+2} = E_{\text{pol}}^{1} + E_{\text{pol}}^{2} + E_{\text{disp}}^{2}$, is plotted for the three rare gas dimers against the interatomic distance. It can clearly be observed in Fig. 4 that in case of He₂ the dispersion contribution to $E_{\text{pol}}^{1+2}$ amounts to about 90% at the equilibrium distance (given by the solid vertical line in Fig. 4), while for Ne₂ and Ar₂, the dispersion energy is only about 80% and 70% of the total polarization energy for the respective distances at the minimum (given by the dashed and dotted vertical lines).

Finally, the interaction energy curves obtained with the DFT-SAPT method are also shown in Figs. 1–3. It can be observed that the DFT-SAPT method somewhat overbinds in the case of He₂ and Ar₂, while it accurately reproduces the CCSD(T) interaction energy curve for the neon dimer. This is also supported by the equilibrium distances and dissociation energies given in Table II.

While so far the effect of the hybrid approach using
Eq. (1) on the total interaction energies has been analyzed, it may be interesting to see how the correction method actually changes the conventional MP2 interaction energies. For this, the difference between the coupled dispersion interaction energies instead of the UCHF energy always rightly corrects the supermolecular MP2 energy toward the more accurate CCSD(T) interaction energies. However, the total amount of the correction can significantly differ depending on the respective method to approximate the dispersion energy. In the case of He₂ and Ne₂ the dispersion corrections from TDHF and LHF are close to each other while the PBE0AC dispersion correction is substantially stronger, in the case of Ne₂ by even more than 300% around the minimum distance of about 6\(a_0\). In contrast to this it can be seen in the diagram in Fig. 7 that for the argon dimer the LHF dispersion correction is closer to the PBE0AC dispersion correction and the TDHF correction is more strongly repulsive in this case.

B. Hydrogen bonded dimers

The total interaction energies for the calculated four, respectively, six structures of the (HF)₂ and the (H₂O)₂ dimer are summarised in Table III. It can be seen that in the case of those structures which are bounded, i.e., where the interaction energy is negative, the MP2 method always underestimates the magnitude of the CCSD(T) interaction energies, while for the unbound structures the opposite is found, except for geometry I of the water dimer. The root mean square (rms) error and the mean absolute error (MAE) of the MP2 method to the CCSD(T) reference values are only 0.25 and 0.22 a.u., respectively, and thus the hydrogen bonded dimers are well described, as expected, on the MP2 level. However, as can be seen in Table III, the correspondence with the CCSD(T) interaction energies can still be improved by using the TDHF dispersion correction. For nearly all structures the TDHF hybrid approach yields total interaction energies which are closer to the CCSD(T) values than with MP2, leading to a total relative deviation of only 5.88% compared to 8.78% as obtained with the MP2 method. However, the asymptotic correction of the dispersion energies using the ratio in Eq. (4) here does not lead to a further improvement of the TDHF energies. On the contrary, the correction leads to much too attractive interaction energies in the case of the bound structures and an absolute relative deviation of over 17% to CCSD(T).

Table III also contains the interaction energies obtained with the TDFF dispersion corrections using the LHF and the PBE0AC functional. For LHF it is evident that the corresponding TDHF interaction energies are nearly reproduced which shows that the LHF/xALDA level very well serves as an exchange-only approximation for the estimation of disper-
sion energies. Correspondingly the LHF hybrid method too improves the MP2 method and even yields an absolute deviation to CCSD(T) of 5.62% only. However, if the dispersion energy is corrected on a more accurate level, here by using the PBE0AC functional, the total interaction energies are significantly worsened, e.g., for the minimum structures (I: (HF)$_2$ and II: (H$_2$O)$_2$) the percentage deviation to CCSD(T) is about −6% with PBE0AC, while with LHF it amounts to only ±1%.

Table III shows also that DFT-SAPT method reproduces the interaction energies for the hydrogen bonded dimers with about the same accuracy as with the TDHF and LHF corrections to the MP2 supermolecular energies. Note that here in the DFT-SAPT approach all corrections are described by using PBE0AC monomer properties (with exception of the third and higher order contributions), i.e., the dispersion interaction contribution is the same as the one added in the MP2($E_{\text{disp}}^{(2)}$[PBE0AC]) hybrid method.

Finally, it is analyzed why the approach of Eq. (1) can also improve the MP2 method for the prediction of interaction energies for hydrogen bonded dimers. First, in Fig. 8 again the ratio of the dispersion energy to the total polarisation energy up to second order for the different structures is displayed. It can be observed that the dispersion interaction for most of the structures amounts to at least 18% of the total sum $E_{\text{pol}}^{(2)}$ and is therefore not negligible in these complexes. The total amount of the dispersion interaction energies of the different methods for the structures is presented in Fig. 9. It can be observed that the UCHF dispersion energies are always corrected to more negative dispersion energies using TDHF, LHF, or PBE0AC, and thus the total supermolecular MP2 interaction energies are always corrected in the right direction. However, while with TDHF and LHF this correction is always small for the hydrogen bonded dimers, with PBE0AC the difference to the UCHF dispersion energy amounts to up to −0.52 mhartree for (H$_2$O)$_2$/II and so significantly affects the magnitude of the total interaction energy in the hybrid approach of Eq. (1).

### IV. SUMMARY AND CONCLUSIONS

In summary it has been shown that the new hybrid method for calculating intermolecular interaction energies, termed MP2[$E_{\text{disp}}^{(2)}(M)$] ($M$=approximation for coupled response), can considerably improve the conventional supermolecular MP2 interaction energies in cases where the dimer is mainly bound through dispersion forces as is the case for the three rare gas dimers He$_2$, Ne$_2$, and Ar$_2$ studied in this work. This finding can be ascribed to the fact that the poor description of the dispersion interaction on the UCHF level of the supermolecular MP2 method is significantly improved by replacing it by a description on the TDDFT level using a proper xc potential and xc kernel. Interestingly the performance of the method often is better if an exchange-only approach is employed for the dispersion correction, i.e., if either TDHF or an exchange-only TDDFT approach

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**TABLE III. Intermolecular interaction energies for different structures of the (HF)$_2$ and (H$_2$O)$_2$ dimer.** See text for explanation of geometries. The aug-cc-pVTZ basis set was used throughout. The last three lines display the rms error, the MAE, and the total relative deviation ($|\Delta|$) to the CCSD(T) reference values for each method. (Energies are in mhartree).

<table>
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<th>Dimer</th>
<th>Geometry</th>
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<th>CCSD(T)</th>
<th>MP2[$E_{\text{disp}}^{(2)}$(TDHF)]</th>
<th>MP2[$E_{\text{disp}}^{(2)}$(TDHF-AC)]</th>
<th>MP2[$E_{\text{disp}}^{(2)}$(LHF)]</th>
<th>MP2[$E_{\text{disp}}^{(2)}$(PBE0AC)]</th>
<th>DFT-SAPT</th>
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termolecular interaction energies which surpass the performance of those from conventional supermolecular MP2 calculations at only a slightly higher computational cost. Especially the latter point is the reason why it is preferable to use dispersion energies from TDDFT instead of the TDHF method: While it has been shown that with density-fitting techniques, it is possible to reduce the former $\Lambda^6$ scaling ($\mathcal{N}$ being a quantity which measures the size of the system) for the calculation of the dispersion energy to a scaling of $\Lambda^5$ if exact Hartree–Fock exchange is used, the TDDFT density-fitting approach enables a further reduction of the scaling behavior by one order of magnitude, i.e., leads to a scaling of $\Lambda^4$ with the system size. This makes the calculation of the dispersion energy also feasible for fairly large molecules and, if combined with efficient MP2 methods, see, e.g., Ref. 56, the dispersion corrected MP2 approach investigated in this work will also be applicable for the study of larger complexes for which also conventional MP2 calculations are still possible.

(LHF/xALDA) is used. In contrast to this the use of the accurate PBE0AC xc potential in combination with the LHF and PBE0AC xc potentials. Note that structure I of the water dimer is left out in the plot due to the large magnitudes of the dispersion energies $E_{\text{disp}}^{(2)}(\text{UHF})=-11.94$ mhartree, $E_{\text{disp}}^{(2)}(\text{TDHF})=-11.76$ mhartree, $E_{\text{disp}}^{(2)}(\text{LHF})=-11.82$ mhartree, and $E_{\text{disp}}^{(2)}(\text{PBE0AC})=-12.70$ mhartree.

![Graph showing dispersion energies for different structures](image)

**FIG. 9.** Dispersion energies for the different structures of the (HF)$_2$ and (H$_2$O)$_2$ dimers obtained from the UCHF, from TDHF, and from TDDFT using LHF and PBE0AC xc potentials. Note that structure I of the water dimer is left out in the plot due to the large magnitudes of the dispersion energies $E_{\text{disp}}^{(2)}(\text{UHF})=-11.94$ mhartree, $E_{\text{disp}}^{(2)}(\text{TDHF})=-11.76$ mhartree, $E_{\text{disp}}^{(2)}(\text{LHF})=-11.82$ mhartree, and $E_{\text{disp}}^{(2)}(\text{PBE0AC})=-12.70$ mhartree.

10. Intermolecular interactions

10.6. Derivation of the dispersion energy as an explicit density- and exchange-hole functional

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- dispersion energy
- fluctuation dissipation theorem
- polarisabilities
- dispersion coefficients
I. INTRODUCTION

The determination of correlation energies plays a crucial role in the estimation of molecular structures and properties. This becomes most obvious if the studied systems contain fragments that are not bound by covalent bonds but are only weakly interacting. In these cases the Hartree–Fock method often fails to describe these interactions, especially if the main source of interaction stems from the so-called van der Waals or dispersion interaction. It has recently been demonstrated using intermolecular perturbation theory, however, that even in classical hydrogen-bonded structures such as the Watson–Crick structures of DNA base pairs, where the main contribution to the total interaction comes from the electrostatic interaction energy, the dispersion energy nevertheless is not negligible and can be of the same order as the total interaction energy itself.\(^1\)

Though there is a common agreement that the capture of long-range correlation energies is desirable in general, in praxis this is often not obeyed. The most important reason for this certainly is that for larger molecular systems, correlation methods are simply not feasible anymore due to their unfavorable scaling behavior with respect to the molecular size. Another reason, which is connected with the former one, may be that often density functional theory (DFT) (Ref. 2) in the generalized gradient approximation (GGA) framework\(^2\) is used as a black-box method since it is has the most favorable scaling behavior of all correlation methods and is available in most quantum chemistry programs. Unfortunately it can easily be shown that GGA methods are unable to describe dispersion interactions.\(^3\) Because of this there is a need to derive new cheap methods that can account for dispersion interaction energies either in the DFT framework or in general.

In the framework of DFT the probably simplest and most efficient approach to include dispersion interactions is to add a long-range multipole expanded correlation term,\(^4\) which is approximated using atom-atom dispersion coefficients. This additional term to the DFT energy has to be properly damped for shorter ranges.\(^5,6,8–10\) This also has to be done in order to avoid any double-counting of correlation effects since current DFT methods based on the GGA are inherently able to describe electron correlation for short interelectronic ranges. Another problem of the damped atom-atom dispersion energy contribution is that it cannot account for a particular polarization of the molecular system, most notably if one of the fragments contains a nonzero charge.

Another approach that derives the dispersion energy as an explicit density functional is to use DFT models of the response function (see Refs. 11–14). While some of these methods still require certain cutoff and damping schemes for shorter interelectronic ranges (see, e.g., Ref. 15), a more general and seamless nonlocal correlation functional was developed by Langreth and co-workers\(^16–18\) and Vydrov et al.,\(^19\) which successfully describes van-der-Waals interaction energies. Note that these approaches may be understood as simple DFT approximations of the more sophisticated way to describe electron correlation effects using the fluctuation dissipation theorem in which the correlation energy is described in terms of the fully interacting many-body response function, which itself does not explicit depend on the density functional but depends on molecular orbitals and orbital energies.\(^20–23\)

Recently Becke and Johnson\(^24\) derived a new model to describe the dispersion energy that is based on the conjecture that the spherical asymmetry of the exchange-hole (Xhole) of the molecules could be the source for the formation of dispersion interactions. The Xhole describes a charge depletion around a reference electron due to the presence of an adjacent electron with equal spin. Since this Xhole is somewhat displaced it describes a dipole together with the instan-
taneous position of the reference electron giving rise to an instantaneous dipole moment. This in turn might be coupled to a corresponding dipole moment of a remote system, leading to an attractive interaction between well separated molecules. From this physical background Becke and Johnson developed a model for the long-range dispersion interaction, which appears to perform particularly well (see Refs. 10 and 24–28).

A thorough analysis of the interplay between the dispersion interaction and the exchange-correlation (xc) hole was previously made by Ángyán29 (see also Ref. 30, which too relates the xc-hole with van der Waals interactions). By approximating the response functions of the subsystems using a generalization of the Unsöld approximation31 followed by a localization over domains, Ángyán29 could show that the asymptotic form of the dispersion energy obtained in this way is different from the empirical Becke–Johnson model. In spite of this finding he tried to explain the undisputed success of the Becke–Johnson model by noting that the dipole moment fluctuations contained in the model may imitate some implicit correlation effects.

In this work a direct relation between the nonexpanded dispersion energy and the Xhole of the interacting monomers will be highlighted. While on this course I will follow similar lines as Ángyán (Ref. 29), the final result will be more general, showing that in fact the nonexpanded dispersion energy can be written as an explicit density and Xhole functional. Therefore the result of this work offers a new possibility to calculate dispersion interactions without using any empirical corrections apart, however, from providing estimates of the mean excitation energies of the subsystems. The usefulness of the approach will be demonstrated by showing calculated polarizabilities and dispersion coefficients of some atomic and small molecular systems.

II. THEORY

The following conventions will be used henceforth: Labels \( i,j, \ldots \) denote occupied orbitals, labels \( a,b,\ldots \) denote unoccupied orbitals, and \( \alpha,\beta,\ldots \) are Cartesian components. For simplicity closed-shell formalism will be used throughout.

Using the fluctuation dissipation theorem (see, e.g., Ref. 22) the correlation energy of an interacting many-body electronic system can be written as

\[
E_c = \frac{1}{2\pi} \int_0^\infty d\alpha \int_0^\infty d\omega \int r_{12} \sum \left[ \alpha \chi_0^a(r_1, r_2, \omega) W(r_3, r_4, \omega) \chi_0^b(r_4, r_2, \omega) + \alpha^2 \chi_0^a(r_1, r_2, \omega) W(r_3, r_4, \omega) \chi_0^b(r_4, r_5, \omega) W(r_5, r_6, \omega) \chi_0^b(r_6, r_2, \omega) + \mathcal{O}(\alpha^3) + \ldots \right],
\]

where \( \alpha \) is the coupling strength, which is 0 for noninteracting and 1 for fully interacting electrons, \( W \) is the electronic interaction operator, and \( \chi_0^a(r_1, r_2, \omega) \) is the (uncoupled) response function of the noninteracting system at an imaginary frequency \( \omega \). The latter can exactly be written in terms of the occupied and unoccupied molecular orbitals \( \phi_i^a \) and \( \phi_i^b \) and their corresponding orbital energies \( e_{i} \) and \( e_{i} \) of the underlying noninteracting system,

\[
\chi_0^a(r_1, r_2, \omega) = 4 \sum \frac{e_{i}^a}{e_{i}^a + \omega} \phi_{i}^a(r_1) \phi_{i}^a(r_2),
\]

where the conventions \( \phi_{i}^a(r) = \phi_i(r) \phi_i^a(r) \) and \( e_{i}^a = e_i - e_a \) are used. The interaction operator \( W = (1/r_{12}) + f_{xc} \) in Eq. (1) comprises Coulomb, exchange, and correlation effects. The latter two are described by the so-called xc kernel \( f_{xc} \). It has now to be noted that Eq. (1) holds exactly, provided that the coupling strength series expansion is truncated and if the exact xc kernel \( f_{xc} \) would be inserted. In praxis the exact \( f_{xc} \) at least its correlation part, is not known and one usually has to resort to approximations. However, since exchange and correlation interactions are more short-ranged compared to Coulomb interactions, they may also give a smaller contribution to long-range correlations. Therefore, since the aim of this work is to derive an expression for the dispersion energy between well separated molecules, the xc contributions will be neglected in the following, that is, \( f_{xc}(r_1, r_2, \omega) = 0 \). Note that this approximation is also known as random-phase approximation.30 Furthermore, the series expansion in Eq. (1) will be truncated after the linear term, obtaining the correlation energy at second order. Using these approximations it is easy to show that the long-range correlation energy between two well separated molecular fragments is given by the widely known Casimir–Polder expression

\[
E_{\text{disp}} = \frac{1}{2\pi} \int_0^\infty d\omega \int r_{12} d\omega d\omega' \chi_0^a(r_4, r_2, \omega) \frac{1}{r_{12} r_{34}},
\]

where now \( \chi_0^a \) and \( \chi_0^b \) are the uncoupled response functions of the monomers A and B, respectively [see Eq. (2)]. Note that an exact expression for the dispersion energy is obtained if the uncoupled response functions are replaced by the fully coupled response functions of the interacting systems of the two monomers. The difference between the uncoupled and coupled response function is implicitly defined by the sum within the square brackets in Eq. (1). The central step that allows to write the dispersion energy as a functional of the electron density and the Xhole of both monomers is now to make the rough estimation that any excitation \( e_{i}^a \) of the non-
interacting system is the same, i.e., one replaces the energy differences in Eq. (2) by a constant mean excitation energy \( \Delta \varepsilon \). This approximation is also known as Unlösöd approximation.\(^{31}\) Then the uncoupled response function can be written as

\[
\tilde{\chi}(r_1, r_2, \omega) = 4 \frac{\Delta \varepsilon}{\Delta \varepsilon^2 + \omega^2} \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) .
\]

This expression can further be transformed if the resolution of the identity in the molecular orbital basis is applied, that is, \( \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) = \delta(r_1 - r_2) \) with \( n \) running over all orbitals. With this the summation over unoccupied orbitals can be replaced by the closure \( \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) = \delta(r_1 - r_2) - \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) \), and the approximate response function becomes

\[
\tilde{\chi}(r_1, r_2, \omega) = 4 \frac{\Delta \varepsilon}{\Delta \varepsilon^2 + \omega^2} \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) \times \left[ \delta(r_1 - r_2) - \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) \right]
\]

\[
= 2 \frac{\Delta \varepsilon}{\Delta \varepsilon^2 + \omega^2} \rho(r_1) \delta(r_1 - r_2)
\]

\[
- 2 \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) ,
\]

where the density \( \rho \) of the noninteracting particle system has been inserted. Note that this result is actually identical to the common energy denominator form of the response function derived by Gritsenko and Baerends\(^{32,33}\) and which has been used to derive an approximate exact exchange density functional method. It can easily be verified that the response function in Eq. (5) satisfies apart from the spatial symmetry two important constraints of the exact response function, namely, the reciprocity and the charge conservation.\(^{34}\)

\[
\chi_0(r_1, r_2, \omega) = \chi_0(r_1, r_2, -\omega) ,
\]

\[
\int dr_1 \chi_0(r_1, r_2, \omega) = 0 \ \forall \ r_2, \omega .
\]

It should be mentioned, however, that in contrast to the exact uncoupled response function, which possesses poles at the orbital energy differences for real frequencies, the approximated response function in Eq. (5) has only one pole at the mean excitation energy \( \Delta \varepsilon \) in the real frequency domain. Now note that the Xhole density is given by

\[
h_X(r_1, r_2) = -2 \sum_{\text{i}} \phi_{\text{i}}(r_1) \phi_{\text{i}}(r_2) \rho(r_1) ,
\]

Insertion into Eq. (5) yields

\[
\tilde{\chi}(r_1, r_2, \omega) = 2 \frac{\Delta \varepsilon}{\Delta \varepsilon^2 + \omega^2} \left[ \rho(r_1) \left( \delta(r_1 - r_2) + h_X(r_1, r_2) \right) \right] ,
\]

which shows that the uncoupled response function can be written in terms of the density \( \rho \) and the Xhole \( h_X \). This result can now be inserted in Eq. (3), thereby carrying out the frequency integration

\[
E_{\text{disp}} = - \frac{1}{4 \pi^2 (\Delta \varepsilon^2 + \omega^2)^2} \int dr_1 dr_2 dr_3 dr_4 \frac{1}{r_{12} r_{34}} 
\times \left[ \rho^A(r_1) \left( \delta(r_1 - r_2) + h_X^A(r_1, r_2) \right) \right] \times \left[ \rho^B(r_2) \left( \delta(r_2 - r_3) + h_X^B(r_2, r_3) \right) \right] .
\]

which is the central result. It justifies the heuristic Xhole model of Becke and Johnson to approximate the dispersion energy. However, the present approach differs from theirs, and this can be seen if the asymptotic form of Eq. (10) is derived. For this it is assumed that the two monomers \( A \) and \( B \) contain no charge and that their centers are well separated by a distance \( R \). Using a change in coordinates the interaction operator between the electrons of both molecules to leading order is then given by\(^{35}\)

\[
\frac{1}{r_{12}} \rightarrow \frac{1}{|\mathbf{R} + r_1 - r_2|} \rightarrow r_0^6 \left( \nabla_a \nabla_b \frac{1}{R} \right)_0^2
\]

\[
\frac{3 R e \rho}{R^5} R e - R^2 \sigma_{ab} \beta_{ab} ,
\]

and the Einstein summation convention is used. Note that the asymptotic interaction operator contains higher order terms involving interactions between higher order multipoles. However, for the current analysis these can be neglected. If one now furthermore assumes that the charge distributions of \( A \) and \( B \) are spherical, i.e., the monomers are atoms, the dispersion interaction simplifies to

\[
E_{\text{disp}}^{\text{asym}} = - \frac{3}{4 \pi R} \int_0^\infty d\omega \left( \frac{2 \Delta \varepsilon^2}{(\Delta \varepsilon^2 + \omega^2)} \right) \int dr_1 dr_2 dr_3 dr_4 \rho^A(r_1) \rho^B(r_2) \left( \delta(r_2 - r_3) + h_X^A(r_1, r_2) \right) \left( \delta(r_2 - r_3) + h_X^B(r_2, r_3) \right)
\]

\[
= - \frac{3}{4 \pi R} \int_0^\infty d\omega \alpha^A(\omega) \alpha^B(\omega) ,
\]

where again the Casimir–Polder integral transform has been used in order to show that the terms in brackets in Eq. (12) can actually be identified as frequency-dependent polarizabilities of the two monomers. Now the dipolar charge distribution produced by the electron and its accompanying Xhole (see Ref. 24) is introduced,

\[
d_X^A(r) = \rho^A \left( \sum_{\text{i}} r_{12}^i \phi_{\text{i}}(r) \right) ,
\]

with \( r_{12}^i = \int dr \rho^A \phi_{\text{i}}(r) \). Moreover, one component of the dipolar charge distribution of the total density shall be defined as \( d^A_0(r) = r^A \rho(r) \) so that Eq. (12) transforms into
10. Intermolecular interactions

The accuracy of the Xhole approximation of the response function in Eq. (9) has been investigated by calculating static isotropic polarizabilities and \( C_6 \) dispersion coefficients of the three rare gas atoms helium, neon, and argon and a number of small molecules with Hartree–Fock densities and orbitals. The geometries for the molecules were taken from Ref. 36. The aug-cc-pVQZ basis set was used in all other cases the aug-cc-pVTZ basis set was used.\(^{37}\) All calculations were carried out using the MOLPRO quantum chemistry program.\(^{38}\) The results are shown in Table I. Note that the mean excitation energies \( \Delta e \) were estimated by an \textit{ad hoc} guess using the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap of the respective system times a factor of two. For comparison Table I also contains reference results from uncoupled Hartree–Fock (UHF), time-dependent Hartree–Fock (TDHF), and dipole oscillator strength distributions (DOSD). It is to be understood that the XHole approach would yield the same result as UHF if the approximations made in Eqs. (4) and (5) would hold exactly. While the results in Table I show that this is not the case, it can nevertheless be seen that with the simple \textit{ad hoc} estimation of \( \Delta e \) the polarizabilities with a few exceptions are fairly close to the UHF results. In those cases where the deviation to the UHF reference results is larger, as for Ar and CH\(_2\), the polarizability is always underestimated, and thus a smaller value of \( \Delta e \) might help to improve the overall results. This is also true if the Xhole values are compared to the accurate reference values from the last column in Table I. It can, however, be seen that in some cases the XHole polarizabilities are in between the coupled and uncoupled HF ones, and so it can be said that by and large they are already good estimates.

The same holds also for the \( C_6 \) coefficients shown in Table I. However, in case of NH\(_3\), for example, where the UHF and XHole polarizabilities are relatively close to each other, the XHole method overestimates the corresponding UHF \( C_6 \) dispersion coefficient by as much as 15 a.u., showing that the frequency dependence of the polarizabilities is clearly different in both cases. Nevertheless the XHole results for the \( C_6 \) dispersion coefficients show about the right tendency already with the rough estimation for the mean excitation energy. In some cases the XHole \( C_6 \) coefficients are even closer to the DOSD reference values from the last column in Table I than both the UHF and TDHF ones. It can be expected that the results can be further improved by a more sophisticated refinement for the determination of mean

<table>
<thead>
<tr>
<th>Property</th>
<th>System</th>
<th>UHF</th>
<th>TDHF</th>
<th>XHole</th>
<th>Reference(^a)</th>
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<tr>
<td>( \alpha )</td>
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<tr>
<td></td>
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<td>5.235</td>
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<tr>
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<td>4.749</td>
<td>4.435</td>
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</tr>
<tr>
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<td></td>
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<tr>
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<td>12.31</td>
<td>9.503</td>
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<tr>
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<td>16.71</td>
<td>14.11</td>
<td>17.5</td>
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<tr>
<td>( C_6 )</td>
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<td>1.375</td>
<td>0.922</td>
<td>1.458</td>
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<tr>
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<tr>
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<tr>
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<td>HCN</td>
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<td>127.0</td>
<td>155.3</td>
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</tbody>
</table>

\(^a\)Values from DOSD (Refs. 39–41) and experimental (HCN molecule) (Ref. 42).
excitation energies. This could be achieved, for example, by fitting the approximate response functions of Eq. (5) to the exact ones of Eq. (2).

IV. SUMMARY

In summary it has been shown that the dispersion interaction energy between two molecules can be approximated in terms of the densities and the Xholes of both monomers. Though this result has been obtained using a series of approximations, most importantly employing the Unsöld approximation in the sum-over-states formulation of the response function, first results for static polarizabilities and \( C_6 \) dispersion coefficients for the rare gas atoms and some small molecules indicate that the approach performs quite well and may be used in the future in order to obtain simple estimations for the dispersion interaction between two molecular systems if higher level methods are not practical anymore due to the size of the studied systems.

The result of this work also confirms the anticipation of Becke and Johnson that the Xhole might be related to the physical origin of the dispersion interaction. However, it should be clear from the above derivations that this is only a first estimate and that the description of the exact dispersion interaction energy requires the knowledge of the fully coupled many-body response functions of the interacting monomers. Nevertheless, the fact that it is possible to directly write the dispersion energy as a functional of the density and the Xhole through some straightforward derivations supports to develop new models of the dispersion energy or even more general the correlation energy in terms of these quantities. The latter can actually be achieved by an insertion of Eq. (5) into Eq. (1), yielding an approximate expression for the correlation energy, which then also transforms into a functional of the density and the Xhole. Such an extension of the approach described in this work can especially be valuable in the framework of DFT in which currently still xc functionals are used most of the time, which are incapable to describe long-range correlation energies.

10.7. SAPT Applied to Endohedral Fullerene Complexes: A Stability Study of $H_2@C_{60}$ and $2H_2@C_{60}$

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- three-body interactions
Symmetry-Adapted Perturbation Theory Applied to Endohedral Fullerene Complexes: A Stability Study of H$_2@C_{60}$ and 2H$_2@C_{60}$

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Abstract: Because of difficulties in a description of host–guest interactions, various theoretical methods predict different numbers of hydrogen molecules which can be inserted into the C$_{60}$ cavity, ranging from one to more than 20. On the other hand, only one H$_2$ molecule inside the C$_{60}$ fullerene has been detected experimentally. Moreover, a recently synthesized H$_2@C_{70}$ complex prevails in the mixture formed with 2H$_2@C_{70}$. To get a deeper insight into the stability of the complexes created from C$_{60}$ and hydrogen molecules, we carried out highly accurate calculations for complexes of one or two hydrogen molecules with fullerene applying symmetry-adapted perturbation theory (SAPT) and a large TZVPP basis set for selected points on the potential energy surfaces of H$_2@C_{60}$ and 2H$_2@C_{60}$. The electron correlation in the host and guests has been treated by density functional theory. Our calculations yield the stability of the recently synthesized H$_2@C_{60}$ complex. In addition, for all tried positions of the H$_2$ dimer inside the C$_{60}$ cage, the 2H$_2@C_{60}$ complex has been characterized by a positive interaction energy corresponding to the instability of this species. Contrary to the conclusions of several theoretical studies, this finding, as well as model considerations and literature experimental data, indicates that only one hydrogen molecule can reside inside the C$_{60}$ cage. The calculated energy components have been analyzed to identify the most important contributions to the interaction energy. Supermolecular interaction energies obtained with MP2, SCS-MP2, and DFT+Disp methods are also reported and compared to those of DFT-SAPT. The DFT-SAPT interaction energy has also been calculated for several points on the potential energy surface for a larger 2H$_2@C_{70}$ complex, confirming, in agreement with recent experimental findings, that this species is stable. The DFT-SAPT approach has been used for the first time to obtain interaction energies for van der Waals endohedral complexes, demonstrating that the method is capable of handling such difficult cases.

Introduction

The possibility of filling a fullerene cage with atomic, ionic, or molecular guests was postulated soon after the serendipitous discovery of C$_{60}$ and development of the procedure for its purification. Since then numerous proposals of possible applications of endohedral fullerene complexes have appeared in different areas of science and technology, ranging from medicine and environmental protection to molecular optoelectronics and renewable energetics. Interestingly, almost none of them have been marketed yet, indicating the immense complexity of the task of filling and subsequent releasing guest molecules from the fullerene cavity. The utilization of fullerenes and carbon nanotubes as hydrogen storage devices has been recently one of the hot topics of research in view of their prospective practical applications. However, the newest experimental evidence damped the expectations for storing a considerable amount of hydrogen inside these carbon forms.
Similarly to the case of nanotubes, a hydrogen molecule can be either chemi- or physisorbed on the fullerene surface. The chemisorption consists in a hydrogenation of the fullerene (i.e., the covalent CH bonds are formed). During the physisorption, a hydrogen molecule is attached to the C_{60} ball without the covalent bond formation. In the latter case, an endohedral van der Waals complex (denoted as H_2@C_{60}) is formed if H_2 is placed inside the fullerene, otherwise a more usual, but weaker exohedral complex is obtained. A synthesis of H_2@C_{60} by Komatsu et al.\textsuperscript{11} consisted in a chemical creation of a hole in the fullerene cage, insertion of a hydrogen molecule,\textsuperscript{12} followed by a chemical closure of the cage.\textsuperscript{11} This process has been called a “molecular surgery” of fullerenes.\textsuperscript{12–14} Note that a parting with an idea of a “brute force” insertion of hydrogen inside the fullerene under extreme conditions (high temperature and pressure) in favor of a milder chemical opening of the cage was suggested some time ago by Patchkovskii and Thiel for He@C_{60}\textsuperscript{26} and by Dodziuk et al.\textsuperscript{16} Very recently, Murata et al.\textsuperscript{17,18} used a similar approach to obtain the 2H_2@C_{70} complex. It is noteworthy that the experimentally observed relative population of H_2@C_{60} and 2H_2@C_{60} (97:3)\textsuperscript{18} is very close to the values which can be deduced from a difference of 1.8 kcal/mol in the steric energy values determined by molecular mechanics.\textsuperscript{19}

Two main issues have been addressed by theoreticians when studying endohedral complexes of fullerenes with hydrogen molecules: a height of the barrier hindering the guest from entering the fullerene cavity and an estimation of the number of hydrogen molecules which can be hosted by the fullerene cage. Both problems can be first analyzed on the basis of simple mechanistic considerations. By taking the length of the H–H bond of about 0.7 Å, the van der Waals radii of the H and C atoms of ca. 1.2 and 1.7 Å, respectively, and assuming the diameter of fullerene (treated approximately as a sphere) as 7.1 Å,\textsuperscript{20} it is easy to estimate that there is no room left for another H_2 molecule inside the cage. Such a simple reasoning shows that only one hydrogen molecule can be hosted by C_{60}. Analogously, a comparison of the radii of the H and C atoms allows one to draw a conclusion that a hydrogen atom or molecule passing through the five- or six-membered ring should exhibit a strong repulsion because of an overlap of the electron clouds of the ring and the H atoms.

The problem of a barrier estimation for a guest entering the C_{60} cage has been studied in several articles\textsuperscript{21–23} yielding barriers of 3 eV\textsuperscript{21} or 2 eV\textsuperscript{23} for a hydrogen atom and 20 eV for H_2\textsuperscript{22} when passing through the six-membered ring. Subsequent molecular dynamics simulations have shown a very low probability for the process of catching a hydrogen atom inside the cage, while the same process in the case of the hydrogen molecule has been not observed in silico at all.\textsuperscript{21} These calculations are in line with a lack of success in obtaining H_2@C_{60} by a direct hydrogen insertion into an intact C_{60} fullerene (i.e., without opening the cage).\textsuperscript{11,18}

The stability of complexes of hydrogen molecule(s) buried inside the C_{60} cage has been studied by various approaches, from molecular mechanics (MM),\textsuperscript{24} through semiempirical and density-functional theory (DFT), to ab initio quantum chemical (QM) methods. At the beginning, it should be stressed that a usage of the semiempirical approach for nonbonding interactions is rather counterproductive, since this method has been developed to provide approximate energies of chemically bonded systems, and for this very reason the calculations of nonbonded complexes performed with this class of methods cannot be reliable. One can also add that semiempirical methods are known to have difficulties even with a satisfactory description of hydrogen bonds,\textsuperscript{25} which are by orders of magnitude stronger than interactions between a hydrogen molecule and a π-electron system. Therefore, the reports of Turker and Erkoc,\textsuperscript{26} who found a stabilization of 24 hydrogen molecules inside C_{60} on the basis of semiempirical AM1 calculations, or those of Ren et al.,\textsuperscript{27} who used the PM3 method combined with DFT and inserted 25 H_2 into the cage, are not reliable. A detailed criticism of the results of Turker and Erkoc can be found in refs 28 and 29. It should be noted that a recently developed OMx class of semiempirical methods compares somewhat better with QM calculations, but still without an empirical dispersion correction they predict no interaction for complexes containing π-electron systems.\textsuperscript{30}

The accuracy of quantum chemical calculations for endohedral fullerene complexes is usually quite limited. The obvious reason for this state of affairs is the size of the system,\textsuperscript{31} which precludes the use of the high-level ab initio electron-correlated theories, such as, for example, coupled cluster\textsuperscript{25} (see, however, ref 33) and large orbital basis sets. The limitations in the choice of ab initio electron-correlated theories are especially serious in the case of nonpolar or slightly polar guest molecules, since in these cases the host–guest interactions are mainly dispersive and exchange ones while it is known that the dispersion energy (and the corresponding exchange-dispersion energy) is not accounted for by the Hartree–Fock method.\textsuperscript{34} For instance, early self-consistent field (SCF) calculations of Cioslowski for H_2@C_{60} yielded incorrectly the instability of this complex.\textsuperscript{35}

Another popular method of accounting for the electron correlation is the DFT approach. The commonly employed DFT in its local density approximation or generalized gradient approximation variant is not an ab initio method, and the accuracy of reproducing the electron energy is strongly dependent on the quality of the functionals used. It is well-known that the DFT approach with commonly used functionals often strongly underestimates\textsuperscript{36} the stabilizing dispersion interaction (and a smaller destabilizing exchange-dispersion contribution) and that a neglect of this part of the interaction energy can lead to qualitatively incorrect results (e.g., destabilization instead of the stabilization effect). It should be also stressed that the existence of a multitude of DFT functionals makes it very difficult for a nonspecialist to select the best one for his or her particular purpose, although recent comprehensive studies on the quality of various functionals for several classes of nonbonding interactions provide some general guidelines.\textsuperscript{37} This situation results, unfortunately, in a broad misuse of functionals, leading to many erroneous conclusions. However, at present the reason why most functionals are incapable to describe dispersion interactions is well-known\textsuperscript{38} and several solutions...
to this problem exist, the most sophisticated of which are possibly the ones which derive nonlocal orbital functionals from many-body perturbation theory, coupled cluster theory, or the fluctuation–dissipation theorem DFT. Another practical solution to the dispersion energy problem with DFT is to use empirical damped multipole expansions of the dispersion energy as a correction term to the DFT energy (see, for example, refs 42–44). In these methods, the dispersion coefficients are often calculated as combinations of atomic dispersion coefficients and thus the dispersion energy can be estimated very efficiently. It has to be added, though, that the dispersion energy obtained in this way should not be confused with the dispersion energy from an intermolecular perturbation theory and has in fact no physical meaning. To our best knowledge, the most popular method from this class (i.e., the DFT + Disp method of Grimme) has not been used to study the stability of endohedral complexes of fullerenes yet. Another modification of the standard DFT method, known as DFT with tight binding (DFTB+), correctly yields only one hydrogen molecule stabilized inside the C_{60} fullerene; however, the latter authors claimed the stability of the highly strained endohedral complexes with up to 20 H \textsubscript{2} which, according to model considerations and available experimental results, cannot be obtained.

The existence of some new promising DFT functionals, which are especially designed to imitate the nonbonding interactions, should be also mentioned here. One of these functionals (MPWB1K, thoroughly tested by Zhao and Truhlar) has been recently used by Slanina et al. to estimate the stabilization energies of H \textsubscript{2}, Ne, and N \textsubscript{2} inside the C_{60} cavity. In agreement with the experimental evidence, MPWB1K predicts that these complexes are stable. The values of the MPWB1K stabilization energies are similar to values obtained from the second-order Møller–Plesset (MP2) and spin-component-scaled MP2 (SCS-MP2) calculations. However, as the authors of ref 47 notice, the MPWB1K functional does not provide a correct description of stacking interactions (like those between two benzene molecules), and therefore it cannot be excluded that sensible values of the interaction energies for three endohedral complexes studied there are just a result of an accidental error cancellation. Additionally, it is known that for complexes involving aromatic molecules the MP2 method often gives too large values of the attractive interaction energies, and therefore a good agreement with MP2 cannot be viewed as an ultimate proof of the usefulness of the MPWB1K functional for such cases.

Unfortunately, DFT with standard functionals is still utilized to calculate energies of endohedral fullerene complexes without taking into account a missing dispersion component of the interaction energy. Among several such works dealing with the stabilization effect for hydrogen molecules in the C_{60} fullerene, one can list, for example, articles of Yang, Pupysheva et al., and Lee and McKee. These authors claim to find stable or metastable structures involving numerous H \textsubscript{2} molecules (plus eventually partly chemisorbed species) inside C_{60} using standard DFT functionals, although in the Yang and Lee and McKee articles starting from the second added hydrogen molecule the energy of the complex is higher than the sum of the energies of isolated molecules. In the work of Pupysheva et al., two H \textsubscript{2} molecules are stabilized inside C_{60}, and for the number of hydrogen molecules in the fullerene cage greater or equal to 15 a partial chemisorption has been obtained yielding unphysically long CH bond of even 1.20 Å. Yang inserted up to 29 hydrogen molecules into the C_{60} cage and claimed that only for 29 guests the cage will be broken. He also modeled the hydrogen entrance into the cage, stating that 19 H \textsubscript{2} molecules can pass through a small opening involving nine bonds. This result contradicts the experimental studies on the orifice size enabling the entrance of one hydrogen molecule inside C_{60}. The paper by Yang has been criticized by Dolgonos, who pointed to the unreliability of the DFT calculations in this case and to very short distances between the seemingly “nonbonded” hydrogen atoms. The Yang reply to the comment of Dolgonos has been unsubstantial. Lee and McKee studied the reactivity of up to six H \textsubscript{2} molecules inside C_{60} using DFT and MP2 methods with unreliable small basis sets. Also, HH distances of 1.6 Å reported by Lee and McKee are certainly too small and should lead to a considerable repulsive destabilization of the systems under consideration. The analyses by the latter authors and Pupysheva et al. of the pressure inside the fullerene cage filled with numerous hydrogen molecules seem immaterial since, as discussed earlier, these complexes cannot be realized. It should be stressed that if an endohedral complex with two or even more endohedral H \textsubscript{2} molecules had been formed, then, despite a high strain, it would not decompose unless the strain of the complex distributed over the whole cage would be sufficiently large to break it. However, no process that could provide complexes with more than one guest inside C_{60} seems feasible. On the other hand, recent claims that endohedral fullerene complexes with hydrogen molecules can be of use for hydrogen storage seem unfounded, since the release of guest hydrogen molecules should lead to an irreversible cage destruction. A recent idea to store hydrogen in chemically opened fullerene cages could be a route to overcome this obstacle.

In this work, the endohedral C_{60} complexes involving one or two hydrogen molecules will be investigated using a computationally efficient variant of intermolecular symmetry-adapted perturbation theory (SAPT), which allows one to reliably estimate the interaction energies in the H_{2}@C_{60} and 2H_{2}@C_{60} species. A simultaneous study of these two complexes allows us to investigate a delicate balance between the dispersion and repulsion energies, which dominate in the intermolecular interactions for these two species, thus demonstrating the applicability of the latter method for such complicated cases.

**Methods**

Let us consider the interaction of two or three closed-shell molecules (denoted A, B, C). In general, the interaction energy of \(n\) molecules A, B, C,... is defined as a difference,

\[
E_{\text{interaction}}(ABC...) = E_{\text{ABC...}} - (E_A + E_B + E_C + ...)
\]

where \(E_{ABC...}\) is the energy of the complex ABC... and \(E_X\) is the energy of the molecule X (X = A, B, C,...). The
interaction energy of the three molecules A, B, and C can be separated into the additive and nonadditive parts:

\[ E_{\text{int}}(ABC) = E_{\text{int}}^{[2, 3]} + E_{\text{int}}^{[3, 3]} \]  

(2)

where \([n,m]\) denotes the \(n\)-body contribution for the complex of \(m\) molecules. The additive part \(E_{\text{int}}^{[2,3]}\) is thus defined as a sum of interaction energies of all pairs:

\[ E_{\text{int}}^{[2, 3]} = E_{\text{int}}(AB) + E_{\text{int}}(BC) + E_{\text{int}}(CA) \]  

(3)

and the nonadditive part \(E_{\text{int}}^{[3,3]}\) accounts for a modification of the interaction caused by the third partner. Note that in eqs 1–3 the intramolecular geometry parameters of A, B, and C have not been changed when calculating energies of complexes (i.e., no geometry relaxation is taken into account).

Equations 1–3 directly define the so-called supermolecular approach (sometimes called supramolecular one) for the calculation of interaction energies. In the supermolecular method, one calculates energies of all molecules and complexes (A, B, AB, etc.) by a given method and just makes the appropriate subtractions, according to eqs 1–3. Although appealing at first look, this approach has several disadvantages (see, for example, ref 58 for a detailed discussion). However, if a suitable theory is selected for the calculation of the electron energies and if the counterpoise correction of Boys and Bernardi\(^5^9\) is used, the supermolecular approach can produce reliable potential energy surfaces (PES) for the van der Waals complexes.

It should be noted parenthetically that endohedral species such as H\(_2\)@C\(_{60}\) are atypical examples of the van der Waals complexes since they cannot be separated into their constituent parts without the cage breaking. However, from the theoretical point of view there is no difference in a treatment of the endo- and exohedral van der Waals species.

**SAPT Treatment of the Interaction Energy of Two Molecules.** Another well-established approach for the calculation of the interaction energy for two closed-shell molecules is symmetry-adapted perturbation theory.\(^5^7,6^0\) In SAPT, the interaction energy is obtained directly as a sum of well-defined physical contributions and not as a difference between two similar numbers (see eq 1). Up to the second order in terms of the intermolecular interaction operator \(V = H_{AB} - H_A - H_B\) (where \(H_X\) is the electron Hamiltonian of a molecule or a complex \(XX = AB, A, B\), these contributions comprise: the first-order electrostatics (\(E_{\text{elst}}^{(1)}\)), second-order induction (\(E_{\text{ind}}^{(2)}\)) and dispersion (\(E_{\text{disp}}^{(2)}\)) energies, and their exchange counterparts: first-order exchange (\(E_{\text{exch}}^{(1)}\)), second-order exchange-induction (\(E_{\text{exch-ind}}^{(2)}\)) and exchange-dispersion (\(E_{\text{exch-disp}}^{(2)}\)), accounting for the electron tunneling between the interacting constituent molecules. The SAPT method up to the second order in \(V\) gives the main part of the interaction energy. As an estimation of the higher-order induction and exchange-induction energies, the Hartree–Fock “delta” correction term \(\delta E_{\text{HF}}\) is usually utilized.\(^3^4,6^1\) Summarizing, the interaction energy in SAPT is calculated as:

\[ E_{\text{int}}^{\text{SAPT}} = E_{\text{elst}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch}}^{(1)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \delta E_{\text{HF}} \]  

(4)

To calculate the energy contributions listed above, the exact wave functions of molecules A and B should be known in principle. Since usually these solutions are not available, one has to resort to some approximate methods. The simplest solution is the utilization of the Hartree–Fock (HF) determinants, in which case the so-called SAPT(HF) method is obtained. In this method, the effect of the electron correlation inside the A and B molecules is completely neglected. Thus far, three methods have been developed which enable to include the effect of the electron correlation inside the interacting molecules: (i) historically the first and the most popular SAPT(MP) approach,\(^6^2,6^3\) where the molecules A and B are treated by Möller–Plesset (MP) theory, (ii) SAPT(CC) approach,\(^6^4\) developed by Korona and Jezierski, where these molecules are described at the coupled cluster level (see also early works\(^6^5,6^6\), and (iii) the SAPT method with intramolecular electron correlation described by DFT. Only the latter method can treat molecules of the fullerene size, and therefore it will be described below in more detail.

A possibility of using DFT to account for the intramolecular correlation in SAPT was first pointed out in ref 66. The formalism of the DFT-SAPT method has been developed independently in two groups: Hesselmann and Jansen\(^5^7,6^8\) and Misquitta et al.\(^6^9\). The implementation of DFT-SAPT, followed by a recent inclusion of the density-fitting (DF) formalism\(^7^0\) for the calculation of two-electron repulsion integrals, allows one to extend treatable sizes of molecules by an order of magnitude. In particular, a DFT-SAPT calculation for a molecule of the C\(_{60}\) size has become feasible. The idea of DFT-SAPT consists in using the Kohn–Sham (KS) and the coupled-perturbed KS (CKS) orbitals instead of the HF and coupled-perturbed HF orbitals in SAPT(HF). In this way, the electron correlation of molecules A and B, present in DFT orbitals, is taken into account in SAPT at cost of the SAPT(HF) method. It should be stressed that DFT-SAPT is a different method from the supermolecular DFT and that the individual interaction energy terms in DFT-SAPT cannot be obtained from an energy decomposition of the supermolecular DFT energy. In particular, DFT-SAPT accounts correctly for the dispersion effect, since the dispersion and exchange-dispersion energies are calculated as the corresponding SAPT corrections. The accuracy of the DFT-SAPT method has been recently confirmed by a comparison with benchmark SAPT(CC) calculations\(^6^4\) and with the supermolecular CCSD(T) approach (see, for example, ref 71).

**Interaction Energies of Three Molecules.** The SAPT method has been extended for the interaction of three molecules in ref 72. In this approach, apart from the calculation of the usual SAPT interaction energies for three pairs of the complexes (AB, BC, and CA), one has to obtain the nonadditive contributions to the interaction energy. However, the program which calculates these corrections is incorporated, along with some higher-order corrections, in the nonadditive part of the supermolecular interaction energies, calculated at various levels of the supermolecular approach. Recently, using this feature,
Podeszwa and Szalewicz developed two hybrid schemes for calculating these contributions. Both schemes divide the nonadditive interaction energy into two parts: one calculated by the supermolecular approach and another part calculated by perturbation theory. For this study, we selected the scheme denoted in ref 73 as MP2+SDFT. In the MP2+SDFT approach, the nonadditive part of the interaction energy is calculated as a sum of the MP2 supermolecular nonadditive interaction energy \( E_{\text{int}}^{\text{MP2}}[3,3] \) and the perturbational three-body dispersion energy \( E_{\text{disp}}^{(3)} \) (CKS)[3,3], calculated from the CKS propagators of constituent molecules

\[
E_{\text{int}}^{[3,3]} = E_{\text{int}}^{\text{MP2}}[3,3] + E_{\text{disp}}^{(3)} (\text{CKS})[3,3]
\]  

(5)

It was stated in ref 73 that the \( E_{\text{int}}^{\text{MP2}}[3,3] \) term provides an estimation for the following nonadditive contributions: first-order exchange, second- and higher-order induction and exchange-induction, and a third-order mixed induction-dispersion terms. The third-order dispersion correction \( E_{\text{disp}}^{(3)} \) is absent in the supermolecular MP2 method, and it should be therefore calculated separately. It should be stressed that at least third-order Möller–Plesset theory (MP3) is required to account for \( E_{\text{disp}}^{(3)} \), which for the nonpolar species is a dominant nonadditive long-range effect. Summarizing, the total interaction energy in the hybrid scheme is obtained as a sum of the following contributions:

\[
E_{\text{int}}^{\text{hybrid}} = E_{\text{int}}^{\text{SAPT}}(AB) + E_{\text{int}}^{\text{SAPT}}(BC) + E_{\text{int}}^{\text{SAPT}}(CA) + E_{\text{int}}^{\text{MP2}}[3,3] + E_{\text{disp}}^{(3)}(\text{CKS})[3,3]
\]  

(6)

### Computational Details

All calculations were performed with the development version of the MOLPRO suite of programs. In addition to the DFT-SAPT calculations, supermolecular calculations were performed with the MP2, SCS-MP2, and dispersion-corrected DFT functional using the damped multipole expansion scheme developed by Grimme to assess the quality of these methods in comparison to DFT-SAPT. The Boys–Bernardi counterpoise correction was used for all supermolecular calculations.

### DFT Calculations for a Fullerene and a Hydrogen Molecule

The \( C_{60} \) and \( H_2 \) molecules in DFT-SAPT were treated with the PBE functional using an additional asymptotic correction of the exchange-correlation (xc) potential, as proposed by Grünig et al. The utilization of this correction is crucial in this method, since otherwise the asymptotic density is in general too diffuse, leading to a poor description of magnitudes of intermolecular interactions. This asymptotic correction is currently performed using a scheme which connects the respective xc potential in the bulk region with an asymptotic xc potential (having a Coulombic \( -1/r \) behavior) by shifting the bulk potential by the so-called derivative discontinuity (i.e., the difference between (negative) ionization potential and HOMO energy of the underlying xc functional). For the case of the \( C_{60} \) molecule, the value of this correction was set to 0.0641 hartree and for the hydrogen molecule to 0.185 hartree. These values were obtained from the experimental vertical ionization potentials of \( C_{60} \) (0.279 hartree) and \( H_2 \) (0.566 hartree) and the corresponding HOMO energies of both systems using the PBE xc functional in the TZVPP basis set (−0.215 and −0.381 hartree, respectively). The latter functional was also used in the DFT+Disp method. A total nonadditive contribution to the interaction energy was calculated by the MP2+SDFT method. Additive (i.e., two-body) contributions were calculated by DFT-SAPT. Because of the absence of the basis-set superposition error in the perturbational approach, the \( \text{H}_2 \cdot \cdot \cdot \text{H}_2 \) and \( \text{H}_2 \cdot \cdot \cdot C_{60} \) interaction energies in the \( 2\text{H}_2@C_{60} \) complex can be calculated without using the basis on the ghost molecule. In this way, we can utilize the results from the \( \text{H}_2@C_{60} \) calculations. The additive contributions of the third order were neglected in the present study, unless they are present in the \( \delta E_{\text{disp}} \) term.

The core electrons (1s) for carbon atoms were frozen in all correlated calculations.

### Choice of the Basis Set and Complex Geometries

The selection of a proper orbital basis set is crucial to obtain reasonable results. Because of the size of the system, we had to find a balance between the accuracy and the computational cost of the method. After some testing, we found that the TZVPP basis set is the smallest reliable basis for our purposes. The corresponding cc-pVTZ/JKFIT DF auxiliary basis set was used for the calculation of Coulombic and exchange integrals in SCF and the first-order interaction energy contributions while all doubly external integrals and all xc-type integrals occurring in the second-order DFT-SAPT were computed using the TZVPP/MP2F182 fitting basis set. With these basis sets, the calculations for a single DFT-SAPT point (without the \( \delta E_{\text{disp}} \) correction) take about 5.5 days on Opteron/2 GHz and 2.5 days on Woodcrest/2.4 GHz computers.

The CC bond lengths of 1.458 and 1.401 Å were assumed for the bonds in a pentagon ring and those between pentagon rings which, due to the \( I_5 \) symmetry, fully determine the \( C_{60} \) geometry. As recommended in ref 84, we use the value of the vibrationally averaged \( R_{\text{H-H}} \) of 0.7668 Å. In view of the large size of the complexes under study, their full PES values could not be calculated. Instead, only few potentially interesting geometries of these two species were analyzed. For the \( \text{H}_2@C_{60} \) complex, these geometries comprise three orientations relative to a selected pentagon ring of the fullerene (with the geometrical center of the hydrogen molecule lying on the fivefold symmetry axis of this pentagon), and two orientations related to a selected hexagon ring of the fullerene (with the geometrical center of the hydrogen molecule lying on the threefold symmetry axis of this hexagon). These orientations will be denoted as:

- **TP**, a hydrogen molecule perpendicular to a selected pentagon ring:
- **PP**, a hydrogen molecule parallel to a selected pentagon ring, \( \text{H}_2 \) lies in one of five symmetry planes of this pentagon;
- **SP**, a hydrogen molecule forming the angle 45° to a selected pentagon ring; as in the case of the PP mutual orientation, \( \text{H}_2 \) lies in one of five symmetry planes of this pentagon;
- **TH**, a hydrogen molecule perpendicular to a selected hexagon ring:
PH, a hydrogen molecule parallel to a selected hexagon ring, H₂ lies in one of three symmetry planes of this hexagon. These orientations are also depicted in Figure 1. For each of these orientations, several distances \( r \) from the center of mass of the hydrogen molecule to the center of the fullerene were used. In two cases also distances \( r > 3.5 \text{ Å} \) were taken into account, which correspond to the C\(_{60}\) complex with a hydrogen molecule outside the cage.

To select potentially interesting structures of 2H\(_2@C_{60}\), we first analyzed the CCSD(T) potential energy surface of the H\(_2\) dimer, published recently by Hinde.\(^8\)\(^5\) The global minimum for this system (\(-0.467 \text{ kJ/mol}\)) occurs for a perpendicular (T) structure (\( \theta_1 = 90^\circ, \theta_2 = 0^\circ \), coordinates defined in ref 85) at a distance of 3.36 Å between the geometrical centers of hydrogen molecules. To select revealing guest positions in the 2H\(_2@C_{60}\) complex, it is also important to know at which point the interaction energy of the H\(_2\)···H\(_2\) dimer is equal to zero. For the case of the T-structure, this happens at 2.92 Å. The minimum is only slightly shallower (\(-0.436 \text{ kJ/mol}\)) for the skew (S) structure (\( \theta_1 = 45^\circ, \theta_2 = 45^\circ, \phi = 0^\circ \)) with the zero point at 2.95 Å. We also found that it will be of interest to check two “crossed” orientations: X1 (\( \theta_1 = 90^\circ, \theta_2 = 90^\circ, \phi = 72^\circ \)) and X2 (\( \theta_1 = 90^\circ, \theta_2 = 90^\circ, \phi = 60^\circ \)). The selected structures of the H\(_2\) dimer were inserted into the fullerene molecule, so that (i) both hydrogen molecules are equidistant from the center of C\(_{60}\), (ii) they are placed at the orientations previously used for H\(_2@C_{60}\), and (iii) their geometrical centers lie on the same symmetry axis of fullerene. In this way, the following structures with two guest molecules were selected (the unspecified details of geometries are the same as for the H\(_2@C_{60}\) case):

- **TP**, a first hydrogen molecule parallel to a selected pentagon ring, the second one perpendicular to it (both H\(_2\) forming the T-structure);
- **SP**, both hydrogen molecules forming the 45° angle with a selected pentagon ring (both H\(_2\) forming the S-structure);
- **XP**, both hydrogen molecules parallel to a pentagon ring form the X1 structure;
- **XH**, both hydrogen molecules parallel to a hexagon ring form the X2 structure.

These orientations are depicted in Figure 2.

**Results and Discussion**

**C\(_{60}\) with One Hydrogen Molecule.** The DFT-SAPT interaction energies for the complex of C\(_{60}\) with one H\(_2\) molecule as a function of a distance from the cage center are presented in Table 1. The examination of this table reveals that there is a small stabilization effect for the endohedral complex of one hydrogen molecule with C\(_{60}\). This effect is not large, since the minimum depth is equal to \(-19.35 \text{ kJ/mol}\), and already at \( r = 1.0 \) or 1.1 Å (depending on orientation), the interaction energy becomes positive. From the five orientations studied in this work, TH gives the lowest interaction energy, corresponding to the largest stabilization, although the differences between various orientations are very small, especially in the center of the fullerene cage. It is interesting to note that there is a shallow secondary minimum (or a saddle point) for the PH orientation, shifted by about 0.1 Å from the center. Another minimum region for this species occurs for the exohedral
10. Intermolecular interactions

SAPT Applied to Endohedral Fullerene Complexes

<table>
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<th>Table 1. DFT-SAPT Interaction Energy for Selected Orientations of the H₂@C₆₀ Complex*</th>
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* Energy values in kilojoules per mole (1 millihartree = 2.6255 kJ/mol); distances in angstroms. Note that for distances r > 3.5 Å the complex is exohedral.

complex at r ≈ 6.5 Å, but in this case the stabilization energy is too small to enable the complex stability at room temperature.

A detailed division of the SAPT interaction energy into components and interaction energies obtained by the supermolecular MP2, SCS-MP2, and DFT¬+Disp[13] approaches are presented in Table 2 for the PP orientation (a parallel orientation was selected for a more detailed analysis since it turns out that this orientation is preferred for the 2H₂@C₆₀ case). The energy components for TH, TP, SP, and PH orientations are very similar to the presented ones and are given in the Supporting Information. A distance dependence of the SAPT corrections for the PP orientation is depicted in Figure 3.

Let us first focus on the supermolecular interaction energies presented in Table 2. An inspection of these data indicates that the MP2 method overestimates the complex binding, which is the common behavior of MP2 for the interaction involving aromatic rings, while SCS-MP2 is in a much better agreement with DFT-SAPT. Next, let us look at the results of the DFT+Disp method of Grimme. It can be observed that DFT+Disp performs well at the center, but for larger distances $E_{\text{disp}}$ increases less steeply than $E_{\text{sapt}}$. The reason for such a behavior of the DFT+Disp method can be ascribed to the “dispersion” contribution of the latter method which rapidly decreases as the H₂ molecule approaches the cage wall. As a result, too much space is available for the hydrogen molecule according to the Grimme method. In the strong repulsive region of $r > 1.5$ Å, the correspondence of DFT+Disp with DFT-SAPT improves because of the switching on the damping function in the DFT+Disp method and a decrease of the dispersion contribution as compared to the other contributions in the supermolecular PBE interaction energy. This behavior is also found for other orientations studied and leads to the conclusion that the DFT+Disp method may not be accurate enough to study PES of endohedral hydrogen molecules in the C₆₀ cage. However, we observed that the agreement of DFT+Disp with our DFT-SAPT reference data can be considerably improved by a modification of the damping parameter α from 20.0 to 9.2 and the prefactor $\lambda$ from $-0.75$ to $-0.63$ of the underlying original Grimme model. While an application of this path may certainly not be advisable in general, it could provide a possible option to investigate the potential energy surface using a quantum chemistry method less expensive than MP2 or DFT-SAPT.

Let us analyze the behavior of the components of the SAPT interaction energy. The stabilization effect in the center of C₆₀ comes mainly from the dispersion energy, while the first-order exchange energy gives the most important repulsive contribution. This trend continues as we approach the cage wall: both corrections grow in absolute values, but the dispersion effect increases slower, and finally the first-order exchange energy prevails leading to the repulsive character of the interaction. The induction energy is almost as important as the dispersion energy, but it is strongly damped by its exchange counterpart (this is a common effect for the short-range induction contribution; see, for example, ref 86). Nonetheless, for $r > 1.5$ Å the effective $E_{\text{disp}} + E_{\text{exch-ind}}$ contribution becomes more important than the dispersion energy.

The above analysis shows that great care should be exercised when modeling PES for endohedral fullerene complexes with a simple repulsion+dispersion model (see, for example, ref 87), since neglected short-range terms may become as large as the included ones, when approaching the cage wall.

An examination of Figure 3 reveals that for the PP orientation there is a shallow well in the attractive region and a steep repulsive potential wall for larger r, where the guest approaches the host cage. A similar pattern is found for other orientations. Table 1 shows that the center of the well is practically isotropic and large enough to allow for an almost free rotation of the H₂ guest. Anisotropy becomes more pronounced for larger distances (i.e., closer to the cage wall). A comparison of the data from the Supporting Information allows us to conclude that, as expected, the dispersion and exchange-dispersion energies are the most isotropic SAPT terms, while the first-order exchange, induction, and exchange-induction energies exhibit the largest anisotropy. However, even at $r = 1.5$ Å (highly repulsive region) this anisotropy does not exceed a few percent (e.g., first-order exchange corrections for the PH and TP orientations differ by 18% for this distance).

Let us analyze how the just presented results can be used to select the most interesting geometries describing the 2H₂@C₆₀ complex. In view of the data from Table 1, shifting of a hydrogen molecule from the center by more than 1.0 Å will cause a strong repulsion from carbon atoms. This means that two hydrogen molecules in the fullerene cage can be separated by at most 2 Å, otherwise a strong repulsion from the cage wall will result. However, the PES for two hydrogen molecules is highly repulsive for such a small distance. On the other hand, the PES for the H₂ dimer passes through zero at about 3 Å. If two hydrogen molecules are placed on
the opposite sides from the center of C_60, at a distance r = 1.5 Å each, they will exhibit a strong repulsion from the cage wall, but the hydrogen molecules will not repel each other. Therefore, the most interesting geometries for the 2H_2@C_60 complex are those with hydrogen molecules at distances from 1.0 to 1.5 Å from the C_60 center. In this region, a minimum of the 2H_2@C_60 interaction energy should be expected.

Accuracy of the Present Calculations. The DFT-SAPT approach is far too expensive to perform a geometry optimization of the H_2@C_60 and 2H_2@C_60 complexes, raising questions about the accuracy of our results. The problem is especially important in the latter case, in which strain should lead to the bond-length distortion. To address this issue, we performed several additional test calculations.

The most important question to be answered is: Does an appropriate deformation of the host and/or guest allow the insertion of a second H_2 molecule into C_60? As already noted, the optimization of the geometry is out of the question in our case, and therefore we tackled this problem in another way. We unphysically enlarged the fullerene cage by increasing all carbon—carbon distances by 5% and calculated the interaction energy for the TP orientation and distances r = 1.1 and 1.25 Å. The resulting DFT-SAPT interaction energies are equal to −1.52 and +4.85 kJ/mol, respectively. This simple test shows that the unphysically large blowup of the cage shifts the zero point of PES from about 1.0 to ca. 1.2 Å, the value still too small to avoid a repulsion between two hydrogen molecules. Therefore, it seems highly improbable that much smaller changes in the geometry of C_60 during the geometry optimization would allow a deformed H_2@C_60 to accept one more hydrogen molecule. Additionally, we found that a change in the distance between the hydrogen atoms (R_H-H = 0.7408 Å) has a negligible effect of 0.1 kJ/mol on the DFT-SAPT energy for the PP orientation at r = 1.0 Å. Summarizing, these data strongly indicate that neither a deformation of the host nor that of the guest would result in stabilizing of the complex of C_60 with two hydrogen molecules.

Finally, the basis set effects were analyzed by performing the DFT-SAPT calculations in a sequence of DZP, TZVP, and TZVPP basis sets for the TP orientation at r = 0. The results presented in Figure 4 indicate that the quality of the dispersion energy depends crucially on the basis set used, while all other SAPT corrections are almost saturated even for the smallest DZP basis set. However, because of the importance of the dispersion energy the DZP basis set cannot be used for the H_2@C_60 complex, as it recovers only 61% of the TZVPP dispersion term. On the other hand, the TZVP $E_{int}^{DFT}$ energy is much closer to the TZVPP value (its absolute

Table 2. Components of the DFT-SAPT Interaction Energy for the PP Orientation of the H_2@C_60 Complex

<table>
<thead>
<tr>
<th>r</th>
<th>$E_{int}^{DFT}$</th>
<th>$E_{disp}^{DFT}$</th>
<th>$E_{ind}^{DFT}$</th>
<th>$E_{DFT}^{disp}$</th>
<th>$\delta E_{F}$</th>
<th>$E_{int}^{MP2}$</th>
<th>$E_{int}^{SAPT}$</th>
<th>$E_{int}^{SCS-MP2}$</th>
<th>$E_{int}^{DFT-Disp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>−7.20</td>
<td>21.16</td>
<td>−5.02</td>
<td>4.50</td>
<td>−36.09</td>
<td>4.13</td>
<td>−0.74</td>
<td>−19.26</td>
<td>−30.69</td>
</tr>
<tr>
<td>0.10</td>
<td>−7.34</td>
<td>21.54</td>
<td>−5.16</td>
<td>4.63</td>
<td>−36.38</td>
<td>4.12</td>
<td>−0.76</td>
<td>−19.25</td>
<td>−30.65</td>
</tr>
<tr>
<td>0.20</td>
<td>−7.77</td>
<td>22.70</td>
<td>−5.54</td>
<td>4.99</td>
<td>−36.81</td>
<td>4.35</td>
<td>−0.80</td>
<td>−18.89</td>
<td>−30.54</td>
</tr>
<tr>
<td>0.25</td>
<td>−8.10</td>
<td>23.58</td>
<td>−5.82</td>
<td>5.24</td>
<td>−37.20</td>
<td>4.46</td>
<td>−0.85</td>
<td>−18.68</td>
<td>−30.44</td>
</tr>
<tr>
<td>0.30</td>
<td>−8.49</td>
<td>24.65</td>
<td>−6.16</td>
<td>5.55</td>
<td>−37.81</td>
<td>4.62</td>
<td>−0.89</td>
<td>−18.52</td>
<td>−30.31</td>
</tr>
<tr>
<td>0.50</td>
<td>−11.12</td>
<td>31.71</td>
<td>−8.66</td>
<td>7.79</td>
<td>−41.34</td>
<td>5.54</td>
<td>−1.17</td>
<td>−17.25</td>
<td>−29.29</td>
</tr>
<tr>
<td>0.75</td>
<td>−17.58</td>
<td>48.81</td>
<td>−14.66</td>
<td>13.15</td>
<td>−47.59</td>
<td>7.39</td>
<td>−1.81</td>
<td>−12.29</td>
<td>−25.76</td>
</tr>
<tr>
<td>0.80</td>
<td>−19.53</td>
<td>53.91</td>
<td>−16.65</td>
<td>14.89</td>
<td>−47.83</td>
<td>7.30</td>
<td>−1.98</td>
<td>−9.88</td>
<td>−24.54</td>
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<tr>
<td>0.90</td>
<td>−24.29</td>
<td>66.30</td>
<td>−21.83</td>
<td>19.39</td>
<td>−53.31</td>
<td>9.00</td>
<td>−2.35</td>
<td>−7.09</td>
<td>−21.29</td>
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<tr>
<td>1.00</td>
<td>−30.28</td>
<td>82.02</td>
<td>−27.82</td>
<td>24.47</td>
<td>−57.90</td>
<td>10.50</td>
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<td>−16.74</td>
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<td>1.10</td>
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<td>102.45</td>
<td>−36.57</td>
<td>31.74</td>
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<td>−3.05</td>
<td>−5.44</td>
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<td>1.25</td>
<td>−54.38</td>
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<td>−55.84</td>
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<td>−73.99</td>
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<td>19.67</td>
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<tr>
<td>1.50</td>
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<td>−114.98</td>
<td>89.25</td>
<td>−97.96</td>
<td>21.35</td>
<td>2.18</td>
<td>62.61</td>
<td>48.95</td>
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<td>1.75</td>
<td>−181.44</td>
<td>476.85</td>
<td>−234.40</td>
<td>156.91</td>
<td>−133.36</td>
<td>28.20</td>
<td>29.79</td>
<td>142.55</td>
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<td>2.00</td>
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<td>−182.68</td>
<td>31.32</td>
<td>121.97</td>
<td>283.67</td>
<td>298.85</td>
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<td>6.00</td>
<td>−7.66</td>
<td>24.68</td>
<td>−5.78</td>
<td>5.24</td>
<td>−15.93</td>
<td>2.47</td>
<td>−1.78</td>
<td>1.25</td>
<td>−0.38</td>
</tr>
<tr>
<td>6.50</td>
<td>−2.00</td>
<td>5.64</td>
<td>−0.76</td>
<td>0.69</td>
<td>−6.99</td>
<td>0.69</td>
<td>−0.34</td>
<td>−3.07</td>
<td>−3.62</td>
</tr>
<tr>
<td>7.00</td>
<td>−0.02</td>
<td>1.25</td>
<td>−0.14</td>
<td>0.12</td>
<td>−2.99</td>
<td>0.18</td>
<td>−0.02</td>
<td>−1.64</td>
<td>−2.51</td>
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<td>8.00</td>
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<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>−0.63</td>
<td>0.01</td>
<td>−0.09</td>
<td>−0.60</td>
<td>−0.77</td>
</tr>
</tbody>
</table>

The total DFT-SAPT energy, as well as MP2, SCS-MP2, and DFT-Disp interaction energies are also given. Energy values in kilojoules per mole; distances in angstroms. Note that for distances r > 3.5 Å the complex is exohedral.

Figure 3. Components of the interaction energy for the PP orientation of H_2@C_60. Energy values are in kilojoules per mole, distances are in angstroms.

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Figure 4. Basis set dependence of the SAPT components for the TP orientation of H2@C60 at distance r = 0. Energies are in kilojoules per mole.

value is smaller by 12%), allowing us to draw a conclusion that the presented results should be reliable. The remaining error resulting from the unsaturation of the basis can be conservatively estimated as about 15%.

C60 with Two H2 Molecules. The results of the calculations of the interaction energy of fullerene and two hydrogen molecules are presented in Table 3. In this table, in addition to the total interaction energy \( E_{\text{int}} \), also the following quantities are presented: a sum of the DFT-SAPT interaction energies of the first and second hydrogen molecule with the fullerene, the DFT-SAPT interaction energy for the dimer of the hydrogen molecule, the MP2 nonadditive contribution, and the nonadditive CKS third-order dispersion term. The total supermolecular MP2 interaction energy is also listed for comparison.

An examination of Table 3 shows that three-body effects for this case are rather small (less than 10% of the total interaction energy). Usually MP2 and third-order dispersion nonadditive effects are of the opposite signs, which makes the total nonadditive contribution even smaller. The third-order dispersion energy is found to be insignificant for almost all tested geometries. However, the MP2 supermolecular method cannot be used for the 2H2@C60 case, anyway, since the two-body energies predicted by MP2 are too attractive for H2@C60 in comparison to the DFT-SAPT reference values.

The shape of the 2H2@C60 potential is determined by the two-body effects. The anisotropy of the three-body interaction energy is quite pronounced. In all tested cases, the interaction energy is positive, denoting that the endohedral complex of fullerene with two H2 molecules is not stabilized. The minimum repulsion (ca. 24.7 \( \text{kJ/mol} \)) occurs for both orientations of the interaction energy of fullerene and two hydrogen molecules.

It is noteworthy that these two orientations are different from the global-minimum orientation of the H2 dimer (corresponding to the TP structure).\(^{15}\) Evidently, the TP orientation is more repulsive (ca. 32.8 \( \text{kJ/mol} \)) since in such an orientation one hydrogen atom (of the H2 molecule perpendicular to a pentagon ring) “touches” the cage wall sooner than in the case of the parallel orientation. Thus, for the “crossed” structures, the minimum is a result of an interplay of the two-body interaction energies of the H2···H2 and H2@C60 (Table 2 and the Supporting Information).

Therefore, one can conclude that the present method does not yield the stabilization of the 2H2@C60 complex. It can also be observed that \( E_{\text{int}}^{\text{MP2}} \) predicts falsely a small stabilization effect for “crossed” structures, which can be explained by too attractive interaction energies predicted for H2@C60 (Table 2 and the Supporting Information).

In view of the recent synthesis of two hydrogen molecules in a closed C60 cage,\(^{16}\) we performed the DFT-SAPT calculations for several points of PES for the 2H2@C60 complex. Because of the limitations of our third-order

### Table 3. Components of the Interaction Energy for Various Orientations of Hydrogen Molecules in the 2H2@C60 Complex\(^a\)

<table>
<thead>
<tr>
<th>r (Å)</th>
<th>( E_{\text{int}} )</th>
<th>( E_{\text{int}}^{\text{SAPT}} )</th>
<th>( E_{\text{int}}^{\text{MP2}} )</th>
<th>( E_{\text{int}}^{\text{SAPT}} )</th>
<th>( E_{\text{int}}^{\text{MP2}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>–33.92</td>
<td>537.66</td>
<td>–1.04</td>
<td>–6.34</td>
<td>496.35</td>
</tr>
<tr>
<td>0.75</td>
<td>–23.07</td>
<td>133.97</td>
<td>4.46</td>
<td>–2.08</td>
<td>113.27</td>
</tr>
<tr>
<td>0.80</td>
<td>–18.95</td>
<td>100.52</td>
<td>4.69</td>
<td>–1.66</td>
<td>84.64</td>
</tr>
<tr>
<td>0.90</td>
<td>–11.50</td>
<td>55.22</td>
<td>4.63</td>
<td>–1.07</td>
<td>47.28</td>
</tr>
<tr>
<td>1.00</td>
<td>–0.04</td>
<td>29.18</td>
<td>4.19</td>
<td>–0.58</td>
<td>32.75</td>
</tr>
<tr>
<td>1.10</td>
<td>15.33</td>
<td>14.64</td>
<td>3.63</td>
<td>–0.25</td>
<td>33.35</td>
</tr>
<tr>
<td>1.25</td>
<td>46.86</td>
<td>4.77</td>
<td>2.85</td>
<td>–0.17</td>
<td>54.31</td>
</tr>
<tr>
<td>1.50</td>
<td>138.60</td>
<td>0.36</td>
<td>2.10</td>
<td>–0.03</td>
<td>141.03</td>
</tr>
<tr>
<td>1.75</td>
<td>305.94</td>
<td>–0.19</td>
<td>1.94</td>
<td>–0.05</td>
<td>307.65</td>
</tr>
</tbody>
</table>

\(^{a}\) The total interaction energy \( E_{\text{int}}^{\text{MP2}} \) is a sum of additive DFT-SAPT energies and nonadditive (\( E_{\text{int}}^{\text{SAPT}} \)) energies; see eq 6. The total supermolecular MP2 interaction energy is listed in the last column. Energy values in kilojoules per mole; distances in angstroms. **A** sum of interaction energies of both fullerene-hydrogen molecule pairs; see eq 4.
dispersion code, only the additive part of the interaction energy was obtained. The geometry of the C_{70} fullerene was taken from ref 88. The X1 structure of the H_2 dimer was used with the geometrical centers of H_2 lying on the fivefold symmetry axis of C_{70}, on the opposite sides from the cage center at distances r = 1.2, 1.3, 1.4, and 1.5 Å from this center. The asymptotic shift of the bulk xc potential of the C_{70} fullerene was taken as 0.0596 hartree. A smaller TZVP basis was used. The additive part of the DFT-SAPT energy for these distances is equal to −16.3, −19.8, −13.6, and −9.1 kJ/mol, respectively. It can be noted that the largest (in absolute value) interaction energy still occurs for the repulsive geometry of the H_2•••H_2 dimer. Since the result is obtained in the TZVP basis and the attractive dispersion energy benefits the most from using the larger TZVPP basis, it can be estimated that the value of the interaction energy can be about 10–20% lower in the full basis set limit. The experience gained from the 2H_2@C_{60} case allows one to estimate the possible nonadditive effects as at most 10% of the total interaction energy. Thus, in agreement with the experimental findings,^{1,15} the DFT-SAPT approach yields the stabilization of two hydrogen molecules inserted into the C_{70} fullerene and the destabilization of the smaller 2H_2@C_{60} complex.

**Summary and Conclusions**

The highly accurate DFT-SAPT method with density fitting used for two-electron repulsion integrals was shown to be applicable for an analysis of selected points of the potential energy surface for the nonbonding interactions of the C_{60} fullerene with hydrogen molecules.

The calculations were performed with DFT-SAPT in a reasonably large TZVPP orbital basis for selected orientations of one and two H_2 molecules inside the C_{60} fullerene. The nonadditive effects were modeled by a recently proposed hybrid method.^{73} For the endohedral complex H_2@C_{60}, a small stabilization effect of about 19.4 kJ/mol (4.6 kcal/mol) was found, with the minimum of PES in the center of the fullerene. It can be noted that this value agrees nicely with a recent estimate of Slanina et al.,^{47} who predicted the stabilization of at least 4 kcal/mol for this species. The PES of H_2@C_{60} is almost flat in the vicinity of the cage center and nearly isotropic, especially in the attractive region. This result is consistent with a recent theoretical study of the translation-rotation spectrum of H_2 confined in C_{60},^{49} where the first rotational level of H_2@C_{60} is virtually identical to the level for the free hydrogen molecule. The hydrogen molecule inside the fullerene is bound mainly by the dispersion interaction, while the first-order exchange term represents the main repulsive component of the interaction energy. However, other SAPT corrections are far from being negligible. For instance, the induction energy is of the same order of magnitude as the dispersion energy, but is strongly quenched by its exchange counterpart in the vicinity of the cage center. A small exohedral minimum, expected on the basis of model considerations, was also observed.

For the 2H_2@C_{60} complex, no stabilization effect was found. This finding is in agreement with the lack of the experimental reports of two H_2 molecules inside the opened and closed C_{60} cage and with only a small amount of the 2H_2@C_{70} obtained in the mixture with H_2@C_{70}. The lowest repulsion for the 2H_2@C_{60} complex occurs for the “crossed” orientation of the hydrogen molecules, which are separated by ca. 2.0 Å from each other. Interestingly enough, the stabilization of H_2@C_{60} and destabilization of 2H_2@C_{60} was also predicted by a simple MM model.^{16,19} For the same orientation of the hydrogen molecules in a larger C_{70} fullerene, separated by 2.6 Å, the DFT-SAPT method yields the negative interaction energy, confirming, in agreement with recent experimental findings, the stability of 2H_2@C_{70}. Interestingly, also in this case the MM method yielded the stabilization of both H_2@C_{70} and 2H_2@C_{70} species, correctly predicting their energy difference.^{19}

**Acknowledgment.** Computations were carried out using the mixed Woodcrest/Opteron cluster at the Lehrstuhl für Theoretische Chemie Erlangen and the Opteron cluster at the Computer Center of the Faculty of Chemistry, University of Warsaw. A.H. gratefully acknowledges the funding of the German Research Council (DFG), through the Cluster of Excellence “Engineering of Advanced Materials” (www.eam.uni-erlangen.de).

**Supporting Information Available:** Results of calculations of DFT-SAPT, MP2, SCF-MP2, and DFT-Disp interaction energies, as well as DFT-SAPT energy components for the TP, TH, SP, and HP orientations of the H_2@C_{60} complex. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

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(48) (a) Yang, C.-K. Carbon 2007, 45, 2451.


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Supporting information for: Symmetry-adapted perturbation theory applied to endohedral complexes of fullerenes: a stability study of H$_2$@C$_{60}$ and 2H$_2$@C$_{60}$

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†Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland
‡Institut für Physikalische und Theoretische Chemie, Universität Erlangen, Egerlandstraße 3, 91058 Erlangen, Germany
§Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warsaw, Poland
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Symmetry-adapted perturbation theory . . .

Table 1: Components of the DFT-SAPT interaction energy for the SP orientation. The total
DFT-SAPT energy, as well as MP2 and SCS-MP2 interaction energies are also given. Energy
values in millihartree. Distances in Å.
r
0.00
0.25
0.50
0.75
1.00
1.25
1.50

(1)

Eelst
−2.74
−3.11
−4.34
−7.01
−12.10
−21.85
−39.58

(1)

Eexch
8.06
9.05
12.37
19.54
33.28
59.52
107.74

(2)

(2)

Eind
Eexch−ind
−1.91
1.71
−2.26
2.03
−3.41
3.04
−6.13
5.43
−11.88
10.27
−24.52
20.21
−50.50
38.17

(2)

(2)

SAPT
Edisp
Eexch−disp δ EHF Eint
−13.76
1.58 −0.28 −7.35
−14.18
1.70 −0.33 −7.09
−15.68
2.12 −0.49 −6.39
−18.26
2.87 −0.82 −4.36
−22.42
4.09 −1.34 −0.10
−28.80
5.92 −1.68
8.80
−38.26
8.27
0.20 26.04

SCS−MP2
MP2
Eint
Eint
−11.69
−8.22
−11.58
−8.04
−11.08
−7.30
−9.57
−5.38
−5.72
−0.93
3.06
8.75
21.57
28.49

Table 2: Components of the DFT-SAPT interaction energy for the PP orientation. The total
DFT-SAPT energy, as well as MP2 and SCS-MP2 interaction energies are also given. Energy
values in millihartree. Distances in Å.
r
0.00
0.25
0.50
0.75
0.80
0.90
1.00
1.10
1.25
1.50
1.75
2.00
6.00
6.50
7.00
8.00

(1)

Eelst
−2.74
−3.08
−4.24
−6.69
−7.44
−9.25
−11.53
−14.53
−20.71
−37.97
−69.11
−120.68
−2.92
−0.76
−0.01
0.02

(1)

Eexch
8.06
8.98
12.08
18.59
20.53
25.25
31.24
39.02
55.14
99.97
181.62
322.58
9.40
2.15
0.47
0.02

(2)

Eind
−1.91
−2.22
−3.30
−5.58
−6.34
−8.31
−10.60
−13.93
−21.27
−43.79
−89.28
−170.50
−2.20
−0.29
−0.05
0.00

(2)

(2)

(2)

SAPT
Edisp
Eexch−disp δ EHF
Eint
−13.74
1.57 −0.28 −7.34
−14.17
1.70 −0.32 −7.12
−15.75
2.11 −0.44 −6.57
−18.13
2.82 −0.69 −4.68
−18.22
2.78 −0.75 −3.76
−20.31
3.43 −0.90 −2.70
−22.05
4.00 −1.04 −0.66
−24.04
4.62 −1.16
2.07
−28.18
5.75 −1.15
7.49
−37.31
8.13
0.83
23.85
−50.79
10.74
11.35
54.30
−69.58
11.93
46.46 108.04
−6.07
0.94 −0.68
0.48
−2.66
0.26 −0.13 −1.17
−1.14
0.07 −0.01 −0.63
−0.24
0.00 −0.03 −0.23

Eexch−ind
1.71
2.00
2.97
5.01
5.67
7.38
9.32
12.09
17.91
33.99
59.76
87.84
1.99
0.26
0.04
0.00

SCS−MP2
MP2
Eint
Eint
−11.69
−8.22
−11.60
−8.05
−11.16
−7.39
−9.81
−5.65
−9.35
−5.09
−8.11
−3.63
−6.35
−1.61
−3.90
1.14
1.63
7.20
18.64
25.36
52.39
60.71
113.82
124.36
−0.15
0.93
−1.38
−0.85
−0.95
−0.70
−0.29
−0.23

Table 3: Components of the DFT-SAPT interaction energy for the PH orientation. The total
DFT-SAPT energy, as well as MP2 and SCS-MP2 interaction energies are also given. Energy
values in millihartree. Distances in Å.
r
0.00
0.10
0.20
0.25
0.30
0.50
0.75
0.90
1.00
1.10
1.25
1.50

(1)

Eelst
−2.74
−2.80
−2.96
−3.08
−3.24
−4.25
−6.67
−9.16
−11.44
−14.36
−20.41
−36.71

(1)

Eexch
8.06
8.21
8.65
8.98
9.39
12.09
18.59
25.17
31.18
38.87
54.72
97.49

(2)

(2)

Eind
Eexch−ind
−1.91
1.71
−1.97
1.77
−2.12
1.91
−2.22
2.00
−2.34
2.11
−3.27
2.95
−5.57
5.00
−8.14
7.24
−10.58
9.30
−13.90
12.08
−20.91
17.63
−41.81
32.53

(2)

(2)

SAPT
Edisp
Eexch−disp δ EHF Eint
−13.47
1.55 −0.28 −7.08
−13.80
1.59 −0.29 −7.29
−13.92
1.64 −0.31 −7.12
−14.22
1.72 −0.32 −7.15
−14.33
1.75 −0.34 −7.00
−15.70
2.11 −0.44 −6.51
−18.12
2.81 −0.69 −4.65
−20.30
3.46 −0.90 −2.63
−22.20
4.03 −1.05 −0.76
−24.22
4.62 −1.19
1.89
−28.13
5.75 −1.25
7.40
−37.04
8.09
0.25 22.81

2

SCS−MP2
MP2
Eint
Eint
−11.69
−8.22
−11.68
−8.19
−11.63
−8.12
−11.60
−8.05
−11.55
−7.97
−11.15
−7.38
−9.80
−5.63
−8.10
−3.61
−6.36
−1.61
−3.96
1.10
1.37
6.97
17.28
24.06


10.8. Accurate Intermolecular Interaction Energies from a Combination of MP2 and TDDFT Response Theory

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- S22 database of intermolecular complexes
- density fitting
- local Hartree-Fock
- adiabatic local density approximation
Accurate Intermolecular Interaction Energies from a Combination of MP2 and TDDFT Response Theory

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Abstract: A new method is presented that improves the supermolecular second-order Møller-Plesset (MP2) method for dimer systems with strong dispersion interactions while preserving the generally good performance of MP2 for other types of intermolecular interactions, e.g., hydrogen-bonded systems. This is achieved by adding a correction term to the supermolecular MP2 energy that is determined using time-dependent density functional (TDDFT) response theory and that accounts for the error of the dispersion energy contained in the supermolecular MP2 method. It is shown for the S22 database set of noncovalent complexes and some potential energy curves of noncovalent bound aromatic dimers that the approach gives strong improvements over MP2 if compared to coupled-cluster singles, doubles, and perturbative triples (CCSD(T)) reference energies. An efficient computer implementation of the method is presented that is shown to scale only with the fourth power of the system size and thus leads only to a slightly higher computational cost than that of the supermolecular MP2 itself.

1. Introduction

Highly accurate interaction energies of noncovalent bound molecular complexes and clusters are of high interest in the wide community of both computational chemists and experimentalists. However, to achieve the desired, so-called chemical accuracy (∼1 kcal/mol) with present wave-function theory (WFT) computational methods is often a very demanding task. For notoriously known problematic interaction types, such as π−π stacking, highly sophisticated theories such as CCSD(T) have to be applied to achieve such an accuracy. But even with ever improving computer technologies and algorithms (as implemented in various computer programs such as MOLCAS,1 PSQ,2 GAMESS,3 ACES3,4 etc.), an $N^{-7}$ scaling of the CCSD(T) method with the system size allows the applicability of this method to be widened very slowly. According to a recently published series of benchmark calculations of noncovalent complexes,5–8 CCSD(T) interaction energies close to the complete basis set (CBS) limit can nowadays be obtained for systems with about 30−50 second row atoms and hydrogen. Though this was just a dream a few years ago, such complexes are still too small to serve even as reliable models in biochemistry, nanoclusters, etc. To extend the investigated systems size beyond models to a “real-life” dimension is clearly impossible. Approximations of the CCSD(T) method within the strict WFT formalism for the calculation of noncovalent interactions is hardly possible. Following the series of increasing order of perturbation theory, i.e., second (MP2), third (MP3, MP4(SD), MP4(SDQ), CCSD), and fourth (MP4, CCSD(T)), none of these methods lower than fourth order is reliable enough.9 For the problematic types of noncovalent interactions, this series often converges in an oscillatory way, third-order “overcorrecting” errors of the second order, etc. According to this, one could conclude that the proper
from ref 22 seems to alleviate the problem of the overestimation of the dispersion contribution in the problematic complexes. It was found that the TDDFT-based approach is most accurate if an exchange-only potential from the localized Hartree–Fock method combined with an exchange-only adiabatic local density approximation (ALDA) kernel is employed. In both works, results for several test cases, such as rare-gas dimers, hydrogen-bonded (H-bonded) complexes of small diatomic molecules, and DNA base pairs, were presented, strongly validating this approach. Similar to this approach, Tkatchenko et al. recently proposed the so-called MP2+ΔvdW method. The main idea is to improve the long-range interaction MP2 potential by using the series of $\Delta C_n R^{-n}$ ($\Delta C_6, \Delta C_8, \ldots$) being differences between the MP2 and the “accurate” dispersion coefficient for $n = 6, 8, \ldots$; $R$ being the distance between the interacting molecules) in combination with a proper damping function for short distances. This approach was shown also to be quite accurate and can, in contrast to the method presented in this work, also be applied to study intramolecular dispersion effects if the scheme presented in refs 29 and 30 is extended by deriving intermolecular dispersion coefficients from atomic contributions. However, as with corresponding DFT+dispersion methods, it relies on an empirically determined damping function which has to reduce the double counting of correlation effects for short intermonomer distances. Moreover, in the MP2+ΔvdW method, the multipolar expansion of the long-range dispersion energy is restricted to the $C_6$ and $C_8$ terms and will therefore not be accurate for short intermonomer distances.

The main goal of this work is to extend the tests of the new MP2 “coupled” (MP2C) approach from ref 23 to the systematic S22 database of noncovalent complexes of Hobza et al. as well as to several challenging noncovalent complexes, such as the benzene dimer in several conformations, the H-bonded and stacked uracil dimer, and the methyl-adene–methyl-thymine dimer (mAmT), for which highly accurate CCSD(T) benchmark interaction energies were published. Because the balanced performance, not only of the equilibrium geometries but over a wide area of the potential energy surface (PES), is important, we selected a few cuts through the PES, i.e., potential energy curves (PEC), of the benzene dimer and nitrogen-substituted heterocyclic derivatives of the benzene dimer as well. Finally, we will also present an efficient implementation of the correction scheme, due to which the overall MP2C method is computationally by 1 order of magnitude less demanding than the supermolecular MP2 itself.

2. Method

The supermolecular MP2 interaction energy can be obtained from the energy difference:

$$E_{int}^{MP2} = E_{AB}^{MP2} - E_A^{MP2} - E_B^{MP2}$$

(1)
elimination of this error can however be achieved by using the Boys–Bernardi counterpoise correction in which all individual energy calculations are done using the same (dimer centered) basis set.

Using intermolecular perturbation theory, it was observed a while ago that the supermolecular MP2 interaction energy of eq 1 contains certain correlation terms that are of second order in the intermolecular interaction, namely the uncoupled Hartree–Fock (UCHF) dispersion energy, the corresponding Hartree–Fock exchange Dispersion energy, and a deformation-correlation term. The exchange-dispersion contribution stems from exchange interactions between the monomers when the monomer distance decreases and vanishes for larger distances while the deformation correlation term includes exchange-penetration, induction, and charge-transfer interactions. The uncoupled Hartree–Fock dispersion energy can exactly be written in terms of the monomer Hartree–Fock orbital and orbital energies:

$$E_{\text{disp}}^{(2)}(\text{UCHF}) = -4 \sum_{iajb} \left( \left( A^a B^b \right) \left( A^a B^b \right) \right)^2$$

where A, B label monomer A or B, indices i, j denote occupied orbitals, a, b denote unoccupied orbitals, \((a|b)\) is a two-electron repulsion integral in chemist’s notation and \(\epsilon_i\) is the orbital energy of orbital i. Note that closed-shell formalism will be used throughout. Using the Casimir–Polder integral transform, it can easily be seen that eq 2 can be rewritten as:

$$E_{\text{disp}}^{(2)}(\text{UCHF}) = -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \chi_0^A(r_1, r_2, \omega) \chi_0^B(r_3, r_4, \omega) \frac{1}{r_{12} r_{34}}$$

where the \(\omega\)-integral runs over imaginary frequencies \(\omega\) and \(\chi_0^A\) and \(\chi_0^B\) are the uncoupled Hartree–Fock response functions of monomers A and B given by:

$$\chi_0^A(r_1, r_2, \omega) = 4 \sum_{ia} \frac{\epsilon_{ia}}{\epsilon_{ia}^2 + \omega^2} \phi_{ir_1}^A(\mathbf{r}) \phi_{ir_2}^A(\mathbf{r})$$

with the occupied-virtual orbital products \(\phi_{ir_1}^A(\mathbf{r}) = \phi_r(\mathbf{r}) \phi_r(\mathbf{r})\) and \(\epsilon_{ia} = \epsilon_a - \epsilon_i\). It is well-known that the dispersion energy on the UCHF level (eq 2) often poorly describes the dispersion energy, e.g., in case of stacked \(\pi-\pi\) interactions the uncoupled HF dispersion energy can overestimate the dispersion energy by 15% and more. Because of this, in refs 22 and 23 a correction was introduced to the supermolecular MP2 interaction energy that replaces the implicitly included UCHF dispersion contribution with the coupled dispersion energy on the time-dependent Hartree–Fock (TDHF) or time-dependent density-functional (TDDFT) level. Using coupled TDDFT dispersion energies, the corrected MP2 interaction energies are thus obtained with:

$$E_{\text{int}}^{\text{MP2C}} = E_{\text{int}}^{\text{MP2}} - E_{\text{disp}}^{\text{UCHF}} + E_{\text{disp}}^{\text{TDDFT}}$$

with the acronym MP2C denoting MP2 ‘coupled’. The decomposition of the supermolecular MP2 energy into the uncoupled HF dispersion energy and a remainder term is based on an explicit decomposition of the total system into two subsystems. Because of this, the approach described in this work is not capable to improve the MP2 method also for intramolecular dispersion effects. The dispersion energies from the TDDFT method can be obtained from:

$$E_{\text{disp}}^{(2)}(\text{TDDFT}) = -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \chi_{\text{coupl}}^A(r_1, r_3, \omega) \chi_{\text{coupl}}^B(r_2, r_4, \omega) \frac{1}{r_{12} r_{34}}$$

where \(\chi_{\text{coupl}}^A, \chi_{\text{coupl}}^B\) denote the coupled response functions of monomers A and B which can be obtained from the Dyson-type equation:

$$\chi_{\text{coupl}}(r_1, r_2, \omega) = \chi_0(r_1, r_2, \omega) + \int d\mathbf{r}_3 d\mathbf{r}_4 \chi_0(r_3, r_4, \omega) W(r_3, r_4, \omega) \chi_{\text{coupl}}(r_3, r_4, \omega)$$

with W denoting the interelectronic interaction operator comprising Coulomb, exchange, and correlation effects:

$$W(r_1, r_2, \omega) = \frac{1}{r_{12}} + f_{\text{xc}}(r_1, r_2, \omega)$$

where \(1/r_{12}\) is the Coulomb-operator and \(f_{\text{xc}}\) is the exchange-correlation (xc) kernel that in general is nonlocal and frequency-dependent. In the framework of TDDFT the xc-kernel almost always is approximated by the adiabatic local density approximation (ALDA) kernel:

$$f_{\text{xc}}(r_1, r_2, \omega) = f_{\text{xc}}^{\text{ALDA}}(r_1) \delta(r_1 - r_2)$$

that is the frequency-independent second derivative of the LDA xc-functional. Note that in order to obtain the coupled response functions via eq 7 an iterative procedure has to be used, as \(\chi_{\text{coupl}}\) appears on both sides of the equation.

It has to be noted here that the MP2C approach (eq 5) does not account for also correcting the corresponding exchange-dispersion energy term \(E_{\text{exch-disp}}^{(2)}\) that is also described on an uncoupled Hartree–Fock level only in the supermolecular MP2 method. The calculation of \(E_{\text{exch-disp}}^{(2)}\) is much more computationally demanding than the calculation of the dispersion energy and would therefore lead to a much more expensive method if explicitly corrected in addition. However, the exchange-dispersion energy is generally much smaller than the dispersion energy itself and decreases exponentially for larger intermonomer distances. It has been found that in the intermediate distance range the ratio between coupled and uncoupled exchange-dispersion energies is about the same as with the corresponding dispersion energies. Because, in contrast to the dispersion energy, the \(E_{\text{exch-disp}}^{(2)}\) contribution is always positive, it is found that in most cases the uncoupled exchange-dispersion energy overestimates the coupled one and leads to slightly higher total intermolecular interaction energies. This may be the reason why it has been found that the correction scheme of eq 5 works best if the TDDFT dispersion energy is calculated with an exchange-only approach and not by using more accurate exchange-correlation (xc) potentials and kernels for the calculation of the coupled response functions of eq 7.23 The
10. Intermolecular interactions
Combination of MP2 and TDDFT Response Theory

TDDFT dispersion energies on the exchange-only level usually are only slightly less negative than the uncoupled HF dispersion energies, while the corresponding dispersion energies from more accurate xc potentials deviate more from the uncoupled HF dispersion energies; see ref 23. Thus the error from the coupled exchange-only approximation in the dispersion energy is reduced by accounting for the exchange-dispersion contribution on an uncoupled Hartree–Fock level.

In the following, a density-fitting implementation for the calculation of uncoupled and coupled dispersion energies will be described that scales only with \( N^3 \), if local xc-kernels are used, and that therefore can be used for relatively large molecular systems. We start by transforming the uncoupled response function of eq 4 in a local auxiliary basis set \( g_P \):

\[
(\chi_0)_{PQ} = \sum_i (P|\eta|ia)(\lambda_{ia}(\eta)|Q) \quad (10)
\]

where \( \lambda_{ia} = 4\epsilon_{ia}(\epsilon_{ia} + \alpha^2) \) and \( (P|\eta|ia) \) is a three-index integral over an auxiliary basis function \( g_P \) (indices \( P, Q, R, \ldots \) are labeling auxiliary basis functions) and the occupied-virtual orbital product \( \phi_{ia} \). The operator \( \eta \) conventionally is chosen as the Coulomb-operator: \( \eta = 1/r_{12} \). The idea is now that the number of auxiliary basis functions \( N_{aux} \) that are used to span the occupied-virtual space is much smaller than the product of occupied times virtual AO functions \( N_{aux} \times N_{virt} \). As the number of auxiliary functions only increases linearly with the system size, it can be shown that the computation of the matrix \( \chi_0 \) scales only as \( N^4 \). Using eq 10, the uncoupled dispersion energy of eq 3 can be written as:

\[
E_{\text{disp}}^{\text{TDHF}} = -\frac{1}{2\pi} \int_0^{\infty} \text{d}Q (S^{-1}_{\text{coup}} J S^{-1}_{\text{coup}} R S^{-1}_{\text{coup}})\J
\]

(11)

where \( S_{PQ} = (P|\eta|Q) \) is the metric matrix in the auxiliary basis set and \( J_{PQ} = (P|1/12|Q) \) is a two-indexed Coulomb matrix in the auxiliary basis. It can readily be seen that the computation of the dispersion energy using eq 11 scales only with \( N^3 \).

In order to obtain the coupled response functions in the auxiliary basis set, the Dyson eq 7 is expanded in this basis and one obtains:

\[
\chi_{\text{coup}} = \chi_0 + \chi_0 W \chi_{\text{coup}} 
\]

(12)

where \( \chi_0 \) is defined in eq 10 and

\[
W_{PQ} = \left( P \frac{1}{r_{12}} | Q \right) + (P|f_{xc}|Q)
\]

(13)

is the interaction operator in the auxiliary basis set. The solution to eq 12 can easily be calculated:

\[
\chi_{\text{coup}} = \chi_0 S^{-1} W (S - \chi_0 S^{-1} W)^{-1} \chi_0 
\]

(14)

requiring only an inversion of a matrix of the dimension \( N_{aux} \). The dispersion energy can then be obtained analogous to eq 11 by:

\[
E_{\text{disp}} = \frac{1}{2\pi} \int_0^{\infty} \text{d}Q (S^{-1}_{\text{coup}} J S^{-1}_{\text{coup}} R S^{-1}_{\text{coup}})\J
\]

(15)

It has been found that the computation of the two-indexed xc-kernel integrals \( (P|\eta|Q) \) turns out to be the computational bottleneck in the calculation of the dispersion energy. As this contribution usually is determined using numerical quadrature, the total cost of its computation is \( N_{grid} \times N_{aux}^2 \) where \( N_{grid} \) is the number of grid points. Though the scaling is only of the order \( N^3 \), the prefactor is rather high because \( N_{grid} \) usually has values of \( 10^2 \) to \( 10^4 \) for larger molecular systems. Therefore, here an alternative way to compute the xc-kernel integrals is presented that reduces the computational cost of numerical quadratures by introducing a gridfree-based algorithm identical to gridfree DFT methods introduced by Almlof and others.37–39 we start by determining the matrix \( (P|\eta|Q) \) where \( \eta \) is the electron density and \( P, Q \) are auxiliary basis functions by:

\[
M_{PQ} = (P|\eta|Q) = (P|\eta|Q) |S^{-1} |_{obs} (S|\eta|\mu\nu) \gamma_{\mu\nu} 
\]

(16)

with \( (P|Q) \) being a three-index overlap integral over three auxiliary functions, \( S^{-1} \) is the inverse of the metric, \( (S|\eta|\mu\nu) \) is a three-index integral over one auxiliary function and two atomic-orbital (AO) basis functions, and \( \gamma_{\mu\nu} \) is the density-matrix in the AO basis. The matrix \( M \) is then transformed into a new matrix \( \tilde{M} \) using an orthonormal basis set:

\[
\tilde{M}[\rho] = V^T M[\rho] V
\]

(17)

with \( V^T SV = 1 \) (note that here \( S_{PQ} = (P|\eta|Q) \)) and diagonalization of \( \tilde{M} \) gives \( \tilde{M} = U \Lambda U^T \) where \( U \) contains the eigenvectors and \( \Lambda \) is a diagonal matrix containing the eigenvalues of \( \tilde{M} \). One can then write any matrix \( (P|\eta|Q) \) of the orthogonal auxiliary basis and functions \( f(\rho) \) as follows:

\[
\tilde{M}[f(\rho)] = U[f(\Lambda)] U^T 
\]

(18)

where the matrix \( f(\Lambda) \) is a diagonal matrix containing the function values \( f(\Lambda_i) \) for each eigenvalue \( \Lambda_i \) in its diagonal. In case of \( f = f_{\text{ALDA}} \) (exchange-only ALDA kernel) the function \( f \) is given by \( f_{\text{ALDA}}(\rho) = -C_1 \rho^{-2/3} \) and \( C_1 \) is the Slater–Dirac constant. Finally the matrix \( \tilde{M}[f(\rho)] \) has to be backtransformed to the original nonorthogonal auxiliary basis set using:

\[
M[f(\rho)] = SVU[f(\Lambda)] U^T V^T S 
\]

(19)

It can be seen that the computational cost of the gridfree-based algorithm is only \( N_{aux}^3 \) and \( N_{aux} \times N_{aux}^2 (N_{aux} \text{ number of AO basis functions}) \) with both \( N_{aux} \ll N_{grid} \) and \( N_{aux} \ll N_{grid} \).

3. Computational Details

Geometries of complexes from the S22 database

\(^{31}\) as well as the geometries of all conformers of the benzene dimer

\(^{5}\) ("TT", "T", "PD", and "S"), the uracil dimer

\(^{5}\) ("HB" and "S"), and the stacked methyl-adene···methyl-thymine dimer

\(^{5}\) ("mAmT") were taken from respective original references.

\(^{31}\) Geometries of complexes from the S22 database

\(^{5}\) as well as the geometries of all conformers of the benzene dimer

\(^{5}\) ("TT", "T", "PD", and "S"), the uracil dimer

\(^{5}\) ("HB" and "S"), and the stacked methyl-adene···methyl-thymine dimer

\(^{5}\) ("mAmT") were taken from respective original references.
PES studies were based on geometries taken from the work of Grimme et al. [40] ("PD-to-IP" and "T-to-S") and on geometries taken from the work of Wang and Hobza, [41] with modified intermonomer distances as explained in detail in section 4.3.

All MP2, MP2C, and CCSD(T) calculations were done in the frozen-core approximation and using the (aug-cc-pVZ) basis sets (aXZ) of Dunning and co-workers. [42] MP2 and MP2C results were obtained with MOLPRO [43] using corresponding JKfit density-fitting basis sets of Weigend [44] for the Hartree–Fock and Localized Hartree–Fock calculations and the MP2fit basis sets from Weigend et al. [45] for the MP2 and TDDFT calculations. For the LHF calculations, the computational-efficient scheme described in ref 46 was used.

CCSD(T) calculations were carried out with the MOLCAS 7.1 package using a Cholesky decomposition of two-electron integrals with a threshold of 10−6 Hartree on both SCF and the CCSD(T) levels. This calculation setup was previously validated to be in agreement with the exact two-electron integral-calculations beyond 0.01 kcal/mol in interaction energies.

4. Results and Discussion

4.1. S22 Test Set. Tables 1–3 show results obtained for the S22 data set in two different ways. In Table 1 total MP2 and MP2C interaction energies with the respective aTZ—ωQZ extrapolations according to Helgaker et al. [47] are presented along with the estimated CCSD(T)/CBS reference values from ref 31. In Table 2 the total MP2 interaction energies are displayed along with the "AMP2C" and "ΔCCSD(T)" energies, defined as ΔX = X-MP2, where X stands for MP2C or CCSD(T). The last table on the S22 results, Table 3, shows a statistical evaluation of errors of estimated MP2/CBS and MP2C/CBS results with respect to the estimated CCSD(T)/CBS for each type of interactions separately as well as for the whole test set.

Let us first analyze the performance of the MP2C method on total interaction energies shown in Table 1. MP2 and MP2C values obtained in the series of aXZ (X = D, T, and Q) basis sets are presented to demonstrate the similar rate of convergence of these methods toward the CBS. Two different numbers appear in the CBS column for MP2, one being obtained by us from the extrapolation from aTZ and aQZ basis sets, another one in parentheses from the original S22 paper. [31] These numbers differ slightly, typically a few hundreds of kcal/mol, at most by 0.1 kcal/mol for the stacked adenine···thymine complex, which is because mostly un-augmented, but of one order of cardinality higher, cc-pVXZ basis sets were used. Another, but less important, deviation could also arise from using different density-fitting basis sets. The performance of MP2C for H-bonded complexes is excellent, just like the performance of uncorrected MP2 itself, with an average error of ~0.2 kcal/mol. The only exception is the 2-pyridoxine-2-amino pyridine, for which the error of MP2 and MP2C is 0.66 and 0.58 kcal/mol, respectively. The performance of MP2 and MP2C is, however, dramatically different for dispersion-dominated complexes, as expected. Here the maximum error of MP2C is obtained for the adenine···thymine stacked complex, being ~0.73 kcal/mol. Note that the actual error is probably by ~0.1 kcal/mol less negative, due to the inconsistency with the MP2/CBS value.

### Table 1. Total MP2, MP2C, and CCSD(T) Interaction Energies (in kcal/mol) for the S22 Complexes. MP2/"CBS S22" and CCSD(T)/CBS Values Were Taken from Ref 31

<table>
<thead>
<tr>
<th>Structure</th>
<th>MP2</th>
<th>MP2C</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH3)2</td>
<td>aDZ</td>
<td>aTZ</td>
<td>aQZ</td>
</tr>
<tr>
<td>(H2O)2</td>
<td>-2.68</td>
<td>-2.99</td>
<td>-3.09</td>
</tr>
<tr>
<td>(2-PO-2-AP)</td>
<td>-15.55</td>
<td>-16.64</td>
<td>-17.06</td>
</tr>
<tr>
<td>(CH3)2</td>
<td>-0.39</td>
<td>-0.46</td>
<td>-0.48</td>
</tr>
<tr>
<td>(ethene)2</td>
<td>-1.17</td>
<td>-1.46</td>
<td>-1.53</td>
</tr>
<tr>
<td>benzene···CH4</td>
<td>-1.47</td>
<td>-1.71</td>
<td>-1.77</td>
</tr>
<tr>
<td>(benzene)2·PD</td>
<td>-4.25</td>
<td>-4.70</td>
<td>-4.85</td>
</tr>
<tr>
<td>(pyrazine)2</td>
<td>-6.00</td>
<td>-6.56</td>
<td>-6.76</td>
</tr>
<tr>
<td>indole···benzene S</td>
<td>-7.14</td>
<td>-7.74</td>
<td>-7.94</td>
</tr>
<tr>
<td>ethene···ethene</td>
<td>-1.39</td>
<td>-1.58</td>
<td>-1.63</td>
</tr>
<tr>
<td>benzene···NH2</td>
<td>-2.21</td>
<td>-2.52</td>
<td>-2.60</td>
</tr>
<tr>
<td>benzene···HCN</td>
<td>-4.38</td>
<td>-4.92</td>
<td>-5.06</td>
</tr>
<tr>
<td>benzene···T</td>
<td>-3.10</td>
<td>-3.46</td>
<td>-3.56</td>
</tr>
<tr>
<td>indole···benzene T</td>
<td>-6.10</td>
<td>-6.71</td>
<td>-6.86</td>
</tr>
<tr>
<td>(phenol)2</td>
<td>-6.79</td>
<td>-7.36</td>
<td>-7.59</td>
</tr>
</tbody>
</table>

a aXZ stands for Dunning’s [46] aug-cc-pVXZ basis sets, X = D, T, Q. MP2/CBS and MP2C/CBS values correspond to Helgaker’s [47] extrapolations from the aTZ and aQZ basis sets. b HB = hydrogen-bonded. c 2-PO-2-AP = 2-pyridoxine-2-amino pyridine. d A···T = adenine···thymine. e In ref 31 for A···T·H and indole···benzene S complexes, −16.37 and −5.22 kcal/mol estimated CCSD(T)/CBS results were calculated as MP2/CBS + ΔCCSD(T)/dz. Because the ΔCCSD(T)/dz values, 0.21 and 2.90 kcal/mol, are significantly underestimated for these systems, more accurate ΔCCSD(T)/aDZ values, of 0.08 and 3.46 kcal/mol, are used instead. f PD = parallel displaced. g S = stacked. h T = T-shaped ~16.37.

10. Intermolecular interactions
The second largest deviation with respect to the S22 CCSD(T)/CBS was found for the phenol dimer, with only 0.25 kcal/mol on average. These large numbers might be a bit misleading, because the ΔMP2C correction changes in absolute values only by −0.04 kcal/mol on average.

### Table 2. Total MP2 and ΔMP2C and ΔCCSD(T) Corrections to the MP2 Interaction Energies (in kcal/mol) for the S22 Complexes

<table>
<thead>
<tr>
<th>Structure</th>
<th>MP2</th>
<th>ΔMP2C</th>
<th>ΔCCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aDZ</td>
<td>aTZ</td>
<td>aQZ</td>
</tr>
<tr>
<td>(NH₄)₂</td>
<td>−2.68</td>
<td>−2.99</td>
<td>−3.09</td>
</tr>
<tr>
<td>(H₂O)₂</td>
<td>−4.37</td>
<td>−4.69</td>
<td>−4.86</td>
</tr>
<tr>
<td>(formic acid)₂</td>
<td>−15.99</td>
<td>−17.55</td>
<td>−18.14</td>
</tr>
<tr>
<td>(formamide)₂</td>
<td>−13.95</td>
<td>−15.03</td>
<td>−15.50</td>
</tr>
<tr>
<td>(uracil)₂ HB³</td>
<td>−18.41</td>
<td>−19.60</td>
<td>−20.07</td>
</tr>
<tr>
<td>2-PO-2-AP²</td>
<td>−15.55</td>
<td>−16.64</td>
<td>−17.06</td>
</tr>
<tr>
<td>A⋯T* HB</td>
<td>−14.70</td>
<td>−15.80</td>
<td>−16.23</td>
</tr>
<tr>
<td>(CH₄)₂</td>
<td>−0.39</td>
<td>−0.46</td>
<td>−0.48</td>
</tr>
<tr>
<td>(ethene)₂</td>
<td>−1.17</td>
<td>−1.46</td>
<td>−1.53</td>
</tr>
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<td>−1.77</td>
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<tr>
<td>(benzene)₂ PD⁴</td>
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<td>(pyrazine)₂</td>
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<td>indole⋯benzene S</td>
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<tr>
<td>A⋯T S</td>
<td>−13.24</td>
<td>−14.26</td>
<td>−14.59</td>
</tr>
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<td>ethene⋯Ethene</td>
<td>−1.39</td>
<td>−1.58</td>
<td>−1.63</td>
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<tr>
<td>benzene⋯H₂O</td>
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<td>−3.46</td>
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<td>benzene⋯HCN</td>
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<td>−4.92</td>
<td>−5.06</td>
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<td>−3.46</td>
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<tr>
<td>indole⋯benzene T</td>
<td>−6.10</td>
<td>−6.71</td>
<td>−6.86</td>
</tr>
<tr>
<td>(phenol)₂</td>
<td>−6.79</td>
<td>−7.36</td>
<td>−7.59</td>
</tr>
</tbody>
</table>

*ΔCCSD(T)/S22 values were taken from the ref 31. * Basis sets used in ref 31 for calculation of ΔCCSD(T), i.e., (a)XZ = (aug-)cc-pVXZ; tz-fd = cc-pVXZ with less diffuse d- and all f-functions removed. * HB = hydrogen-bonded. ² 2-PO-2-AP = 2-pyridoxine-2-aminopyridine. ³ A⋯T* = adenine⋯thymine. ⁴ PD = parallel displaced. ⁵ S = stacked. ⁶ T = T-shaped.

### Table 3. Root Mean Squared Errors (RMS), Mean Absolute Deviations (MAD), Mean Signed Deviations (MSD), and Maximum Absolute Errors (MAX) (in kcal/mol) to the Estimated CCSD(T) Interaction Energies of the S22 Complexes from Table 1

<table>
<thead>
<tr>
<th>H-bonded</th>
<th>dispersion</th>
<th>mixed</th>
<th>all</th>
</tr>
</thead>
<tbody>
<tr>
<td>rms</td>
<td>0.26/0.25</td>
<td>1.86/0.34</td>
<td>0.71/0.17</td>
</tr>
<tr>
<td>MAD</td>
<td>0.16/0.18</td>
<td>1.48/0.24</td>
<td>0.61/0.15</td>
</tr>
<tr>
<td>MSD</td>
<td>0.08/0.17</td>
<td>1.47/−0.16</td>
<td>0.61/0.15</td>
</tr>
<tr>
<td>MAX</td>
<td>0.66/0.58</td>
<td>2.87/0.73</td>
<td>1.24/0.25</td>
</tr>
</tbody>
</table>

* MP2 values are the first and the MP2C errors are the second number in each column.

10. Intermolecular interactions

Combination of MP2 and TDDFT Response Theory

Trends in the basis set convergence of the ΔMP2C term can be better observed for the dispersion-dominated complexes, because of much larger absolute values of the interaction energies, especially for the \( \pi-\pi \) stacked complexes. First of all, in all \( \pi-\pi \) stacked complexes investigated by us\(^5–8\) or other authors (for instance see ref 49), the \( \Delta \text{CCSD(T)} \) (thus \( \Delta \text{MP2C} \) as well) values are repulsive. What is different is that the \( \Delta \text{CCSD(T)} \), unlike the \( \Delta \text{MP2C} \), converges with the basis set from below, i.e., the repulsion is increasing with the basis set size. Surprisingly (see, for instance, results for the stacked uracil dimer in Table 2), the \( \Delta \text{MP2C} \) correction decreases when going from the aDZ to the aQZ basis set. This means that for these kinds of complexes the total MP2C interaction energy (in attractive equilibrium complex geometries) is increasing with the basis set size, unlike the total CCSD(T) interaction energy, which is decreasing. Because we do not have systematic CCSD(T) results for the whole S22 set, few selected complexes, shown in Table 4, will be analyzed separately in section 4.2. The \( \Delta \text{MP2C} \) values for dispersion-dominated complexes converge rather fast, both in percentile and absolute scale. The average change of \( \Delta \text{MP2C} \) for the dispersion-bound complexes (methane and ethene dimers, benzene•••methyl-thymine) from the aDZ to the aTZ basis set is \(-0.03 \text{ kcal/mol (}\sim15\%)\), while from the aTZ to the aQZ basis set it is only \(-0.01 \text{ kcal/mol (}\sim13\%)\). For the stacked complexes (benzene, pyrazine, and uracil dimers and adenine•••thymine complex), the average change of the \( \Delta \text{MP2C} \) from aDZ to aTZ basis set is only \(0.08 \text{ kcal/mol (}\sim3\%)\), while from aTZ to aQZ it is even less, \(0.05 \text{ kcal/mol (}\sim2\%)\). This is similar to the rate of convergence of the \( \Delta \text{CCSD(T)} \) term, as discussed further. The largest error from the dispersion dominated complexes as well as for the whole S22 set is obtained for the adenine•••thymine stacked complex, estimated to be about 0.6 kcal/mol. As in case of 2-pyridoxine-2-aminopyridine, we have no clear explanation where this discrepancy stems from. We can only hypothesize that here maybe contributions to the intermolecular interaction other than the dispersion energy are approximated poorly on the intra- and/or intermolecular MP2 level. The convergence of \( \Delta \text{MP2C} \) for the “mixed” complexes is also monotonous and “from above” (the repulsion due to the corrected dispersion energy decreases with the basis set size). Changes of \( \Delta \text{MP2C} \) from aDZ to aTZ are on average 0.05 kcal/mol (\sim9\%), while from the aTZ to aQZ basis sets, the average change decreases to only 0.02 kcal/mol (\sim4\%).

A statistical evaluation of errors via rms (root-mean-squared deviation), MAD (mean absolute deviation), MSD (mean signed deviation), and MAX (maximum absolute error) is summarized in Table 3. It is found that errors similar to those of the SCS(M1)-MP2\(^{14}\) or the MP2.5\(^8\) are obtained. However, both of these two methods contain empirical parameters, and furthermore the spin energy component scaling parameters utilized in the SCS(M1)-MP2 method were optimized exactly for the S22 data set. The performance of the first of these methods on complexes outside its training set is clearly deteriorating, as shown in the footnote of Table 4. Results for several systems from the S22 can also be compared with those used for the testing of the MP2+\( \Delta \text{vdW} \) method in ref 29. For water and ammonia H-bonded dimers errors of the best and the worst performing damping functions are \(0.09–0.21 \text{ kcal/mol and }0.09–0.23 \text{ kcal/mol, respectively.} \) For “mixed” and dispersion bound complexes such as “T”-shaped benzene dimer and parallel-displaced (PD) conformations, errors of \(0.09–0.35 \text{ kcal/mol and }0.05–0.60 \text{ kcal/mol were obtained.} \)

### 4.2. Other Benchmarks

The growing number of highly accurate, systematically calculated CCSD(T)/CBS benchmarks for medium-sized (according to the applicability of the coupled-cluster theory) noncovalent complexes allows us to assess the accuracy of the MP2 approach even more critically. Table 4 shows the comparison of MP2C with the CCSD(T)/CBS results gathered from a few publications.\(^5,7,8\) The first four lines show the performance of the MP2C method on various conformers of the benzene dimer. The rates of convergence of the \( \Delta \text{MP2C} \) and \( \Delta \text{CCSD(T)} \) terms are very similar, values being practically converged toward the CBS already in the aTZ basis set. A further increase of the basis set size amounts to changes of only 0.01–0.03 kcal/mol. Comparing the MP2C and the CCSD(T) values in the CBS limit, an almost uniform overestimation of 0.15–0.20 kcal/mol by the MP2C method is observed. When \( \Delta \text{MP2C} \) and \( \Delta \text{CCSD(T)} \) values are compared, for instance, in the aQZ basis set, a similar underestimation of the \( \Delta \text{CCSD(T)} \) by \(0.09–0.17 \text{ kcal/mol is found.} \) What is, however, of key importance is that the CCSD(T)/CBS relative stability of different structures is well reproduced by the MP2C method. PD and T, almost isoeconomic structures according to the

| Table 4. Total MP2C and CCSD(T) Interaction Energies and Respective \( \Delta \text{MP2C} \) and \( \Delta \text{CCSD(T)} \) Energy Corrections (in kcal/mol) for a Few Selected Benchmark Complexes |
|---|---|---|---|---|---|---|---|---|---|
| Structure | MP2C | CCSD(T) | \( \Delta \text{MP2C} \) | \( \Delta \text{CCSD(T)} \) |
| | aDZ | aTZ | aQZ | CBS | aDZ | aTZ | aQZ | CBS | aDZ | aTZ | aQZ | CBS |
| B\(_2\) T | \(-2.53\) | \(-2.81\) | \(-2.90\) | \(-2.97\) | \(-2.44\) | \(-2.66\) | \(-2.75\) | \(-2.78 \pm 0.03\) | \(0.68\) | \(0.65\) | \(0.63\) | \(0.75\) |
| B\(_2\) S | \(-2.37\) | \(-2.72\) | \(-2.82\) | \(-2.89\) | \(-2.28\) | \(-2.57\) | \(-2.65\) | \(-2.69 \pm 0.02\) | \(0.72\) | \(0.69\) | \(0.68\) | \(0.82\) |
| U\(_2\) mAmT | \(-2.06\) | \(-2.58\) | \(-2.74\) | \(-2.85\) | \(-2.15\) | \(-2.49\) | \(-2.63\) | \(-2.70 \pm 0.04\) | \(2.20\) | \(2.11\) | \(2.09\) | \(2.11\) |
| U\(_2\) S | \(-1.19\) | \(-1.58\) | \(-1.70\) | \(-1.79\) | \(-1.27\) | \(-1.51\) | \(-1.61\) | \(-1.64 \pm 0.04\) | \(1.70\) | \(1.61\) | \(1.58\) | \(1.62\) |
| mAmT | \(-8.60\) | \(-9.89\) | \(-9.32\) | \(-9.55\) | \(-8.54\) | \(-9.33\) | \(-9.68\) | \(-9.86 \pm 0.11\) | \(1.71\) | \(1.63\) | \(1.58\) | \(1.26\) |

\(a\) B\(_2\) = benzene dimer, TT = ‘T’-shaped tilted, T = ‘T’-shaped, PD = parallel displaced, S = sandwich. For details on structures, see ref 5. \(b\) U\(_2\) = uracil dimer, HB = hydrogen-bonded, S = stacked. For details on structures, see ref 7. \(c\) mAmT = methyl-adenine•••methyl-thymine. For details on structure, see ref 8. \(d\) \(\Delta \text{SCS(M1)-MP2/cc-pV(DT)Z} \) and \(\Delta \text{SCS(M1)-MP2/cc-pVQZ} \) values are 2.87 and 2.65 kcal/mol, respectively.
CCSD(T)/CBS results, differ only by 0.04 kcal/mol with MP2/CBS. The energetic separation of the TT structure from both PD and T, being ~0.1 kcal/mol on the CCSD(T)/CBS level, is well reproduced on the MP2/CBS level, with values of 0.08–0.12 kcal/mol.

An excellent agreement of the MP2/CBS and the CCSD(T)/CBS within ~0.1 kcal/mol is achieved also for the H-bonded and stacked uracil dimers. For these complexes the CCSD(T)/aQZ results are not available because of the enormous computational requirements. At least for the stacked structure, judged according to the convergence of the ΔCCSD(T) correction in aDZ and aTZ basis sets, the estimated CCSD(T)/CBS value is supposed to be very close to its exact basis set limit. The accuracy of the CCSD(T)/CBS value for the H-bonded dimer is, however, a bit more uncertain.

The last of the complexes in Table 4, the stacked methyladenine···methyl-thymine dimer, was thoroughly investigated in ref 8, motivated by its previously estimated31 large repulsive higher-order correlation contribution to the interaction energy. The difference between ΔCCSD(T) and ΔMP2C is decreasing from ~0.55 kcal/mol in the aDZ to ~0.32 kcal/mol in the aTZ basis set. Just like for the rest of the complexes in Table 4, the same inverse slope of convergence of ΔMP2C compared to ΔCCSD(T), as for the S22 data set, is observed. The total MP2/CBS interaction energy is finally only slightly underestimated by ~0.25 kcal/mol (~2%) compared to the CCSD(T)/CBS value. This is an excellent result, especially taking into consideration that the total MP2C/aTZ calculation of the BSSE corrected interaction energy was done in 12 h on a single Intel Core2 Quad 2.40 GHz processor, while only the (T) part of the coupled-cluster calculation of this complex in the aTZ basis set took almost 7 days on 80 four-core Xeon E5430 2.66 GHz processors.

4.3. PEC for Dimers of Aromatic Systems. Generally applicable methods for calculating noncovalent interactions should deliver accurate results not only for the minima but also over the wide region of the PES. This is a strong requirement for applications, for instance in biology, where the interacting fragments of protein, DNA, etc., often appear in distorted geometries or where a superposition of weak but numerous middle- to long-range interactions occurs. The first three figures show the “dissociation” of the parallel-displaced conformation of the benzene dimer (Figure 1), benzene···pyrimidine (Figure 2), and benzene···1,2,4,5-pentazine (Figure 3) calculated with MP2/CBS (aTZ–aQZ extrapolation) and estimated with CCSD(T)/CBS (MP2 from aTZ–aQZ extrapolation, ΔCCSD(T) calculated in the aDZ basis set). For a more refined view, ΔMP2C and ΔCCSD(T) curves are plotted along the curves of total interaction energies. These systems were selected for known strong π·π interactions41 which increase with the number of nitrogen heteroatoms. The increase of polarity from benzene to 1,2,4,5-pentazine results in a decrease of the optimal vertical displacement of the rings in the complex and consequently an increase of the interaction energy from ~2.32 through ~3.50 to ~5.13 kcal/mol. Starting from the optimized structures of Wang and Hobza41 (the acronyms “B0P”, “B2P”, and “B5P” were used in this publication), the distance between the centers of mass of the stacked rings was sampled by 0.2 Å to cover both repulsive and attractive regions around ~1.2 R₀ (R₀ being the equilibrium distance) in both directions. As can be clearly seen from Figures 1–3, MP2C well reproduces the CCSD(T) curve. Some deviations can be seen, for instance, in the strongly repulsive region for benzene···pyrimidine (more clearly visible on the ΔMP2C and ΔCCSD(T) curves) or as a small constant shift of ~0.2 kcal/mol along the whole PEC for benzene···1,2,4,5-pentazine. Deviations in the repulsive region probably originate from
the intrinsic error of the MP2C method, while the constant shift on the curve for benzene···1,2,4,5-pentazine could be caused by a deficiency of the aDZ basis set used in the calculation of the estimated CCSD(T)/CBS reference.

The last two examples are PECs of the T-shaped benzene dimer conversion to the sandwich (S) structure, Figure 4 and Figure 5, and the parallel displaced (PD) benzene dimer conversion to the in-plane (IP) arrangement, Figure 6 and Figure 7. Geometries for all structures on these PECs were taken from the work of Grimme et al.40 On both Figure 5 and Figure 7, MP2 and MP2C total interaction energies in the aDZ to aQZ basis sets are shown, along with the corresponding $\Delta$MP2C correction. As references, CCSD(T) and $\Delta$CCSD(T) in the aDZ basis set (unlike the estimated CCSD(T)/CBS used in previous figures, i.e., Figure 1–3) are plotted as well. A common feature in Figures 5 and 7 is the trend of convergence of the MP2 and the $\Delta$MP2C energies with an increase of the basis set size. For the total MP2 interaction energy, a convergence toward a stronger stabilization is observed and in the case of MP2C a decrease of the “destabilization” due to a decrescent value of $\Delta$MP2C occurs. As analyzed by Grimme et al.,40 the contribution from the intermolecular interaction of $\pi-\pi$ orbitals is doubled (from 17% to 36% of the MP2/aDZ level) going from the T to the S structure. This can be tracked by more than a doubled rise of the $\Delta$CCSD(T) (and $\Delta$MP2C as well) in Figure 5.

The error of the MP2C is also following this trend, being the largest for the sandwich structure, 0.12 kcal/mol in the aDZ basis set. On the basis of the trends of convergence of the $\Delta$CCSD(T) and $\Delta$MP2C correction terms (see Table 4), this discrepancy has a tendency to further increase upon an improvement of the basis set quality, because they converge in opposite directions. The overall quality of the total MP2C interaction energy is still excellent, with an error compared to the CCSD(T)/aDZ being smaller than 6% along the whole PEC.

The character of interaction is also significantly changing along the PD-to-IP PEC; the PD structure (A) has a strong $\sigma-\pi$ (49%) and $\pi-\pi$ (34%) character,40 while for the IP structure (D) the importance of the intermolecular $\pi-\pi$ interaction decreases only to 9% ($\sigma-\pi$ decreases only slightly to 36%). This change of interaction character can be tracked in Figure 7 by a decrease of the $\Delta$CCSD(T) and $\Delta$MP2C term from 1.84 and 1.87 kcal/mol for PD to almost zero for the IP structure. However, at the same time the total CCSD(T) and MP2C interaction energies decrease by $\sim$2 kcal/mol, because the repulsive $\Delta$CCSD(T) and $\Delta$MP2C terms correct the overestimation of the interaction energy on the MP2 level occurring only for structures with significant overlap of the stacked rings. MP2C/aDZ accurately reproduces the CCSD(T)/aDZ values along the whole PEC within 0.04 kcal/mol, leading to percentile errors of at most 8% (obtained for the IP structure).

5. Conclusions

The recently developed dispersion correction scheme (termed MP2C, i.e., MP2 ‘coupled’, in this work) for the supermolecular MP2 method has been extensively tested for different types of dimer systems containing both strong electrostatic and/or strong dispersion interaction energy contributions. While it is well-known that the supermolecular MP2 method is for some types of noncovalent interactions (such as hydrogen-bonding, etc.) capable of accurately reproducing CCSD(T) interaction energies, it has been shown in this work that the correction used in the MP2C approach does not worsen this performance. In fact it has been found that for the set of seven hydrogen-bonded complexes contained in the S22 benchmark set (see Table 1) the root
mean squared errors to the estimated CCSD(T)/CBS results for MP2 and MP2C are of about the same magnitude and amount to 0.25 kcal/mol.

In contrast to this, a clear difference between the MP2 and MP2C method is observed for the $\pi \pi^* \pi$ stacked complexes where the intermolecular dispersion interactions are dominant. Here the MP2 method does not give reliable estimates of the interaction energy because of large overestimations of the dispersion interaction component contained in the supermolecular MP2 energy. This stems from the fact that the MP2 method accounts for dispersion interactions only on an uncoupled Hartree–Fock level, and this can typically lead to errors of 15% and more in this interaction energy component. In the MP2C method the uncoupled Hartree–Fock dispersion energy contribution is replaced by the coupled dispersion energy calculated using the exchange-only time-dependent density functional theory employing local Hartree–Fock (LHF) orbitals and eigenvalues and the exchange-only adiabatic local density approximation kernel (ALDAx). It has been shown that this approach leads to strong improvements over the MP2 method for the dispersion-dominated and mixed complexes of the S22 dimer set. Root mean square errors of MP2 to the CCSD(T) reference interaction energies are reduced from 1.86 to 0.36 kcal/mol for the dispersion-dominated complexes and from 0.71 to 0.17 kcal/mol for the mixed type complexes. Therefore, in contrast to the supermolecular MP2 method, the MP2C approach yields accurate and balanced estimates of the intermolecular interaction energy for all diverse types of interactions.

While the S22 benchmark data set contains only complexes in their equilibrium geometries, we have extended the testing of the MP2C method on several cuts through the potential energy surface of the benzene dimer and benzene···pyrimidine and benzene···1,2,4,5-pentazine dimers. In all three cases the MP2C curves do not only agree well with the CCSD(T) reference curves in the region of the minimum of the potential, but they also nicely reproduce the CCSD(T) curves for repulsive and stretched dimer distances. Another challenging test presented here are the potential energy curves corresponding to the transition of the benzene dimer from ‘‘T’’-shaped to sandwich arrangement and from the parallel-displaced to the in-plane arrangement. CCSD(T) reference curves are reproduced within ~0.1 kcal/mol accuracy, despite the fact that the character of interaction, especially for the latter one, is changing from strong $\pi \pi^* \pi$ to $\sigma \sigma^* \sigma$ dominated. These examples strongly support the validity of the MP2C approach even for the prediction of wide areas of potential energy surfaces of noncovalent complexes with a good accuracy.

A computer implementation of the correction term used in the MP2C method is presented that scales only as $1/N^4$ with the system size and is therefore 1 order of magnitude lower than that of conventional density-fitting MP2 implementations. As an example, the additional computational cost over the standard supermolecular MP2 in the calculation of one of the largest dimers studied in this work, namely the adenine···thymine base pair, amounts to only ~27% of the total CPU time. Moreover, it was found that the basis set dependence of the $\Delta$MP2C correction is less dependent on the basis set size than the total interaction energy (compare Table 1 and Table 2) and therefore can be, if needed, accurately approximated using smaller basis sets.

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10. Intermolecular interactions

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10.9. Interaction energies of endohedral complexes of the $C_{60}$ fullerene with a rare gas atom

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- endohedral
- symmetry-adapted perturbation theory
- three-body interactions
On the accuracy of DFT-SAPT, MP2, SCS-MP2, MP2C, and DFT + Disp methods for the interaction energies of endohedral complexes of the C$_{60}$ fullerene with a rare gas atom

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Selected points on the potential energy surface for the complexes Rg@C$_{60}$ (Rg = He, Ne, Ar, Kr) are calculated with various theoretical methods, like symmetry-adapted perturbation theory with monomers described by density functional theory (DFT-SAPT), supermolecular Møller–Plesset theory truncated on the second order (MP2), spin-component-scaled MP2 (SCS-MP2), supermolecular density functional theory with empirical dispersion correction (DFT + Disp), and the recently developed MP2C method that improves the MP2 method for long-range electron correlation effects. A stabilization of the endohedral complex is predicted by all methods, but the depth of the potential energy well is overestimated by the DFT + Disp and MP2 approaches. On the other hand, the MP2C model agrees well with DFT-SAPT, which serves as the reference. The performance of SCS-MP2 is mixed: it produces too low interaction energies for the two heavier guests, while its accuracy for He@C$_{60}$ and Ne@C$_{60}$ is similar to that of MP2C. Fitting formulas for the main interaction energy components, i.e. the dispersion and first-order repulsion energies are proposed, which are applicable for both endo- and exohedral cases. For all examined methods density fitting is used to evaluate two-electron repulsion integrals, which is indispensable to allow studies of noncovalent complexes of this size. It has been found that density-fitting auxiliary basis sets cannot be used in a black-box fashion for the calculation of the first-order SAPT electrostatic energy, and that the quality of these basis sets should be always carefully examined in order to avoid an unphysical long-range behavior.

I. Introduction

The endohedral complexes of fullerenes are interesting objects from the theoretical point of view, since the encapsulation of the guest “binds” it to the host in a mechanical way, irrespective of the strength and the sign of interactions. Fullerenes complexes with rare gas atoms are models in the sense that they cannot create a chemical bond with the carbon atoms from the cage, as can many other trapped species. Rg@C$_{60}$ serve therefore as examples of pure noncovalent endohedral complexes. All these complexes have been obtained experimentally, usually under high pressure and temperature conditions and/or by high-energetic collisions of ionized fullerene with a rare gas atom.$^{1-6}$ For the lightest rare gas atom, helium, two atoms inside C$_{60}$ have been observed, although with much lower yield.$^{6}$ The rare gas complexes with C$_{60}$ have also been studied theoretically in e.g. ref. 7–15 by methods like density-functional theory (DFT), second-order Møller–Plesset theory (MP2), or DFT with an empirical dispersion correction (DFT + Disp). However, these methods are not reliable enough for a description of weak noncovalent interactions of nonpolar molecules.

Recently$^{16}$ we investigated selected cuts through the potential energy surface of the endohedral complexes of one or two hydrogen molecules inside the C$_{60}$ fullerene by utilizing the density fitting DFT-SAPT (DF-DFT-SAPT) method$^{17,18}$ as implemented in the molpro suite of codes.$^{19}$ We also compared SAPT interaction energies with various supermolecular approaches, frequently utilized for studying complexes of these sizes. The main conclusion from ref. 16 is that the results obtained with the standard supermolecular (SM) approach to the interaction energy $E_{int}$, i.e.

\[ E_{int} = E_{AB} - (E_A + E_B), \]  

(1)

(where $E_X$ denotes the Born–Oppenheimer energy for a molecule $X$) should always be critically examined when applied to the nonpolar complexes. In particular the MP2 and DFT + Disp$^{20,21}$ methods do not provide accurate values for $E_{int}$. In this work we continue to investigate endohedral complexes of fullerenes by turning to the rare gas atoms guests. Several issues should be clarified by this investigation. First it is interesting to see if the overbinding of the MP2 method, which has been already reported for several stacked $\pi$ complexes$^{22}$ and which we have found for the case of H$_2$@C$_{60}$,$^{16}$ occurs also for the Rg@C$_{60}$ class of noncovalent complexes. Second, since this behavior of MP2
in many instances is corrected by the spin-component-scaled MP2 (SCS-MP2)\textsuperscript{23} we included this method in our check-out list, too. Finally, we examine the MP2C method, developed very recently by one of us\textsuperscript{24,25} which has already shown promising results for smaller noncovalent complexes. Since the C\textsubscript{60} fullerene can be treated as a sphere in some applications (see \textit{e.g.} ref. 26–28), we also propose fitting formulas for two major SAPT components, which can be used for endohedral complexes with a spherical host.

\section{Methods}

A well-established method of calculating the interaction energy of noncovalent complexes is symmetry-adapted perturbation theory (SAPT) developed by Jeziorski \textit{et al.}\textsuperscript{29–32} An important advantage of SAPT in comparison to the SM approach is that the SAPT interaction energy is obtained directly as a sum of physically sound contributions, and is by definition free from the basis-set superposition error (BSSE), while in the SM the interaction energy is calculated as a difference of two similar numbers (eqn (1)), which puts rather severe requirements on the quality of these energies. In practice, the following energy components are calculated for the production-level SAPT

\begin{equation}
E_{\text{int}}^{\text{SAPT}} = E_{\text{elst}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch}}^{(1)} + E_{\text{exch–ind}}^{(2)} + E_{\text{exch–disp}} + \delta E_{\text{HF}},
\end{equation}

where the number in parenthesis refers to the order of the intermolecular interaction operator $V$. The first three components of the r.h.s. of eqn (2) are the electrostatic, induction and dispersion energies, respectively, which are obtained from Rayleigh-Schrödinger perturbation theory applied with the zeroth-order Hamiltonian being a sum of the monomer Hamiltonians and $V$ serving as the perturbation operator. The next three components, \textit{i.e.} the first-order exchange energy, the second-order exchange-induction and exchange-dispersion energies, are the counterparts of the first three terms, resulting from an imposition of the antisymmetry on the approximate dimer wave function. Finally, the $\delta E_{\text{HF}}$ contribution\textsuperscript{33,34} is a small term accounting approximately for the higher than second-order Hartree-Fock (HF) induction and exchange-induction effects, and is calculated as the difference between the SM HF interaction energy and the sum of the electrostatic, induction, first-order exchange, and second-order exchange-induction components obtained at the HF level for monomers (see below). Past investigations of the convergence of the SAPT series with respect to $V$ have shown that this series truncated after the second order usually provides a reliable estimate to the interaction energy of two closed-shell monomers (for open-shell monomers the situation is less favorable, see \textit{e.g.} ref. 35).

Monomers in SAPT should ideally be described by exact (full configuration interaction) wave functions. Since this is, of course, not feasible in the majority of cases, some additional approximations are introduced in SAPT, leading to various SAPT\textit{(method)} approaches, where the \textit{method} in parenthesis denotes the approach utilized to describe intramonomer electron correlation. So far the following methods have been applied for a description of monomers within SAPT: HF, MP, coupled cluster (CC), and DFT. Because of the high scaling behavior of MP and CC theories with the molecular size only HF and DFT can be used for large monomers. From the two remaining methods the SAPT(HF) approach does not account for electron correlation effects inside the monomers, so rather significant errors are expected (and observed) in this case. This leaves SAPT(DFT),\textsuperscript{36} also called DFT-SAPT,\textsuperscript{17} as the only method capable to treat large molecules. Recent investigations on small model complexes with an accurate, but computationally very expensive SAPT(CCSD) model\textsuperscript{37–43} reveal that the energy components of DFT-SAPT and SAPT(CCSD) resemble close to each other. It has also been found that DFT-SAPT agrees well with the CCSD(T) SM calculations for such noncovalent complexes like argon or benzene dimers.\textsuperscript{17,18} Therefore, the DFT-SAPT method with a suitable density functional, like \textit{e.g.} PBE\textsubscript{0},\textsuperscript{44–45} and an additional asymptotic correction of the underlying exchange-correlation potential (see \textit{e.g.} ref. 46–49) (in this work the non-hybrid asymptotically corrected PBE functional is used, termed as PBEac in the following) is a reliable method for the calculation of the intermolecular energy. For this reason, the DFT-SAPT approach is used in this work as a benchmark for other methods under investigation. Among these approaches the first one is the very popular MP2 SM method, where the interaction energy is obtained from eqn (1) by utilizing MP2 energies for the dimer and both monomers. The corresponding spin-component-scaled MP2 (SCS-MP2)\textsuperscript{23} interaction energies can be obtained from the MP2 energies at no cost. It should be noted that some theoretical justification for SCS-MP2 has been recently given by Szabados\textsuperscript{50} and Fink.\textsuperscript{51} SCS-MP2 is not an \textit{ab initio} method in a proper sense, since it involves a rescaling of singlet and triplet components of the MP2 correlation energy using fitted parameters. It has been found in various studies that in many cases SCS-MP2 gives results close to CCSD(T).\textsuperscript{52} Also in our recent study of H\textsubscript{2}@C\textsubscript{60} we found a very favorable agreement between the SCS-MP2 interaction energies and DFT-SAPT. It is therefore interesting to investigate if this trend holds for other endohedral fullerene complexes. The supermolecular DFT method is known to miss the important long-range dispersion contribution, which should be recovered in one way or another in order to obtain sensible results. To this end various \textit{a posteriori} correction schemes were proposed, among which the Grimme DFT + Disp method\textsuperscript{20,21} gained the most popularity.

The last applied method, termed as MP2C (“coupled” supermolecular second-order Möller-Plesset perturbation theory), has been recently developed by one of us.\textsuperscript{24,25} The approach directly accounts for the deficiency of MP2 in describing the intermolecular dispersion contribution on the uncoupled HF level, see ref. 53 and 54. The appropriate correction is done by combining the supermolecular MP2 interaction energy with a correction term determined from second-order intermolecular perturbation theory, see ref. 24 and 25 for more details.
III. Technical details

All calculations have been performed with the development version of the MOLPRO suite of programs. In addition to the DFT-SAPT calculations, supermolecular calculations have been performed with the MP2, SCS-MP2, and with the dispersion-corrected DFT functional utilizing the damped multipole expansion scheme developed by Grimme. As outlined before, the primary goal of the SM calculations was to assess the quality of these methods in comparison to DFT-SAPT. The Boys-Bernardi counterpoise correction was used for all SM calculations to reduce the BSSE.

In DFT-SAPT the asymptotic correction for the exchange–correlation functional has been utilized, as described by Grüning et al. For all monomers we took the experimental ionization potentials from ref. 57, while the HOMO energies have been calculated in the same basis as used in DFT-SAPT. The difference of the ionization energies and the HOMO energies are used in order to shift the bulk exchange–correlation (exc) potential of the underlying xc-functional in order to correct the lacking derivative discontinuity shifts of continuous standard density functionals, see ref. 56. The exchange–correlation functional used in the DFT-SAPT and in SM calculations has been approximated by using the PBE generalized gradient functional. The difference of the ionization energies and the HOMO energies are used in order to shift the bulk exchange–correlation (exc) potential of the underlying xc-functional in order to correct the lacking derivative discontinuity shifts of continuous standard density functionals, see ref. 56. The exchange–correlation functional used in the DFT-SAPT and in SM calculations has been approximated by using the PBE generalized gradient functional.44

The MP2C interaction energies were obtained by combining the MP2 interaction energies with a correction term which has been calculated as the difference between the uncoupled HF with coupled time-dependent density functional theory (TD-DFT) dispersion energies. The latter were obtained by using orbitals and orbital energies determined with the density-fitted localized HF method (LHF) and an exchange-only adiabatic local density approximation exchange–correlation (xc) kernel (xALDA). This choice for the xc-potential and kernel was found to yield highly accurate interaction energies for the S22 data base set containing both hydrogen-bridged and dispersion dominated complexes (see ref. 25 for an explanation to this behavior).

A relation between the DFT-SAPT method and the MP2C method can be established if both methods are viewed as a supermolecular approach which is enhanced using correction terms calculated on the intermolecular perturbation theory level. In particular the DFT-SAPT interaction energy from eqn (2) can be written as:

\[ E_{\text{int}}^{\text{DFT-SAPT}} = E_{\text{int}}^{\text{HF}} + [E_{\text{exc}}^{\text{exc}}(\text{DFT}) - E_{\text{exc}}^{\text{exc}}(\text{HF})] + [E_{\text{disp}}^{\text{disp}}(\text{DFT}) - E_{\text{disp}}^{\text{disp}}(\text{HF})] + [E_{\text{exch-ind}}^{\text{exch-ind}}(\text{DFT}) - E_{\text{exch-ind}}^{\text{exch-ind}}(\text{HF})] + E_{\text{disp}}^{\text{disp}}(\text{DFT}) + E_{\text{exch-disp}}^{\text{exch-disp}}(\text{DFT}) \]

where the first term on the right hand-side is the supermolecular HF interaction energy. Since \( E_{\text{int}}^{\text{HF}} \) does not account for intermolecular correlation effects to \( E_{\text{exc}}^{\text{exc}} \) and \( E_{\text{exch-disp}}^{\text{exch-disp}} \) and \( E_{\text{exch-disp}}^{\text{exch-disp}} \) calculated also on the (TD-)DFT level and which are of second-order in the intermolecular potential but take into account all orders in the intramonomer fluctuation potentials as in the corresponding SAPT(CCSD) method. In comparison to this, the MP2C interaction energy is determined using:

\[ E_{\text{int}}^{\text{MP2C}} = E_{\text{int}}^{\text{MP2}} + [E_{\text{disp}}^{\text{disp}}(\text{DFT}) - E_{\text{disp}}^{\text{disp}}(\text{UCHF})] \]

Since the MP2 interaction energy \( E_{\text{int}}^{\text{MP2}} \) already accounts for intramolecular correlation effects to the electrostatic, induction, and corresponding exchange contributions, these are not corrected in the MP2C method. However, \( E_{\text{int}}^{\text{MP2}} \) does account for the (exchange-)dispersion interaction on the uncoupled, i.e. uncorrelated (for monomers) HF (UCHF) level. Therefore the correction term in square parenthesis on the right hand-side of eqn (4) improves the MP2 interaction energy with a dispersion energy term calculated using TD-DFT including intramonomer correlation. While the terms \( E_{\text{disp}}^{\text{disp}}(\text{DFT}) \) in eqn (3) and (4) are formally identical, in this work they were calculated using different approximations for the xc-potential and xc-kernel, see above. Thus, while DFT-SAPT and MP2C both can be viewed as hybrid methods of a supermolecular method and intermolecular perturbation theory, their interaction energy contributions are calculated quite differently in praxis.

The orbital basis set utilized in this study for carbon is the TZV Karlsruhe basis. Since the preliminary calculations with the def2-TZVP basis set for He yielded a very inaccurate dispersion energy for He\(_{\text{2}}@C_{60}\), which in turn resulted in a much too shallow potential well, the augmented correlation-consistent Dunning basis sets for all rare-gas atoms were used instead. As the TZV basis for carbon contains \( s, p \), and \( d \) functions, we decided to replace the helium TZV basis set with the corresponding augmented correlation-consistent Dunning basis containing the same angular momentum functions as TZVP for helium, i.e. the aug-cc-pVDZ basis. Similarly, the TZVP basis set for neon has been replaced by the corresponding aug-cc-pVTZ basis. However, the TZVP basis sets for argon and krypton also contain only the \( s, p, d \) set, while we feel that in order to obtain at least a semiquantitative description of the dispersion interaction involving these atoms, a basis set of \( spdf \)-quality has to be used. Therefore we selected the aug-cc-pVTZ basis for these two atoms. Although this selection does not provide a near-CBS (complete basis set) accuracy, it is nonetheless sufficient for the comparison of various theoretical methods, which is one of the main goals of this work. In order to estimate the accuracy of the obtained interaction energies we have performed test calculations by varying the basis sets for helium in the center of the fullerene cage. Similarly to the \( H_{\text{2}}@C_{60} \) complex it turned out that the dispersion component is the most basis-set dependent, while other components of the interaction energy given in eqn (2) change by much lesser extent in a better basis set. The best tested basis set (TZVPP for carbon and aug-cc-pV5Z for helium) gives an about 15% lower interaction energy than the basis selected by us for production, while the cost of one DFT-SAPT calculation (without \( \delta E_{\text{HF}} \)) increases by a factor of 2.5 (up to about 4 CPU days on the Opteron cluster) when
going from the aug-cc-pVDZ/TZVP to aug-cc-pV5Z/TZVPP basis sets. It should be noted parenthetically that the poor quality of the def2-TZVP and def2-TZVPP basis sets for rare gas atoms explains the fact why the MP2 and SCS-MP2 interaction energies of Wang et al.13 (see Table 16 of this reference) obtained with the def2-TZVPP basis for both He and C are smaller by 15% than the respective energies from our Table 2 in spite of utilizing a more expensive basis for the carbon atom. Summarizing, one can estimate that the unsaturation of the dispersion energy causes an underestimation of the interaction energy in the cage center by about 15–30%.

The density-fitting method, that has been applied to all two-electron repulsion integrals in this work, requires auxiliary basis sets, each corresponding to a given orbital basis. All doubly-external integrals and all x-type integrals occurring in the second-order DFT-SAPT were computed using the TZVP/MP2FIT65 fitting basis set for carbon, aug-cc-pVDZ/MP2FIT for He and Ne, and aug-cc-pVTZ/MP2FIT for Ar and Kr.66 For Coulomb and exchange integrals in Hartree–Fock and in the DFT-SAPT first-order interaction energy we took the recommended cc-pVTZ/JKFIT66 DF auxiliary basis set for carbon and all rare-gas atoms with the exception of helium. For helium we developed an even-tempered basis set (10x5p2d) with the highest exponents equal to 77,12,1.1, respectively, and the ratio equal to 2.5 by optimizing the weighted sum of the electrostatic energies of He$_2$ for several selected distances.

Usually for the first-order SAPT energies the corresponding JKFIT basis sets are utilized in a "black-box" fashion, while MP2FIT basis sets are used for the second-order energy components. Our preliminary calculations have shown, however, that some of these basis sets are not optimized well enough for the rare-gas atom case. We recommend therefore to perform some security checks of the quality of auxiliary DF basis sets before starting the main calculations. A simple test showing the problem consists in calculating the DF-DFT-SAPT potential energy curve for two helium atoms. If the def2-TZVPP orbital basis67 and the def2-TZVPP/JKFIT68 auxiliary basis for Coulomb and exchange integrals and first-order SAPT energies are employed, nonsense density-fitted electrostatics are predicted. This shows that this auxiliary basis is completely inappropriate for the calculation of the electrostatic energy. In particular, the DF $E^{\text{elst}}_{\text{DF}}$ component decreases much too slowly with the interatomic distance $R$ (approximately as $R^{-1}$), while for two ground-state atoms the electrostatic contribution should be a short-range effect vanishing exponentially with $R$. For instance, at the large interatomic distance of $R = 20$ bohr the DF electrostatic energy dominates the total interaction energy, while for this distance the only remaining contribution should be the second-order dispersion energy (decreasing as $R^{-6}$). For smaller distances (around the van der Waals minimum) DF errors are also unacceptable large, e.g. for $R = 6$ bohr the DF value is almost 4 times higher in absolute value than the correct result. Only for the region of the strong valence repulsion both non-DF and DF electrostatic energies become similar. Interestingly, the augmentation of the Def2-TZVPP/JKFIT basis by only one $s$ gaussian function (with an exponent 0.08) corrects the wrong behavior for all but the largest distances. More precisely, it causes the $R^{-1}$ part of the electrostatic energy to be effectively damped, so that only for the largest distances it again becomes larger than the total interaction energy. Unfortunately, this exponent is not transferable to other complexes containing helium. It should be stressed that for the def2-TZVPP basis set this incorrect behavior (the wrong description of electrostatics) is magnified because of the poor quality of the basis, but the effect is probably present in all density-fitted methods, although for good-quality auxiliary basis sets the erroneous part of electrostatics is damped to such extent that it does not count in the total interaction energy any more. One should however be careful when fitting individual components of the DF-DFT-SAPT energy, as it is often done when producing SAPT potential energy surfaces (see e.g. ref. 69). Since in molpro it is possible to obtain non-DF Coulomb matrices with an arbitrary one-electron density in an integral-direct way by using the matcrop program facility, we were able to calculate both DF and non-DF electrostatic energies for the complexes of the size of C$_60$ with a manageable additional cost (the non-DF $E^{\text{elst}}_{\text{DF}}$ term has been obtained using the methodology described in ref. 70). If the def2-TZVPP orbital and auxiliary basis sets are used for helium, an error of 4% is found for $r = 0$. The error becomes smaller than 1% for the repulsive region, similarly to the He$_2$ case, but for the exohedral complex the DF and non-DF electrostatic terms are completely different and much too large in an absolute value for the DF case (e.g. $-0.11$ and $-0.06$ kJ mol$^{-1}$ for $r = 7$ Å, $-0.06$ and $-0.002$ kJ mol$^{-1}$ for $r = 8$ Å), which leads to the wrong results for total DF-DFT-SAPT interaction energies.

Fortunately, for the more carefully optimized basis sets the errors of the electrostatic components are within 1% for all but the largest distance $r = 9$ Å for the case of He@C$_60$, where the DF-DFT-SAPT value is even of a wrong sign, but luckily in this case the absolute value of electrostatics is small and this error “dissolves” in the much larger values of the dominating dispersion contribution. Note that the same problem with the inappropriate representation of long-range two-electron repulsion integrals has been described by Jung et al.,71 who observed a $R^{-1.25}$ decay in DF calculations for a series of hydrocarbons.

The carbon–carbon bond lengths of 1.458 Å and 1.401 Å have been used72 for the bonds in a pentagon ring and those between pentagon rings which, due to the $I_h$ symmetry, fully determine the C$_{60}$ geometry. The rare gas atom is placed in the line connecting the center of the fullerene and the center of one of the carbon hexagons. Because of the high symmetry of fullerene similar results are expected also for other geometries.

Core orbitals were frozen in all correlated calculations.

IV. Results and discussion

A. Rg@C$_{60}$ interaction energies

The SAPT components of the interaction energies, as well as total energies calculated with various methods are presented in Tables 2–5. It can be observed that all methods yield a
minimum of the interaction energy for the centered structure of \( r = 0 \), the only exception is found for \( \text{He}@C_{60} \) MP2C where a slightly lower interaction energy is found for the distance of \( r = 0.2 \) Å, see Table 2. Among the potential energy curves the one for the \( \text{He}@C_{60} \) complex shows the least increase when the guest is moved towards the fullerene wall and becomes positive at a distance of about 0.9 Å. This corresponds to a volume of about 3.1 Å\(^3\) in which the \( \text{He}@C_{60} \) complex is stable (interestingly, the same size of the systems volumes of 1.8 Å\(^3\) (Ne@C\(_{60}\)), 1.1 Å\(^3\) (Ar@C\(_{60}\)) and 0.7 Å\(^3\) (Kr@C\(_{60}\)) are found. The main reason for the increasing constriction of the rare-gas atom with the atomic number is the very large contribution of the first-order exchange energy contributions that are found in the second line in Table 1 for the centered structures of the \( \text{Rg}@C_{60} \) complexes (individual interaction energy contributions for all distances are compiled in Tables 1–4 in the supplementary material). This can also be observed in Fig. 1(a) and (b) which show the four contributions \( E_{\text{exch}} \), \( E_{\text{disp}} \), \( E_{\text{int}} \), \( E_{\text{disp}} \) and \( E_{\text{exch-ind}} \) for \( \text{He}@C_{60} \) complexes for respectively two distances of the rare gas atom from the center, \( r = 0.0 \) Å and \( r = 0.4 \) Å. As can be seen in the figures, the first-order exchange energy contribution is always larger than the sum of all other interaction energy terms (which holds true for all distances \( r = 0–2.0 \) Å) excluding the dispersion energy which itself is always the most stabilizing term. It can therefore be argued that the \( \text{Rg}@C_{60} \) complexes are mainly stabilized by dispersion while the electrostatic and induction energy contributions are totally quenched by their exchange counterparts. In particular, the first-order electrostatic energy is overcompensated by the first-order exchange contribution while the sum of the induction and exchange-induction energies are very small for the binding regions of the interaction energy curves, see Table 1, Fig. 1(a) and (b), and Tables in the supplementary material. All \( \text{Rg}@C_{60} \) complexes studied here show also stable exohedral structures at a distance of about \( r = 7.0 \) Å of the rare-gas atom from the center. These structures are, however, much weaker than the corresponding endohedral ones: for \( \text{He}@C_{60} \) and \( \text{Ne}@C_{60} \) by a factor of about 10 and for \( \text{Ar}@C_{60} \) and \( \text{Kr}@C_{60} \) by factors of 7.5 and 6.0, respectively.

It can be observed that the dispersion energy for \( r = 0 \) shows an interesting almost-linear dependence on the size of the rare-gas atom (measured by its covalent radius, \( r_{\text{cov}} \)) times the number of electrons. This can be explained qualitatively by the dipole model of dispersion: an instantaneous dipole on a carbon atom creates an instantaneous dipole on the atom in the cage and the length of this second dipole is proportional to the number of electrons (\( q \)) and the possible extent of charges (\( r_{\text{cov}} \)).

A comparison of the SAPT interaction energies with the supermolecular MP2 and SCS-MP2 interaction energies from the columns 7 and 8 of Tables 2–5 for the different complexes shows that the MP2 energies are always much larger in magnitude than the corresponding SAPT values while for \( \text{He}@C_{60} \) and \( \text{Ne}@C_{60} \) a rather good correspondence between the SAPT and SCS-MP2 interaction energies is found with deviations of no more than 1 kJ mol\(^{-1}\) in the attractive region of the interaction potential. As it has been shown above, the dispersion energy is the main stabilizing interaction energy contribution for the \( \text{Rg}@C_{60} \) complexes, so the deviations between the SAPT and MP2 energies likely stem from the erroneous description of dispersion in the MP2 method. It is known on the other hand that the SCS-MP2 method improves supermolecular MP2 for dispersion-dominated complexes and thus both SAPT and the SCS-MP2 interaction energies can be regarded as being more accurate than the MP2 interaction

### Table 1

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<td>-11.95</td>
<td>-32.97</td>
<td>-34.57</td>
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### Table 2

| \( r \) | \( E_{\text{exch}}^{\text{int}} \) | \( E_{\text{ind}} \) | \( r_{\text{disp}}^{\text{MP2}} \) | \( E_{\text{exch}} \) | \( E_{\text{SAPT}} \) | \( E_{\text{MP2}} \) | \( E_{\text{SCS-MP2}} \) | \( E_{\text{DFT + Disp}} \) | \( E_{\text{MP2C}} \) |
|------|----------------|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0.0  | -1.17          | -0.56  | -10.75         | -6.61          | -8.77          | -6.07          | -8.51          | -7.07          | -7.00          |
| 0.2  | -1.24          | -0.63  | -10.64         | -6.23          | -8.66          | -6.28          | -8.26          | -7.09          | -7.09          |
| 0.4  | -1.62          | -0.87  | -11.49         | -5.86          | -7.84          | -5.36          | -5.75          | -7.91          | -5.75          |
| 0.6  | -2.41          | -1.39  | -12.73         | -6.64          | -7.20          | -4.09          | -7.09          | -6.41          | -6.41          |
| 0.8  | -3.89          | -2.47  | -14.78         | -8.18          | -9.40          | -5.90          | -9.24          | -2.18          | -2.18          |
| 1.4  | -21.04         | -17.54 | -27.68         | -16.23         | -16.23         | -15.78         | -16.04         | -1.10          | -1.10          |
| 2.0  | -106.22        | -95.83 | -60.48         | -70.02         | -70.02         | -69.12         | -70.27         | -1.00          | -1.00          |
| 5.0  | -26.30         | -25.50 | -22.17         | -130.99        | -130.99        | -129.91        | -130.99        | -2.00          | -2.00          |
| 6.0  | -1.32          | -1.17  | -2.47          | -7.21          | -6.50          | -1.00          | -0.80          | -1.00          | -1.00          |
| 7.0  | -0.06          | -0.05  | -0.85          | -0.35          | -0.62          | -0.54          | -0.37          | -1.00          | -1.00          |
| 8.0  | 0.00           | 0.00   | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           |
| 9.0  | 0.00           | 0.00   | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           |

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energies. However, both for Ar@C_{60} and Kr@C_{60} larger differences between the SAPT and SCS-MP2 interaction potentials are found, see Tables 4 and 5. For example at the endohedral minima the differences are $-13$ and $-19$ kJ mol$^{-1}$, respectively, while the corresponding exohedral interaction energies of SAPT and SCS-MP2 again are relatively close to each other. Because of this we have done additional calculations for the Rg@C_{60} complexes using the MP2C method which, in contrast to SCS-MP2, directly corrects the dispersion energy contained in the supermolecular MP2 method. As it has been found that the MP2C method yields a fairly accurate and balanced description of the interaction energy of different types of noncovalent complexes, see ref. 25, it can be expected that it should also give reliable results for the Rg@C_{60} complexes. In Tables 2–5 it can be seen that at the endohedral minima the SAPT interaction energies are always close to the corresponding SAPT values and only in case of Ne@C_{60} a slightly larger difference of 1.1 kJ mol$^{-1}$ is found that is, however, only about 10% of the total interaction energy of $-11.95$ kJ mol$^{-1}$ in case of DFT-SAPT. In particular, for Ar@C_{60} and Kr@C_{60} the SAPT and MP2C interaction potentials agree very nicely (if the high repulsive part of the potential is excluded). Since the SAPT and the MP2C method principally are two clearly different methods for calculating intermolecular interactions (see a discussion of their relation in section III), this result indicates that both the SAPT and the MP2C interaction energies are the most accurate in Tables 2–5, while the larger deviations between SAPT and SCS-MP2 in case of Ar@C_{60} and Kr@C_{60} probably are due to inherent errors of the SCS-MP2 method. For comparison Tables 2–5 also contain interaction energies determined with the semiempirical DFT + Disp method for some chosen distances. If the SAPT values are taken as reference, the DFT + Disp interaction energies at the endohedral minima are clearly too low, for Ne@C_{60} even by $-11.5$ kJ mol$^{-1}$, that is about 100% of the total interaction energy. It should be noted, however, that the DFT + Disp interaction energies are less basis-set dependent than the other methods used here (the “dispersion” correction for the Grimme method$^{22}$ is independent of the basis set size), and so the deviations to the SAPT interaction energies will likely become smaller in the CBS limit.

Fig. 2(a) and (b) show the total interaction energies for the four Rg@C_{60} complexes for the various methods for the two distances $r = 0.0$ A and $r = 0.4$ A of the rare gas atom to the center. As can be seen in Fig. 2(a), in case of the centered structures the total interaction energies decrease from He@C_{60} to Kr@C_{60}, but for DFT-SAPT and MP2C the
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The interaction energy of Kr@C60 is only slightly lower than the interaction energy of Ar@C60, while for DFT + Disp, the curve decreases almost linearly. Considering the DFT-SAPT and MP2C methods as most reliable among the methods used in this study, it can therefore be anticipated that for corresponding Rg@C60 complexes with larger rare gas guest atoms than Kr, the interaction energy will even increase again in case of \( r = 0.0 \) Å. However, DFT-SAPT test calculations for Rg-benzene complexes, which serve as model systems for the endohedral Rg@C60 complexes, have shown that with larger basis sets than those used in this study, the Kr-benzene dimer is much more stabilised in comparison to the Ar-benzene complex than with smaller basis sets. This indicates that the turnover of the interaction energy is not yet reached for the Kr@C60 complex. See also a recent work by Grimme.73 For the distance of \( r = 0.4 \) Å of the rare gas atom from the fullerene center one can observe in Fig. 2(b) that now for DFT-SAPT and MP2C the Ar@C60 complex is more stable than the Kr@C60 complex while the other methods still yield lower interaction energies for Kr@C60 than for Ar@C60 (in case of SCS-MP2 the interaction energy of the Ar and the Kr complex is almost identical for this distance).

**B Comparison to results of Wang et al.**

It is interesting to compare our DFT-SAPT energies with the results of Wang et al.15 for the center and off-center components of the interaction energy. In Table 16 of ref. 15 the asymptotic dipole–dipole and quadrupole–quadrupole contributions to the dispersion energies for the centered structures of the Rg@C60 complexes are shown. These contributions are obtained from eqn (69) and (72) of ref. 15, which are based on a modified asymptotic formula built from monomer properties, like e.g. polarizabilities and “irregular polarizabilities” (with e.g. an \( x/r^3 \) operator instead of \( x \) for dipole polarizabilities, see ref. 15 for details). Wang et al. use polarizabilities calculated with the BLYP density functional that enters the asymptotic dispersion formula. It is known, however, that BLYP and other GGA-type functionals yield (dipole) polarizabilities that are generally too large because of the wrong asymptotic behavior of the underlying exchange–correlation potentials, see e.g. ref. 74. As a consequence, dispersion coefficients and therefore asymptotic dispersion energies can be expected to be overestimated if calculated from BLYP polarizabilities.74 Since we have used an asymptotically corrected exchange–correlation potential in our SAPT calculations (see section III) a direct comparison of our nonexpanded dispersion energies and the asymptotic dispersion energies of Wang et al. is difficult. Because of this, it is not surprising that relatively large deviations are found: the dispersion energies of Wang et al. (a sum of dipole–dipole and quadrupole–quadrupole terms: He@C60: \(-5.2 \) kJ mol\(^{-1}\), Ne@C60: \(-10.4 \) kJ mol\(^{-1}\), Ar@C60: \(-34.1 \) kJ mol\(^{-1}\), Kr@C60: \(-68.1 \) kJ mol\(^{-1}\)) are roughly by a factor of 2 smaller than the nonexpanded dispersion energies in Tables 2–5 (\( r = 0 \), an exception is the Ar@C60 complex where a factor of 2.7 is found. This indicates that on the one hand the higher order multipole–multipole contributions to the asymptotic dispersion energy are not negligible and on the other hand even for the centered endohedral structures the use of multipole-expanded dispersion energies is not completely valid. In Table 18 in ref. 15 Wang et al. present also interaction energy contributions of the He@C60 complex in which the helium atom is displaced from the center. Here, however, the dispersion energy is determined from the difference between the supermolecular MP2 and HF energies. Though this difference, which may be termed as intermolecular correlation energy, also contains correlation contributions other than the dispersion (e.g., it will contain also correlation contributions to the electrostatic and induction interaction) a nice agreement between these results and our dispersion energies from Table 2 is observed: \(-9.9 \), \(-16.0 \), and \(-51.8 \) kJ mol\(^{-1}\) for distances \( r = 0.0 \), \( 1.0 \), \( 2.0 \) Å were obtained in ref. 15 from the difference of the MP2 and HF interaction energies, while the DFT-SAPT results are \(-10.8 \), \(-17.8 \), and \(-60.5 \) kJ mol\(^{-1}\), respectively. The agreement between the first-order exchange energy in Table 2 and the Pauli repulsion of Wang is not so good, and this is clearly due to an incorrect definition of the Pauli repulsion energy in the work of Wang et al.:15 the Hartree–Fock interaction energy sums up all interaction energy terms in eqn (2) with exception of \( E_{\text{disp}} \) and \( E_{\text{exch-disp}} \) if calculated with Hartree–Fock (response-)densities and density matrices. In particular, it
contains the attractive interaction energy contributions $E_{\text{elst}}$, $E_{\text{ind}}$ and higher order induction interaction energy terms\(^{(3)}\) which are, however, small in magnitude as can be seen in Table 2 (containing, however, the interaction energy terms calculated with the PBE1ac density functional). We have verified that indeed the numbers denoted in ref. 15 as Pauli repulsion agree very well (errors less than 1%) with the HF interaction energy, which we obtain as an intermediate value when calculating the $\delta E_{\text{HF}}$ correction. Such a good agreement in spite of utilizing different basis sets reflects the fact that the first-order and the second order induction and exchange-induction energies are not sensitive to the choice of the basis sets and are saturated already for basis sets of medium sizes.

### C He\(_2@C\)\(_{60}\) trimer interaction energies

Although not the main topic of this paper, it is interesting to estimate the stabilization effect for two helium atoms inside fullerene. The stability of He\(_2@C\)\(_{60}\) and other trimers with two endohedral rare gas atoms has been analysed in a number of previous works both by means of theoretical and experimental methods.\(^{6,9,11,13,75}\) The first experimental evidence of the endohedral He\(_2@C\)\(_{60}\) complex has been made by Sternfeld et al. using \(^{3}\)He NMR spectroscopy.\(^{75}\) However, a di-helium signal could only be observed for the hexa-anion $^{12}$He\(_2@C\)\(_{60}\) while in the neutral species the mono- and di-helium signals could not be separated from each other due to the low net aromatic character of C\(_{60}\).\(^{75}\) The ratio of He\(_2@C\)\(_{60}\) and He\(_{2}@C\)\(_{60}\), however, was 200 : 1, while it was 20 : 1 for the corresponding C\(_{70}\) compounds. This indicates that the He\(_2@C\)\(_{60}\) complex is much less stabilized than the corresponding dimer due to strong repulsive interaction contributions of the helium atoms confined in the C\(_{60}\) cage.

Some results for the He\(_2@C\)\(_{60}\) trimer for a couple of geometries are presented in Table 6. The interaction energy for a trimer can be divided into the additive and nonadditive parts, denoted as $E_{\text{int}}[2,3]$ and $E_{\text{int}}[3,3]$, respectively. For the additive parts the DFT-SAPT energies from Table 2 are utilized. The interaction energy between two helium atoms is taken from the fit of the potential energy curve given in ref. 76. For the nonadditive part of the interaction energy we utilize the pragmatic approach of Podeszwa and Szalewicz,\(^{77}\) who proposed to estimate the nonadditive effects as a sum of the nonadditive MP2 energy and the third-order nonadditive dispersion contribution. In the resulting so-called hybrid (SAPT and SM) approach the nonadditive part of the interaction energy is therefore obtained as the sum,

$$E_{\text{int}}[3,3] = E_{\text{int}}^{\text{MP2}}[3,3] + E_{\text{disp}}^{(3)}(\text{CKS})[3,3]$$

### Table 5 Components of the DFT-SAPT interaction energy for the Kr\(_@C\)\(_{60}\) complex. For definitions of $E_{\text{elst}}$ and $E_{\text{ind}}$ see Table 2. The total DFT-SAPT energy, as well as MP2, SCS-MP2, DFT + Disp, and MP2C interaction energies are also given. Energy values in kJ mol\(^{-1}\), distances in Å.

Note that for distances $r > 3.5$ Å the complex is exohedral.

![Fig. 2](image_url) Interaction energies of the four Rg\(_@C\)\(_{60}\) complexes calculated with various methods for the distances $r = 0.0$ Å and $r = 0.4$ Å of the rare gas atom to the center.
so that the total interaction energy of the trimer in this hybrid approach is given by

\[ E_{\text{int}}(\text{trimer}) = E_{\text{int}}^{\text{SAPT}[2,3]} + E_{\text{int}}^{[3,3]} \]  

(6)

The results listed in the last row of Table 6 show that the molecule He@C\(_{60}\) is thermodynamically unstable, although the instability is quite small and it is expected to become even smaller in the CBS limit. Note that all distances reported in Table 6 correspond to repulsive distances between two helium atoms (the negative interaction energies for He\(_2\) start from a distance of about 2.6 Å). Additionally, given the small magnitude of the effect, a more accurate description of the additive and (especially) nonadditive contributions may still play a role. The existing investigations of the nonadditive SAPT effect show that sometimes even the \(E^{(4)}\) components have to be included. 78,79 Also unknown are the magnitudes of the intramonomer electron correlation effects for the \(E^{(3)}\) and \(E^{(5)}\) additive and nonadditive terms, which can constitute a significant part of the total component in some cases. 77 Finally, the estimation of the additive effects in a larger aug-cc-pVTZP/TZVPP basis for one distance suggests strongly that the basis set limit is not yet achieved. Unfortunately, the necessary extension of the basis set for carbon to QZVPP is beyond our computer capacities.

Table 6 also contains the total trimer interaction energies obtained using MP2, SCS-MP2 and MP2C for the respective distances. In case of MP2C the interaction energy of the trimer ABC was calculated with the following scheme:

\[
E_{\text{int}}^{\text{MP2C}}(ABC) = E_{\text{int}}^{\text{MP2C}}(ABC) + (E_{\text{disp,LHF}}^{(2)}(AB) - r^{(2)}_{\text{disp,UCHF}}(AB)) + (E_{\text{disp,LHF}}^{(2)}(AC) - r^{(2)}_{\text{disp,UCHF}}(AC)) + (E_{\text{disp,LHF}}^{(2)}(BC) - r^{(2)}_{\text{disp,UCHF}}(BC)) + E_{\text{disp,LHF}}^{(3)}(ABC)[3,3] 
\]  

(7)

where \(E_{\text{disp,LHF}}^{(2)}\) and \(r^{(2)}_{\text{disp,UCHF}}\) are the dispersion energies obtained using coupled TD-DFT with LHF orbitals and uncoupled HF, respectively. Note that \(E_{\text{disp,LHF}}^{(3)}(ABC)[3,3]\) denotes the three-body coupled dispersion energy calculated with LHF orbitals that is absent in the supermolecular MP2 trimer interaction energy (see above). The comparison of the MP2, SCS-MP2 and MP2C results from Table 6 shows again that the SCS-MP2 and MP2C interaction energies are close to each other while the MP2 interaction energies are much lower in magnitude, though still repulsive for the distance of \(r = 1.0\) Å. This indicates in concordance with the hybrid-SAPT results that the endohedral He\(_2@C_{60}\) complex remains unstable even if the uncompleteness error of the basis set is corrected. The table shows also nonadditive third-order dispersion energies, missing in the SM MP2 energy. Large values of this correction would indicate that MP2 cannot be used for the calculations of trimer interaction energies. The nonadditive third-order dispersion energy listed in Table 6 has been calculated for the LHF functional, used also within the MP2C scheme, and for the PBEAc functional, utilized in DFT-SAPT. It can be seen that this component is sensitive to the choice of the functional, but since its absolute value is small in comparison to the total interaction energy, this dependence does not play any significant role.

### D Estimation formulas for the dispersion and exchange energies for the A@B endohedral complexes

From Tables 2–5 it is clear that the main contributions for the interaction energy in the Rg@C\(_{60}\) complexes are the attractive dispersion and repulsive exchange energies. It is therefore of interest to be able to model these contributions of \(E_{\text{int}}\). In this section it will be shown that the two main components of the interaction energy for Rg@C\(_{60}\), i.e. dispersion and the first-order exchange, can effectively be modelled by applying a straightforward modification of the analytical forms, used for fitting ‘normal’ (not endohedral) van der Waals complexes. The presented formulas can be helpful in a future modelling of potential energy surfaces of endohedral and exohedral fullerene complexes, when the fine deviations from spherical symmetry can be ignored.

Let us find an asymptotic form of the dispersion and first-order exchange energies for an endohedral complex A@B, where all anisotropies of the guest molecule A are...
neglected and where the host molecule $B$ is modelled by a spherical cage with a radius $R$. The molecule $A$ is shifted from the center of the host molecule by some distance $r$ (see Fig. 3). Each infinitesimal array $dS$ of the sphere $B$ interacts with the molecule $A$, giving a contribution of $-C dS/(4\pi R^2 r^6)$ to the dispersion energy, where $C$ is a constant and $x$ a distance between $A$ and the array $dS$ ($x^{-6}$ is a usual asymptotic dependence of the dispersion energy and $C/(4\pi R^2)$ is a contribution to the dispersion energy from a unit array of the cage). After the integration over the whole sphere the following formula for the dispersion energy is obtained,

$$E_{\text{disp}}^{(2)} = -\int_0^\pi C \sin \theta \frac{1}{2 (R^2 - 2 R r \cos \theta + r^2)} d\theta.$$  

(8)

Similarly, if the exchange contribution resulting from the array $dS$ is modelled as $ae^{-b r} dS/(4\pi R^2)$, then

$$E_{\text{exch}}^{(1)} = \int_0^\pi \frac{1}{2} ae^{-b \sqrt{R^2 - 2 R r \cos \theta + r^2}} \sin \theta d\theta = \exp(-b R) \left[ e^{-b R} - \frac{a}{b} e^{-b R} (b R - 1) + \frac{a}{b^2} e^{-b R} (b R - 1) \right].$$

(9)

For a small $r$ (molecule $A$ situated close to the center of the sphere) the functions obtained can be expanded into the Taylor series around $r = 0$ giving,

$$E_{\text{disp}}^{(2)} = \frac{C}{R^6} \frac{5 R^2}{r^8} + C(r^4),$$

(10)

$$E_{\text{exch}}^{(1)} = ae^{-br} + ab(6R)^{-1} e^{-b R} (b R - 2) r^2 + C(r^4).$$

(11)

It should be noted that recently Pyykkö et al.\textsuperscript{12,15} presented an approximate formula for the dispersion energy of the endohedral complex, being a generalization of the famous London expression\textsuperscript{10} for the case when the molecule $A$ is located in the center of the $B$ molecule. Since in eqn (10) the distance $R$ is constant, the first term on the r.h.s. of eqn (10) corresponds to the term of Pyykkö et al. It is also interesting to note that terms of the $r^2$ type (see eqn (10)) have also been obtained recently by Wang et al.\textsuperscript{15} in a generalization of the approach presented in ref. 12. According to eqn (10), the dispersion energy curve should be almost flat for small $r$ and it should grow rapidly (as $C(r^4)$) for somewhat larger $r$. Note that if we assume $r \gg R$ (the guest atom outside the cage), then the leading term in the Taylor expansion will become again the usual textbook $-C r^{-6}$ term. Therefore, eqn (8) covers all $r$ distances. Similarly, the exchange contribution is almost constant in the vicinity of the cage center, then it grows quadratically for larger $r$. For $r \gg R$ this term behaves as $ae^{-br}$. We have estimated the parameters $C$, $a$, and $b$ by fitting eqn (8) and (9) to DFT-SAPT dispersion and first-order exchange energies, respectively. The resulting curves and the DFT-SAPT dispersion and first-order exchange contributions are plotted in Fig. 4–7. In the fits the $R$ value of 3.56208 Å (the distance from the center of fullerene to any carbon atom)
has been used. As can be seen from these figures, the accuracy of both formulas is remarkably good for all distances under consideration.

\[ C = 9.2 \times 10^8 \text{ A}^2 \text{ kJ mol}^{-1}, a = 2.2 \times 10^8 \text{ kJ mol}^{-1}, b = 4.0 \text{ A} \].

V. Conclusions

We have calculated the interaction energies for endo- and exohedral complexes of the C\textsubscript{60} fullerene with rare-gas atoms using various quantum chemistry methods. The endohedral complex is stabilized in all cases with the minimum corresponding to the center of the fullerene. A secondary minimum outside the fullerene cage at about \( R = 7 \) Å has also been detected. The DFT-SAPT interaction energies, which serve as a benchmark, are in a good agreement with a newly developed hybrid MP2C method. On the other hand, the SCS-MP2 method, which performed well for the case of H\textsubscript{2}@C\textsubscript{60},\textsuperscript{16} behaves not so well for the Rg@C\textsubscript{60} systems. It can be noted that the worse performance of the SCS-MP2 method has also been established for other types of complexes, like saturated compounds (e.g. alkane dimers).\textsuperscript{31} The MP2 method overbinds both endo- and exohedral complexes by even 50%. The performance of the DFT + Disp method is mixed: while for all studied Rg@C\textsubscript{60} complexes a strong underestimation of the interaction energies for the dimer case the DFT-SAPT approach should therefore be advertised here as a best-suited method for \textit{ab initio} investigations of stabilization energies of complexes with fullerene.

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10. Intermolecular interactions


73 S. Grimme, not yet published.
On the accuracy of DFT-SAPT, MP2, SCS-MP2, MP2C, and DFT+Disp methods for the interaction energies of endohedral complexes of the C$_{60}$ fullerene with a rare gas atom. Supplementary material.

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TABLE I: Components of the DFT-SAPT interaction energy for the He@C60 complex. The total DFT-SAPT energy, as well as MP2, SCS-MP2, DFT+Disp, and MP2C interaction energies are also given. Energy values in kJ/mol, distances in Å. Note that for distances $r>3.5$ Å the complex is exohedral.

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TABLE II: Components of the DFT-SAPT interaction energy for the Ne@C\textsubscript{60} complex. The total DFT-SAPT energy, as well as MP2, SCS-MP2, DFT+Disp, and MP2C interaction energies are also given. Energy values in kJ/mol, distances in Å.

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TABLE III: Components of the DFT-SAPT interaction energy for the Ar@C$_{60}$ complex. The total DFT-SAPT energy, as well as MP2, SCS-MP2, DFT+Disp, and MP2C interaction energies are also given. Energy values in kJ/mol, distances in Å.

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TABLE IV: Components of the DFT-SAPT interaction energy for the Kr@C\(_{60}\) complex. The total DFT-SAPT energy, as well as MP2, SCS-MP2, DFT+Disp, and MP2C interaction energies are also given. Energy values in kJ/mol, distances in Å.

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10. Intermolecular interactions

10.10. Comparison of intermolecular interaction energies from SAPT and DFT including empirical dispersion contributions

journal: Journal of Physical Chemistry A

author(s): A. Heßelmann

year: 2011

note: published online, to appear in the Pavel Hobza Festschrift

Key words:

- empirical dispersion correction
- symmetry-adapted perturbation theory
- S22 database of intermolecular complexes
- force field
Comparison of Intermolecular Interaction Energies from SAPT and DFT Including Empirical Dispersion Contributions

Andreas Hesselmann*
Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen

ABSTRACT: The dispersion correction based on damped atom–atom long-range interaction contributions has been tested for an extended S22 database of intermolecular complexes using density functional theory (DFT) and symmetry adapted perturbation theory (SAPT) to account for the remaining interaction energy contributions. In the case of DFT, the dispersion correction of Grimme (J. Comput. Chem. 2006, 27, 1787) was used, while for SAPT, another damping function has been developed that has been optimized particularly for the database. It is found that both approaches yield about the same accuracy for the mixed-type complexes, while the DFT plus dispersion approach performs better for the dispersion-dominated complexes if compared with coupled cluster singles-doubles with perturbative triples interaction energies as a reference.

1. INTRODUCTION

The accurate description of electron correlation effects is of crucial importance for the determination of intermolecular interaction energies. While in many cases, like the interaction of aromatic π rings, the intermolecular correlation effects are the main source of stabilization, also intramolecular correlation effects should accurately be accounted for. A prominent example for this is the CO dimer, where not even the coupled cluster singles-doubles with perturbative triples (CCSD(T)) method, which is often used as a reference approach, is accurate enough to reproduce the rovibrational spectrum qualitatively correctly. Moreover, even in intermolecular complexes that are mainly bound by electrostatic interactions, the long-range dispersion energies cannot be neglected and can amount to 20–30% of the total interaction energy. Because of this, usually, it would be desirable to use high-level ab initio methods to study weak interactions between molecules. Unfortunately, however, these methods commonly have a high scaling behavior with respect to the molecular size, which grows at least with the fifth power of the cheapest approaches, namely, second-order Møller–Plesset perturbation theories. Moreover, conventionally large basis sets are required to describe electron correlation effects with ab initio approaches in order to accurately model the interelectronic cusp. Therefore, ab initio correlation methods often can only be applied to study rather small systems.

Compared to this, common density functional theory methods (DFT) possess a much more favorable scaling behavior of with respect to the molecular size. This stems from the fact that in these methods, electron correlation is not explicitly modeled through the description of a many-body wave function, but it is hidden in the so-called exchange-correlation (xc) functional, which solely is approximated as a functional of the density and its gradient. Gradient approximation (GGA) functionals. More modern (meta-GGAs and hybrid GGAs) functionals also depend on the kinetic energy density or on occupied molecular orbitals, but still, the favorable scaling behavior in these DFT methods is conserved. It turns out, however, that such functionals are not capable to describe long-range correlation effects. This means that they can principally not account for the important long-range dispersion interaction energy between two molecules. In the asymptotic range, this correlation contribution can be described with the expansion

where are the dispersion coefficients depending on the frequency-dependent polarizabilities of the monomers A and B and is the distance between the monomers. For smaller distances the expansion in eq 1 gets damped but still significantly contributes to the stabilization of the two monomers in the equilibrium region. A potential remedy to the long-range correlation problem of standard DFT methods is therefore to simply add the expansion of eq 1 to the DFT interaction energy but damp it in the short-range region. A number of such methods, which will be termed as DFT+D approaches in this work, have been derived in recent years, and they appear to be almost always better to describe intermolecular interactions than corresponding uncorrected DFT methods. However, DFT+D approaches are no longer within the realm of Kohn–Sham (KS) electronic structure methods.

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DFT because they combine DFT with an empirical force field term that itself does not contribute to the xc potential and therefore KS orbitals. The dynamic polarization that is the source for the intermolecular correlation effects is therefore not described explicitly through the KS system but is empirically determined by using atom–atom dispersion coefficients that are (usually) optimized against some reference data. A number of other approaches exist that try to model the long-range correlation effects by the xc functional itself. For example, some recent (hybrid-)GGA functionals by Troullier et al. are parametrized in such a way that they are more accurate for the description of intermolecular bonding. This approach, however, appears to be a bit questionable because the corresponding xc functionals do not qualitatively correctly describe the interaction in the asymptotic region (see above). In contrast to this, a number of nonlocal xc functionals have been derived that explicitly describe the long-range correlation through the Coulombic interaction between charge distributions that are functionals of the electron density. While DFT methods using these functionals are somewhat more computationally demanding than standard DFT methods, it has been shown that they can accurately describe intermolecular interactions.

A completely different approach to describe the interaction between molecules is symmetry-adapted intermolecular perturbation theory (SAPT). Here, in contrast to supermolecular methods where the interaction energy is calculated by subtracting the monomer energies from the energy of the supermolecule, the interaction energy is described by a sum of physically interpretable terms that can be obtained from monomer properties; see section 2.1 for details. This offers a number of advantages in comparison to the supermolecular approach. For example, by definition, in SAPT, there can be no basis set superposition error, and in fact, each interaction energy term could be calculated within its own basis set. Second, the different interaction terms that contribute to the total interaction energy in SAPT can principally be calculated using any quantum chemistry approach. A very favorable approach with respect to the computational cost therefore is to combine SAPT with DFT (DFT–SAPT), in which the DFT monomer description accounts for the intramolecular correlation effects. Thus, the DFT–SAPT method can be used in conjunction with any kind of xc functional because the intermolecular correlation is not described by the functional but explicitly by the perturbation expansion. However, it has been shown that the accuracy of the interaction energy from DFT–SAPT very much depends on the underlying xc potentials used in the monomer calculations. If these accurately yield molecular multipoles and, depending on their asymptotic behavior, accurate polarizabilities, it has been shown in a number of works that the DFT–SAPT method describes intermolecular interactions exceedingly well if compared to high-level ab initio methods.

A further advantage of the DFT–SAPT method (and SAPT in general) is that it yields directly a decomposition of the interaction energy into terms that can be interpreted on the basis of physical intuition. For example, the terms appearing in the SAPT expansion, that is, electrostatics, polarization, dispersion, and repulsion terms, can in principle directly be related to terms that appear in common intermolecular force fields. Indeed, in refs 70 and 71, new force fields were developed that are (partially) fitted to SAPT interaction energy terms. In ref 71, it was shown that the force field derived in this way agrees well with full DFT quantum chemistry calculations for the description of the interaction of glycopeptide fragments with small peptide ligands. A very thorough comparison of DFT–SAPT interaction energy terms with corresponding force field contributions of the AMBER force field has been made by Zgarbova et al. Here, it was shown that for larger monomer distances, there is a nice agreement of the electrostatic and dispersion terms, while in shorter regions (approaching the equilibrium), the different description of the intermolecular repulsion leads to larger differences in both cases. However, it has been observed that these differences cancel each other when summing up all terms such that the total force field interaction energy and the DFT–SAPT interaction energy deviate less from each other than the individual interaction terms.

In this work, a hybrid method will be investigated in which the electrostatic, induction, and corresponding exchange-repulsion interaction terms are calculated with DFT–SAPT, while the dispersion and exchange–dispersion interaction contribution will be modeled by an empirical damped atom–atom dispersion interaction energy term. Because the dispersion and exchange–dispersion terms are computationally the most expensive interaction energy terms in DFT–SAPT, this hybrid method would extend the applicability of DFT–SAPT to larger molecular systems. Moreover, it is well-known that paradoxically “classical” electrostatic and polarization effects are more difficult to describe with intermolecular force fields than van der Waals interactions that originate from quantum mechanical effects. In the case of the electrostatic interactions, this mainly stems from the fact that at shorter ranges, there is a significant contribution due to charge penetration effects that can not be described by a point charge model. These effects, of course, are accurately accounted for by SAPT methods, and thus the hybrid DFT–SAPT–force field method, which will be termed as SAPT+D in this work, would also be an alternative approach to force field methods if quantum chemistry methods are still feasible. Some first results showing the performance of a combined DFT–SAPT and damped dispersion method for the helium dimer were presented by Misquitta et al. The corresponding interaction energy curves showed a nice agreement with the full many-body SAPT curve; however, the damping coefficient was explicitly optimized for that single system.

This work is organized as follows: in section 2, the different methods are described that are used in this work, namely, SAPT (section 2.1), DFT+D (section 2.2), and SAPT+D (section 2.3). Section 3 describes the reference systems that were used in this work to assess the performance of the different methods. Section 5 discusses the results, and section 6 summarizes.

2. METHODS

2.1. Symmetry-Adapted Perturbation Theory. In SAPT, the total interaction energy between two molecules A and B is described by a sum of well-defined interaction contributions

\[ E_{\text{int}}(A \cdots B) = E_{\text{diss}}^{(1)} + E_{\text{ind}}^{(1)} + E_{\text{disp}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{exch-ind}}^{(1)} + E_{\text{exch-ind}}^{(2)} + \Delta(3 - \omega) \]

where the sum of the first three terms on the righthand side of eq 2 is the polarization energy up to second order in the intermolecular perturbation expansion, with \( E_{\text{diss}}^{(1)} \) as the electrostatic interaction energy, which can be obtained from the densities of the monomers, \( E_{\text{ind}}^{(1)} \) as the induction energy described by static response propagators of the monomers, and \( E_{\text{disp}}^{(1)} \) as the dispersion energy curve showed a nice agreement with the full many-body SAPT curve; however, the damping coefficient was explicitly optimized for that single system.
interaction energy requiring the frequency-dependent response propagators of the two monomers. These terms are accompanied by the additional exchange terms $E_{\text{exch}}^{(1)}(\rho)$ and $E_{\text{exch}}^{(2)}$ which arise due to the tunnelings of the electrons from one monomer to the other if the densities of the monomers overlap with each other. Conventionally, in SAPT, the third- and higher-order contributions with respect to the perturbation expansion in the intermolecular potential are not explicitly calculated, but they can be approximated by a supermolecular Hartree–Fock calculation in the following way

$$
\Delta^{(3-\infty)}_{\text{xc}}(\rho) = E_{\text{HF}} - E_{\text{int}}^{(1)}(\rho) - E_{\text{ind}}^{(2)}(\rho) = E_{\text{exch}}^{(1)}(\rho)
$$

where $E_{\text{HF}}$ is the supermolecular Hartree–Fock interaction energy and the other terms on the right-hand side of eq 3 are the first- and second-order interaction energy contributions calculated on the Hartree–Fock level (excluding $E_{\text{disp}}^{(2)}$ and $E_{\text{exch}}^{(2)}$ because these terms are not contained in $E_{\text{HF}}$).

In general, the interaction terms in eq 2 could be calculated using any quantum chemistry method, and originally, SAPT methods were developed that account for the intramonomer correlation effects using a double-perturbation expansion both for the intermolecular potential and for the intramonomer fluctuation potential. In more recent developments, the individual interaction energy terms were derived in terms of coupled cluster (response) densities and density matrices. It has been found, however, that as an alternative to the ab initio approaches to account for the intramonomer electron correlation in SAPT, one can also use DFT. While this method, termed DFT–SAPT, is computationally much cheaper than corresponding many-body or coupled cluster SAPT methods, it was found that it also yields fairly accurate interaction energies under the condition that accurate (meaning particularly asymptotically corrected) exchange-correlation potentials are used in the DFT calculations of the monomers. This observation was somewhat surprising because (even exact) Kohn–Sham DFT does not yield the exact density matrices of an electron system, and therefore, the exchange interaction energy terms in eq 2, in contrast to the polarization terms, cannot be calculated exactly, even if the exact exchange-correlation potentials and kernels of the monomers would be employed.

**2.2. Dispersion Correction in DFT.** It is well-known that standard (local density approximation (LDA) or generalized gradient approximation (GGA)) Kohn–Sham DFT methods, in which the exchange-correlation ($xc$) energy is expressed as

$$
E_{\text{xc}}^{\text{LDA,GGA}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \nabla^2 \rho(\mathbf{r}), \ldots) \, d\mathbf{r}
$$

where $\epsilon_{\text{xc}}$ is the xc energy density, $\rho(\mathbf{r})$ is the electron density, and $\nabla^n \rho(\mathbf{r})$ are its nth derivatives, cannot account for the long-range intermolecular correlation effects between two interacting molecules, which is simply due to the (semilocal) nature of the form of the functional in eq 4. This can easily be shown for the Slater–Dirac exchange functionals as an example; for a large distance $r_{\text{AB}}$ between two monomers A and B, the electron density $\rho_{\text{AB}}(\mathbf{r})$ of the total dimer system will approximately be the sum of the densities of the two monomers

$$
\rho_{\text{AB}}(\mathbf{r}) \approx \rho_{\text{A}}(\mathbf{r}) + \rho_{\text{B}}(\mathbf{r})
$$

and the Slater–Dirac exchange energy of the dimer will take the form (with $C_6$ being a constant)

$$
E_{\text{exch}}^{\text{LDA}}(\mathbf{r}) = -C_6 \int \delta(x/\rho_\text{A}(\mathbf{r}) - \rho_\text{B}(\mathbf{r})) = -C_6 \int \delta(x/\rho_\text{A}(\mathbf{r}) + \rho_\text{B}(\mathbf{r}))\n$$

$$
\approx -C_6 \int \delta(x/\rho_\text{A}^{4/3}(\mathbf{r}) + \rho_\text{B}^{4/3}(\mathbf{r})) = E_{\text{exch}}^{\text{LDA}}(\mathbf{r}) + E_{\text{exch}}^{\text{LDA}}(\mathbf{r})
$$

(6)

where $\rho_\text{A}(\mathbf{r}) + \rho_\text{B}(\mathbf{r})^{4/3}$ is because the two densities, practically, do not overlap with each other. Thus, there can be no long-range intermolecular correlation contribution from a functional of the form of the Slater–Dirac exchange energy functional. While a bit more complicated to verify, this holds true for any functional of the form of eq 4 because the xc energy density $\epsilon_{\text{xc}}$ here is defined to be only locally dependent on the density and its gradients and thus cannot contain any long-range correlation effects. Therefore, standard DFT methods perform particularly worse for intermolecular complexes with a strong dispersion interaction contribution, while they do better describe situations where other interaction contributions are more important.

The most economical approach from a computational point of view is the addition of a simple damped force field contribution to the DFT interaction energy

$$
E_{\text{DFT}} + D = E_{\text{DFT}} + E_{\text{disp}}(DFT + D)
$$

where

$$
E_{\text{disp}}(DFT + D) = -\kappa \sum_{\text{monomer A}}^{\text{monomer B}} f_{\text{disp}}(r_{ij}) \frac{C_6}{r_{ij}^6}
$$

(8)

where $\kappa$ is a global scaling parameter that is adapted for a specific density functional, $r_{ij}$ is the distance between two atoms of the molecular system, $C_6$ is an atom–atom-based dispersion coefficient (see below), and $f_{\text{disp}}(r_{ij})$ is a damping function that properly damps the dispersion interaction for short atom–atom distances. Note that here, the summations in eq 8 are restricted to $i \in A$ and $j \in B$, with A and B denoting the two subsystems, while eq 8 would also be valid to account for intramolecular long-range correlation energies; see, for example, ref 4. Note also that, while most of the dispersion corrections that have been developed only contain the $-1/r^6$ leading-order term of eq 1, more recently developed methods also employ higher-order terms in the long-range expansion.

The $C_6$ coefficient can be calculated, for example, using the following approximations:

$$
C_6^{\text{eff}} = 2 \frac{C_6}{C_6 + C_6^{\text{eff}}}
$$

(9)

$$
C_6^{\text{eff}} = \sqrt{C_6^{\text{eff}}}
$$

(10)

where the atomic $C_6$ coefficients are usually determined by fitting to some data set of intermolecular complexes. In this work, eq 10 has been used in conjunction with the $C_6$ parameters developed by Grimme. The damping function $f_{\text{disp}}(r_{ij})$ in eq 8 is a very crucial part of the dispersion correction to DFT because it not only ensures finiteness for short distances, but the damping at short distances

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The implementation of the DFT with in ref 33. The atomic van der Waals radii parameter that has been optimized to values of 23 in ref 29 and 20 in ref 33. The atomic van der Waals radii \( r_{vdW} \) are derived from the radius of the 0.01 \( e \) electron density contour from restricted open-shell Hartree–Fock densities.

2.3. Dispersion Correction in SAPT. The density-fitting implementation of the DFT–SAPT method significantly reduces the computational cost of the individual interaction energy terms of eq 2, which then possess a scaling behavior of \( 1/r^6 \) for \( E_{disp} \), \( E_{exch} \), \( E_{vdW} \), and \( \delta(HF) \). However, for \( E_{disp} \) and \( E_{exch} \) with \( r_{vdW} \) being a measure of the molecular size (refer to ref 87 for a corresponding density-fitting many-body SAPT method). While this makes DFT–SAPT calculations feasible also for quite large intermolecular complexes comprised of up to about 150 electrons and 2000 basis functions, the generation of potential energy surfaces for such systems or the treatment of even larger systems is certainly limited. The main reason for this is the high (in comparison with the other contributions) computational cost of the dispersion and exchange–dispersion interaction terms. Because of this, in this work, it is tested whether these two contributions can be accurately modeled using a damped force field term, as described in the last section. In order to do this, however, it is important to point out the differences between the role of the dispersion correction in DFT and SAPT methods; in DFT, the dispersion correction in eq 7 shall contribute only to the long-range part of the intermolecular interaction energy, while in SAPT, a strict separation of interaction energy contributions exists, such that the sum of \( E_{disp} \) and \( E_{exch–disp} \) totally contains all intermolecular correlation effects (up to second order).

In Figure 1, the sum of the second-order dispersion and exchange–dispersion interaction energy from a very accurate DFT+D calculation of Korona et al.\(^{88}\) is compared to the damped dispersion correction of eq 8 using the damping function of eq 11. While the two curves in Figure 1 show some quantitative difference from each other already close to the minimum (taking into account the problem of double counting in the case of DFT) of the total interaction energy curve (shown also in the diagram), there is an apparent qualitative difference of \( E_{disp} \) and \( E_{disp-exch-disp} \) in the shorter strong-repulsive part. Namely, the DFT+D dispersion correction is damped to zero, while the term \( E_{disp-exch-disp} \) stays finite for small distances (note, however, that for very small monomer distances, the SAPT perturbation expansion may break down\(^{89–91}\)). Because of this, the dispersion correction to be used in conjunction with SAPT requires a qualitatively different damping function than that of eq 11. In this work, the following expression is used

\[
f_{damp}(r_{ij}) = \frac{1}{1 + \exp[-\alpha(r_{ij}/(r_{vdW}^6 + r_{vdW}^6) - 1)]} \quad (11)
\]

with \( r_{vdW} \) being the van der Waals radius for atom \( i \) and \( \alpha \) as a parameter that has been optimized to values of 23 in ref 29 and 20 in ref 33. The atomic van der Waals radius \( r_{vdW} \) are derived from the radius of the 0.01 \( e \) electron density contour from restricted open-shell Hartree–Fock densities.

\[
f_{damp}(r_{ij}) = \text{erf} \left( \frac{\alpha}{\sqrt{2}} \frac{r_{ij}}{r_{vdW}^6 + r_{vdW}^6} \right) \quad (12)
\]

where \( \alpha \) is a parameter to be optimized and the same van der Waals radii as those in eq 11 (according to ref 33) were used. The behavior of the two different damping functions according to eqs 11 and 12 are shown in Figure 2 for the helium dimer, which has a minimum at the distance of about 3 Å. The total dispersion correction to be used as replacement for the sum \( E_{disp-exch-disp} \) in SAPT is proposed as

\[
E_{disp}(\text{SAPT} + D) = -s_{eff} \sum_{\text{monomer A}} \sum_{\text{monomer B}} \text{erf} \left( \frac{\alpha}{\sqrt{2}} \frac{r_{ij}}{r_{vdW}^6 + r_{vdW}^6} \right) C_{ij}^6 
\]

containing the three global parameters \( s_{eff}, \alpha, \) and \( \beta \) to be fitted. The fitting parameter \( \beta \) has been introduced because the asymptotic \(-1/r^6\) behavior usually is observed only for very large distances (beyond the equilibrium), while for shorter distances, it is known that higher-order multipole terms can contribute with about 20–30% to \( E_{disp} \) so that a single-term expansion as in eq 13 cannot be accurate in the middle range region. Note that there also exist force fields that use different power laws for the dispersion interaction.\(^{92} \) Note also that \( E_{disp-exch-disp} \) is a repulsive short-range contribution to the intermolecular correlation energy that decays exponentially with the monomer distance. Thus, if the total sum \( E_{disp} + E_{exch-disp} \) is
The damping function of eq 12 actually diverges for very small values of \( r_{ij} \), if \( \beta > 1 \). However, because here the dispersion contribution shall only describe the intermolecular long-range correlations, this unphysical behavior of eq 12 is not taken into account. In practice, even for very small values of \( r_{ij} \), the damping function of \( 1/(\beta \ln 1/r_{ij}) \) will not get much smaller than the sum of van der Waals radii for two atoms even at very short distances. As can be observed, the dispersion correction of eq 13 is much closer to the sum of dispersion-dominated complexes, as can be seen in the middle group of complexes in Figure 3. For the mixed-type complexes (see the right-hand side of the diagram in Figure 3), most cases, the electrostatic and dispersion contribution to the total sum \( E_{\text{pol}} \) is of about the same importance. One notable exception to this is, however, observed for the T-shaped benzene dimer bound by a C–H⋯\( \pi \) interaction. As can be seen in Figure 3, for this system, the dispersion interaction contributes stronger to the total polarization sum, and it could therefore also be categorized in the group of dispersion-dominated complexes.

### 4. COMPUTATIONAL DETAILS

The interaction energies for the complexes from the S22+ set (see section 3) have been calculated using the methods described in section 2. The DFT–SAPT calculations were done using the localized and asymptotically corrected LPBE0AC exchange-correlation potential for the monomer calculations. The vertical ionization energies required for the asymptotic correction were taken from ref 96. See ref 94 for further details. The supermolecular DFT calculations were done using the Becke97 (B97) hybrid xc functional, which is also the functional that is proposed in Grimme’s second work about DFT +D. However, while Grimme reparametrized the functional in combination with the dispersion correction, the other Becke parametrization of the B97 functional is used. Because of this, the scaling parameter of eq 8 has been optimized explicitly for the S22+ database (excluding, however, the problematic short-range complexes) by measuring absolute percent deviations of the total DFT+D interaction energies to the extrapolated CCSD(T) reference interaction energies. The optimal values for the parameters were taken from ref 33.

In case of the SAPT dispersion correction of eq 13, the parameters \( s, \alpha, \beta \) were optimized by fitting the total SAPT+D interaction energies to the CCSD(T) reference interaction energies again by measuring the absolute percent deviations. This strategy has been preferred over a least-squares fit in order to achieve a more balanced fit for the weaker and more strongly interacting systems. The results for the optimization are \( s = 0.67, \alpha = 1.087, \beta = 5.67 \). The optimized value for the exponent \( \beta \) shows that obviously a more strong interaction than the exact asymptotic \(-1/r^6\) dependence is required to obtain good agreement with the reference values. Note, however, that this result cannot be interpreted by physical means because the optimization depends also on the underlying atomic van der Waals radii and dispersion coefficients used in eq 13. These were taken from ref 33 and are therefore probably not optimal because they were determined for use in DFT+D calculations. Indeed, as can be seen in Figure 1 for He\(_2\), as an example, the damped...
dispersion energy from the DFT+D method is much weaker than the sum $E_{\text{disp+exch}}/C_{\text{disp}}$ (2) in the minimum region, and thus, vice versa, this explains the stronger $-1/r^n$ ($n < 6$) dependence for the fit of eq 13 if used in conjunction with $r_{\text{vdW}}^{\text{atomic}}$ and $C_6^{\text{atomic}}$ from DFT+D methods. Because of this, it might be advantageous to also reoptimize the atomic van der Waals radii and dispersion coefficients explicitly for use in SAPT+D calculations in future work.

In all calculations, the aug-cc-pVTZ basis set of Dunning et al.98 has been used. In case of the dispersion and exchange--dispersion interaction energies, the two-point extrapolation of Bak et al.99 with the aug-cc-pVDZ and aug-cc-pVTZ basis sets from Dunning et al.98 has been employed to obtain results that are closer to the basis set limit.

All calculations were done using the Molpro quantum chemistry program.100 Core electrons were kept frozen for the intermolecular correlation contributions.

5. RESULTS

Figure 4 shows the average absolute percent deviations of the interaction energies from SAPT (eq 2), DFT+D (eq 7), and SAPT+D (eq 2 using eq 13 instead of $E_{\text{disp+exch}}/C_{\text{disp}}$) to the

Figure 5. Absolute average percent deviations to complete basis set extrapolated CCSD(T) interaction energies with respect to different interaction types (excluding short-range geometries).

Figure 6. $E_{\text{int}}(\text{SAPT})$ versus $E_{\text{int}}(\text{CCSD(T)})$. The top diagram shows the correlation with respect to the five individual monomer distances (1: small; 2: equilibrium; 3–5: larger distances), and the bottom diagram shows the correlation with respect to the different interaction types of the extended S22+ database.
CCSD(T) reference values for the five different distances used for each dimer of the S22+ database. As can be seen, for the smallest distance, the errors for the different methods are 1 order of magnitude larger than those for the other distances. This comes from the rather small interaction energies that are found for most of the dimers of the dispersion-dominated and mixed-type group, which are all still negative but close to zero in the respective cases. As can be seen in Figure 4, the SAPT+D method has the smallest error to the CCSD(T) results for the short-range geometries, while the error of over 130% for DFT+D is very large. For the distances 2−5 (2 being close to the equilibrium and 3−5 being three additional distances at a longer range), the deviations of the SAPT+D and DFT+D interaction energies to CCSD(T) are about the same and vary between 6 and 10%. In comparison to this, the SAPT method always has smaller deviations for the distances 2−5 of only 3.6−5%.

In Figure 5, the overall performance of the different methods is shown with respect to the three groups, hydrogen-bridged, dispersion-dominated, and mixed-type complexes of the S22+ database. Note that in this diagram the respective short-range geometries were excluded, see above. As can be seen in Figure 5, the performance of DFT+D and SAPT+D is quite different with respect to the type of interaction; in the case of the hydrogen-bridged systems, the DFT+D method performs exceedingly well and deviates from the CCSD(T) reference energies by only about 3% on average, while it has much larger errors in case of the dispersion-dominated group of complexes. Contrary to this, the SAPT+D method is better in the case of the dispersion-dominated complexes but worse for the more strongly interacting hydrogen-bridged systems. The bottom diagram in Figure 5 shows, in addition to SAPT, DFT+D, and SAPT+D, also the deviations of the standard DFT functional without dispersion correction. As expected, the standard DFT method performs very poorly for the dispersion-dominated and also the mixed-type systems with errors of 90 and 50% from the CCSD(T) reference values. This gets much better for the hydrogen-bridged dimers, but even here, the DFT functional does not give very accurate interaction energies in comparison to the DFT method including the dispersion correction. This shows the importance of the dispersion correction also for systems where electrostatic interactions dominate. Figure 5 shows that the SAPT method shows the most balanced
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Figure 9. $E_{\text{disp}}$ (damped) versus $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ (SAPT). The top diagram shows the correlation with respect to the five individual monomer distances (1: small; 2: equilibrium; 3–5: larger distances), and the bottom diagram shows the correlation with respect to the different interaction types of the extended S22+ database.

The performance of SAPT, SAPT+D, and DFT+D is also displayed in Figures 6–8, which show correlation diagrams for the interaction energies of all 110 calculated systems of the respective methods plotted against the CCSD(T) reference interaction energies. In the two correlation diagrams in Figure 6, it can be observed that in the case of the more strongly interacting dimers, the SAPT method only slightly underestimates the CCSD(T) values for the equilibrium and larger-distance geometries, while it tends to overestimate the interaction energies for some of the hydrogen-bridged dimers in their short-range geometry.

The bottom diagram of Figure 8 shows a very good correlation between the DFT+D and CCSD(T) interaction energies for the hydrogen-bridged group indicated by the red dots in the diagram at larger interaction energies, while for some of the dispersion-dominated dimers, the DFT+D method underestimates the CCSD(T) interaction energies; see the green dots in the bottom diagram in Figure 8. In comparison to this, the SAPT+D method mostly underestimates the CCSD(T) interaction energies in the case of the hydrogen-bridged systems but has a more balanced description for the dispersion-dominated systems; see the bottom diagram in Figure 7. For the mixed-type complexes, the SAPT+D method performs only slightly better than the DFT+D method; see the top diagram in Figure 5.

The two diagrams in Figure 9 show the correlation between the sum $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ and the fitted damped dispersion energies of eq 13 with respect to the monomer distances (top diagram) and the type of interaction (bottom diagram). It can be observed that for most of the more strongly interacting dimers, the fitted SAPT dispersion correction tends to underestimate the sum of the dispersion and exchange—dispersion energy from the SAPT calculation. Again, this might indicate that the atomic dispersion coefficients and van der Waals radii assumed from the fit for the DFT+D method are not optimal for use in SAPT+D. Nevertheless, the SAPT+D method already seems to perform as good as corresponding DFT+D methods on average and, as indicated by Figure 5, appears to be even better in cases where the dispersion interaction dominates the total interaction.

In order to test the transferability of the SAPT dispersion correction, eq 13 has been evaluated for the 10 different DNA base tetrarmers of ref 65. In ref 65, the interaction energy between DNA base pair steps has been calculated with DFT−SAPT (using a slightly different xc potential than the one used in this work), considering each Watson−Crick pair as a monomer. Figure 10 compares the sum of $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ from the DFT−SAPT calculation and the SAPT+D dispersion correction. Note that in ref 65, an aug-cc-pVTZ basis set was used, which roughly yields basis set errors of 10%. Because of this, the DFT−SAPT values plotted in Figure 10 were corrected by multiplication of the aug-cc-pVTZ values by a factor of 1.1. While this, of course, is only a very rough estimate for the exact basis set limit of $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$, the diagram in Figure 10 nevertheless indicates a nice correspondence of $E_{\text{disp}}^{(2)}$ (SAPT+D) and $E_{\text{disp}}^{(2)}$ with the exception of the CG−GC base pair step. Thus, though further tests are certainly desirable, the dispersion correction to SAPT appears to give reasonable results also for other intermolecular complexes not contained in the S22+ database.

6. SUMMARY

The performance of atom−atom damped dispersion corrections used in conjunction with density functional theory (DFT)
and symmetry-adapted perturbation theory (SAPT) has been tested for an extended S22 (S22+) database of intermolecular complexes including electrostatic-dominated, dispersion-dominated, and mixed-type dimer systems at equilibrium and nonequilibrium structures. It has been shown that the damping functions in DFT+D and SAPT+D methods qualitatively differ from each other in the short-range region due to the different description of intermolecular correlation in DFT and SAPT. Therefore, a new (eq 13) dispersion correction has been proposed that may be used in SAPT calculations in order to approximate the computationally expensive dispersion and exchange−dispersion interaction energies for large systems. The parameters of this dispersion correction were optimized against accurate extrapolated CCSD(T) interaction energies for the S22 set of dimers.

While in total not as accurate as the full SAPT method, it has been found that the SAPT+D approach performs similar as the DFT+D method for the S22+ dimers if compared to extrapolated CCSD(T) reference interaction energies. However, while the DFT+D approach very well describes the interaction energies of the hydrogen-bridged systems in the S22+ database, it is found that the SAPT+D method yields smaller errors for the dispersion-dominated complexes. Possibly, this stems from the fact that in DFT+D methods, one has to assume possible double countings of electron correlation effects for short ranges. This problem, by definition, cannot occur in SAPT+D approaches.

It should be noted that, as with corresponding DFT+D approaches, the optimal parameters of the SAPT dispersion correction will depend on the underlying exchange-correlation (xc) functional used for the monomer calculations and are therefore not unique. However, in contrast to DFT+D, the dispersion correction in SAPT totally accounts for all intermolecular correlation effects and should therefore be more independent from the xc functional used to describe the other interaction energy contributions. Indeed, the nice agreement between the SAPT dispersion correction and the (estimated) intermolecular correlation contributions from a different DFT−SAPTC calculation for DNA base tetramers indicates that the SAPT dispersion correction can also be used in conjunction with other xc functionals.

**ASSOCIATED CONTENT**

* Supporting Information. Geometries for the extended S22 set, CCSD(T) interaction energies, and the extrapolation scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**

10.11. Long-range correlation energies from frequency-dependent weighted exchange-hole dipole polarisabilities

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Long-range correlation energies from frequency-dependent weighted exchange-hole dipole polarisabilities

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Long-range correlation energies between two molecules are calculated using an approximation of the single-particle density-density response function of the two systems that leads to an expression requiring only occupied orbitals and eigenvalues of the respective monomers. Dipole-dipole polarisabilities and isotropic leading-order dispersion coefficients obtained from this approximation are shown to be in a reasonable agreement with corresponding values from the experiment or dipole oscillator strength distributions. The combination of the dispersion interaction term, calculated from corresponding localised polarisabilities and properly damped at short ranges, with a hybrid-GGA functional gives a hybrid DFT+Dispersion method that has a comparable accuracy than high-level ab-initio wave function methods at a much lower computational cost. This has been analysed for a number of dimer systems from the S22 and S66×8 benchmark databases and the acetylenedicarbaldehyde dimer at equilibrium and non-equilibrium geometries.

I. DESCRIPTION OF LONG-RANGE CORRELATION ENERGIES WITHIN DENSITY FUNCTIONAL THEORY METHODS

It has now been well established that standard density functional theory (DFT) methods [1–4] based on the local density approximation (LDA) or the generalised gradient (GGA) approximation are incapable to (completely) describe the important long-range correlation contributions that occur between molecular systems that are not bound by covalent bonds [5–12]. More recent (semi-local) hybrid functionals [13–16] or meta GGA’s [17, 18], depending on the Kohn-Sham orbitals or the kinetic energy density, yield some improvement over standard functionals, yet this improvement does not originate from the correct description of the long-range correlations but from a more accurate modelling of the mid-range regions of the interaction potentials through the introduction of more parameters in the functional. The exchange-correlation functional for all these functionals can be written in the general form

\[ E_{\text{xc}}[\rho] = \int dr \rho(r) \varepsilon_{\text{xc}} \left[ \rho, \nabla^n \rho, \ldots, \phi_i, \tau \right] \]

where \( \varepsilon_{\text{xc}} \) is the exchange-correlation (xc) energy density, \( \rho \) is the electron density, \( \nabla^n \rho \) are its \( n \)-th derivatives, \( \phi_i \) is an occupied Kohn-Sham orbital and \( \tau = \sum_i |\nabla \phi_i|^2 \) is the kinetic energy density. The crucial point is now, that the xc energy density in the standard approach is only locally dependent on the density and its derivatives. Thus it can easily be verified that there can be no long-range correlation interaction contribution from the xc energy in a supermolecular Kohn-Sham calculation, i.e.

\[ \Delta E_{\text{xc}} = E_{\text{xc}}(AB) - E_{\text{xc}}(A) - E_{\text{xc}}(B) \xrightarrow{R_{AB} \to \infty} 0 \]  

where \( E_{\text{xc}}(AB) \) is the xc energy for the dimer, \( E_{\text{xc}}(A, B) \) are the xc energies for the monomers and \( R_{AB} \) denotes the distance between the two molecules.

A number of methods were developed in recent years to improve density functional theory methods to describe long-range correlation energies. Without the claim for completeness they can be categorised as follows:

- Functionals that directly incorporate nonlocal correlation energy terms, depending, however, only on the electron density and its derivatives [19–24].
- Orbital-dependent density functionals in which the functional is written in terms of Kohn-Sham orbitals and eigenvalues, e.g. functionals derived from many-body perturbation theory or the random-phase approximation [25–33].
- Hybrid methods using a mixing of standard GGA correlation functionals with a second-order perturbation theory functional [34].
- Range-separated density functionals in which the long-range correlation contribution is not described with DFT but using ab-initio wave function methods [35–42].
- Functionals in which the long-range correlation contribution is calculated separately using sums over damped atom-atom dispersion interaction energy terms (termed as DFT+D methods in this work).
- Using empirically determined atomic dispersion coefficients [43–52].
- Using dispersion coefficients determined by the exchange-hole model by Becke and Johnson [53–58].
- Methods using dispersion-correcting atom-centered one-electron potentials [59, 60].
- Symmetry-adapted intermolecular perturbation theory [4, 61] in which the intermolecular correlation contributions are calculated explicitly.
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via a perturbation theory ansatz while the intramolecular correlation energy contributions are calculated using DFT [62, 63].

Certainly, functionals that fall into the first category of the above given list lie most within the realm of density functional theory. While these nonlocal functionals are more computationally expensive than standard DFT methods, recent developments in this field have shown that they can be efficiently implemented exploiting the sparsities of quantities on the molecular quadrature grid [23, 24]. It has also been demonstrated by several groups that the functionals quite accurately describe intermolecular interaction energies [21, 23, 24]. Note that actually two types of nonlocal functionals exist: functionals that also include short-range electron-electron interaction contributions [19, 20, 22] and functionals that use a cutoff for short interelectronic distances and in which the short-range part is described by standard DFT [10, 21, 64]. Functionals of the latter type are therefore similar to range-separated functionals or DFT+D methods, however, they approximate the long-range correlation contribution by a density functional expression.

Probably the most accurate functionals describing van-der-Waals interactions are orbital-dependent density functionals depending, in contrast to hybrid functionals, also on unoccupied Kohn-Sham orbitals [25–33, 65]. These functionals are directly related to wave function theory methods as they (usually) adopt the functional form from wave function theory, e.g., many-body perturbation theory or the random-phase approximation (note that in the latter case the functional can also be more rigorously be derived starting from the fluctuation dissipation theorem [66–69]). Functionals of this form still are within the realm of DFT since the density explicitly depends on the Kohn-Sham orbitals. Therefore, via the optimised effective potential method [70–74], it is possible to derive the functional derivative for orbital-dependent functionals yielding very accurate xc potentials [75]. Unfortunately, these functionals also import the unfavourable scaling behaviour of corresponding wave function methods and can therefore be used only for the study of small molecular systems.

This problem is solved in range-separated density functionals in which the short-range part is described on the DFT level and only the long-range part is described using wave function methods [35–37, 39–42]. Thus, in these methods the problematic modelling of the interelectronic cusp explicitly present in orbital-dependent functional theory does not occur, so that a much faster convergence with respect to the basis set size is achieved. A number of range-separated methods have now also been used with success to describe intermolecular interaction energies [40, 76, 77]. The currently most popular and computationally most efficient DFT methods that include long-range correlations are methods that contain damped atom-atom dispersion interaction energy terms. Conventionally, the atomic dispersion coefficients were obtained by fitting procedures to reproduce molecular $C_6$ values, binding energies and bond distances for a number of (usually small) systems [44, 45, 47]. The coefficients obtained in this way are thus fixed values that do not depend on the chemical environment. A more recent DFT+D method by Grimme et al. uses data from time-dependent density functional theory to obtain atom-atom dispersion coefficients using frequency-dependent polarisabilities calculated for corresponding hydride molecules of the two interacting atoms [52]. While less empirical than older DFT+D methods, this approach allows also to describe hybridisation states within the molecule and should therefore be more generally applicable than DFT+D methods including fixed atomic dispersion coefficients.

Another approach that may be categorised as DFT+D method is the exchange-hole model by Becke and Johnson [53–58]. In this method the long-range interaction between two molecular systems is related to the interaction of the exchange-hole dipole moments of the two systems. This (at first sight) heuristic ansatz was used to calculate dispersion coefficients that were distributed between the atoms and combined with an empirical damping term to calculate interaction energies for a range of systems using an accompanying xc functional to account for the remaining interaction contributions [54]. The results for dispersion coefficients and intermolecular interactions obtained by this method were remarkably good [54, 55, 78]. In Ref. [56] this approach was also extended by including $C_8$ and $C_{10}$ coefficients as well.

In recent independent works Angyan [79], Ayers [80] and I [81] have analysed the origin of the exchange-hole model by Becke and Johnson starting from the exact nondamped long-range correlation energy expression to the intermolecular interaction energy (see Ref. [82] for an analysis of the link between the dispersion interaction energy with the full exchange-correlation hole). It was found that indeed the dispersion interaction energy can be related to the exchange-hole dipole moments of the interacting monomers if a number of simple approximations for the response functions of the two monomers are employed. However, the functional form for the asymptotic dispersion interaction energy obtained in this way differs from the one reported by Becke and Johnson [79–81]. It has been shown that this more rigorously derived expression yields quite accurate static polarisabilities and isotropic dispersion coefficients for a number of small molecules if the underlying mean excitation energy is approximated by the scaled HOMO-LUMO gap of the systems calculated from Hartree-Fock theory [81].

In this work the approach from Ref. [81] will be refined by using a more realistic approximation to the response function than the Unsöld approximation [83] used in Ref. [81], see section II A. Section II B shows the performance of this new approach for predicting atomic and molecular polarisabilities and dispersion coefficients. A localisation scheme is then employed, section II C, to enable the calculation of atom-atom long-range correlation energies, see section II D. This method combined with a
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proper damping function and a hybrid density-functional was then used to calculate intermolecular interaction energies for a number of systems from the S22 and S66×8 databases as well as the acetylenedicarbaldehyde dimer as a test case, see section III. Section IV summarises the results.

II. DISPERSION INTERACTIONS FROM APPROXIMATE SINGLE-PARTICLE RESPONSE FUNCTIONS

A. The weighted exchange-hole approximation to the response function

Consider two separated sybsystems $A$ and $B$ with non-overlapping electron densities $\rho_A$ and $\rho_B$. The exact correlation contribution in second order of the intermolecular fluctuation potential to the interaction energy of this system is then given by

$$
E^{(2)}_c(A - B) = -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \times \chi_A(\mathbf{r}_1, \mathbf{r}_3, \omega) \chi_B(\mathbf{r}_2, \mathbf{r}_4, \omega) \frac{1}{r_{12}} \frac{1}{r_{34}}
$$

(3)

where $\frac{1}{r_{ij}}$ is the Coulomb-interaction operator and $\chi_A(\mathbf{r}_1, \mathbf{r}_2, \omega)$ and $\chi_B(\mathbf{r}_1, \mathbf{r}_2, \omega)$ are the density-density response functions of the two systems evaluated at imaginary frequencies $\omega$. Eq. (3) is the well known Casimir-Polder expression of the dispersion interaction between two molecules $A$ and $B$ [84, 85] and apparently appeared first in a seminal work by Longuet-Higgins [86]. It is an exact equation for the second-order intermolecular correlation energy provided that the exact response functions $\chi_A$ and $\chi_B$ of the subsystems $A$ and $B$ are known. In praxis, however, the response functions of the monomers have to be approximated. Basically there exist two options for this: the uncoupled approach in which the response function is written in terms of orbitals and orbital energies that are the eigenfunctions and eigenvalues of a single-particle operator and the coupled approach where (at least partially) the electron-electron interactions neglected in the uncoupled approach are accounted for. The most often used coupled methods are time-dependent Hartree-Fock [84] (also known as random-phase approximation) and time-dependent density functional theory [87]. Both methods start from the same expression for the uncoupled response function

$$
\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = -4 \sum_{ia} \frac{\epsilon_{ia}}{\omega^2 + \epsilon_{ia}^2 + \omega^2} \phi_{ia}(\mathbf{r}_1) \phi_{ia}(\mathbf{r}_2)
$$

(4)

and then take higher order electron-electron interactions into account through the solution of a Dyson-type equation that can be solved in several ways [88]. In Eq. (4) indices $i, (j, k, \ldots)$ label occupied orbitals and indices $a, (b, c, \ldots)$ label unoccupied indices and the convention is used that $\epsilon_{ia} = \epsilon_a - \epsilon_i$ and $\phi_{ia}(\mathbf{r}) = \phi_i(\mathbf{r})\phi_a(\mathbf{r})$ with $\epsilon_{ia}$ and $\phi_{ia}$ denoting occupied/unoccupied orbital energies and orbitals, respectively. Closed-shell formalism is used throughout in this work unless otherwise noted. Moreover it is assumed that the orbitals are real-valued without loss of generality.

If the response functions of the monomers $A$ and $B$ are approximated by Eq. (4) and inserted in Eq. (3) then the so-called uncoupled dispersion interaction energy is obtained that is of zeroth order in the intramonomer fluctuation potential. This is the intermolecular correlation contribution that is contained in supermolecular second-order perturbation theory methods, e.g., second-order Møller-Plesset perturbation theory [89, 90]. In Ref. [81] the uncoupled response function of Eq. (4) has been approximated by replacing the orbital energy differences $\epsilon_{ia}$ all by a constant mean excitation energy $\Delta \epsilon$ which corresponds to the so-called Unsöld approximation [83, 85, 91] or CEDA (common energy denominator approximation) [92, 93] to the response function:

$$
\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = -4 \frac{\Delta \epsilon}{\Delta \epsilon^2 + \omega^2} \sum_{ia} \phi_{ia}(\mathbf{r}_1) \phi_{ia}(\mathbf{r}_2)
$$

(5)

This is a rather crude approximation since it assumes that the response function, if evaluated at real frequencies, has only one single pole while the true response function has infinitely many (at the excitation energies of the many-body system). Nevertheless, using Eq. (5) with a proper choice for $\Delta \epsilon$ it has been shown in Ref. [81] that reasonable dipole-dipole polarisabilities and $C_6$ dispersion coefficients can be obtained for a range of small molecules. Sylvain et al. have, after applying the orbital basis set completeness relation (see below), investigated modifications to Eq. (5) using some scaled sums over inverse occupied orbital energies instead of the term $\Delta \epsilon/(\Delta \epsilon^2 + \omega^2)$ and obtained reasonable results for static dipole polarisabilities by this approach using, however, very small basis sets (this work was done in 1987) [91]. In this work a more reasonable approximation is used by retaining the occupied orbital energy shifts and replacing only the unoccupied orbital energies in Eq. (4) by a constant value $\overline{\epsilon}$: $\epsilon_{ia} \approx \overline{\epsilon} - \epsilon_i = \Delta \epsilon_i$. With this the uncoupled response function can be written as

$$
\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = -4 \sum_{ia} \frac{\Delta \epsilon_i}{\Delta \epsilon_i^2 + \omega^2} \phi_{ia}(\mathbf{r}_1) \phi_{ia}(\mathbf{r}_2)
$$

(6)

and using the completeness relation of the orbital basis $\sum_i \phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2) + \sum_a \phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$:
with the electronic density $\rho(\mathbf{r}) = 2\sum_i \phi_i^2(\mathbf{r})$. The second term in parenthesis in Eq. (9) has the same form as the exchange hole density [53, 81] but with weight factors $\lambda_i(\omega)$ within the summation that emphasize orbital contributions with higher lying orbital energies. Because of this, I will term this quantity as a ‘weighted’ exchange-hole approximation are given by

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -4\sum_i \frac{\Delta \epsilon_i}{\Delta \epsilon_i^2 + \omega^2} \left[ \phi_i^2(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \sum_j \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2) \right]$$  \hspace{1cm} (7)

$$= -\sum_i \lambda_i(\omega) \left[ \phi_i^2(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \sum_j \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2) \right]$$  \hspace{1cm} (8)

$$= -\rho(\mathbf{r}_1) \left[ \frac{2\sum_i \frac{1}{2} \lambda_i(\omega) \phi_i^2(\mathbf{r}_1)}{\rho(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2) - \frac{2\sum_{ij} \frac{1}{2} \lambda_i(\omega) \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2)}{\rho(\mathbf{r}_1)} \right]$$  \hspace{1cm} (9)

in parenthesis in Eq. (9), which is a local contribution to the response function, weights energetically higher lying orbital contributions favoured in comparison to lower lying orbital contributions. The expression in Eq. (9) may be compared with the Unßöld approximation to the response function in Ref. [81], Eq. (9) in which the first term from Eq. (9) reduces to a scaled delta operator and the second term to the exchange-hole density.

The response function of Eq. (8) fulfills the desired symmetry, reciprocity and charge condition [68, 94]:

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = \chi_0(\mathbf{r}_2, \mathbf{r}_1, i\omega)$$  \hspace{1cm} (10)

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, -i\omega) = \chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega)$$  \hspace{1cm} (11)

and

$$\int d\mathbf{r}_1 \chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -\int d\mathbf{r}_1 \sum_i \lambda_i(\omega) \left[ \phi_i^2(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \sum_j \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2) \right]$$

$$= -\sum_i \lambda_i(\omega) \phi_i^2(\mathbf{r}_2) + \sum_{ij} \lambda_i(\omega) \phi_{ij}(\mathbf{r}_2) \delta_{ij}$$

$$= 0$$  \hspace{1cm} (12)

### B. Dipole polarisabilities and dispersion coefficients from weighted exchange-hole response functions

Generally, frequency dependent dipole(-dipole) polarisabilities can be computed from the response function $\chi(\mathbf{r}_1, \mathbf{r}_2, i\omega)$ using

$$\alpha_{\alpha\beta}(\omega) = \int d\mathbf{r}_1 d\mathbf{r}_2 r_{1\alpha}^* r_{2\beta}^* \chi(\mathbf{r}_1, \mathbf{r}_2, i\omega) \quad \alpha, \beta \in \{x, y, z\}$$  \hspace{1cm} (13)

and thus, using Eq. (8), dipole polarisabilities from the weighted exchange-hole approximation are given by

$$\alpha_{\alpha\beta}(\omega) = -\sum_i \lambda_i(\omega) \langle \phi_i | r^\alpha r^\beta | \phi_i \rangle + \sum_{ij} \lambda_i(\omega) \langle \phi_i | r^\alpha | \phi_j \rangle \langle \phi_j | r^\beta | \phi_j \rangle$$  \hspace{1cm} (14)

with $\langle \phi_i | r^\alpha r^\beta | \phi_i \rangle = \int d\mathbf{r} r^\alpha r^\beta \phi_i^2(\mathbf{r})$ which is a simple second moment integral and $\langle \phi_i | r^\alpha | \phi_j \rangle = \int d\mathbf{r} r^\alpha \phi_{ij}(\mathbf{r})$ which is a simple dipole moment integral over two occupied orbitals $i$ and $j$. The isotropic (average) dipole polarisabilities are given by $\bar{\alpha} = \frac{1}{3} \sum_{\alpha\alpha} \alpha_{\alpha\alpha}$.

The asymptotic form of the long-range correlation energy of Eq. (3) between two closed-shell molecules $A$ and $B$ is given by [85]

$$E_{\text{disp}}(A - B) = \frac{C_0^{AB}}{r_{AB}^6} - \frac{C_6^{AB}}{r_{AB}^8} - \frac{C_8^{AB}}{r_{AB}^{10}} - \ldots$$  \hspace{1cm} (15)

where $r_{AB}$ denotes the distance between the two monomers and $C_0, C_6, \ldots$ are the isotropic dispersion coefficients. The leading-order $C_0$ coefficient can be obtained from the frequency-dependent dipole polarisabilities $\Pi^A(i\omega)$ and $\Pi^B(i\omega)$ of the monomers using the Casimir-Polder expression [85]:

$$C_0^{AB} = \frac{3}{\pi} \int_0^\infty d\omega \Pi^A(i\omega) \Pi^B(i\omega)$$  \hspace{1cm} (16)

Higher-order polarisabilities are obtained using similar
equations as Eq. (16) by replacing the dipole polarisabilities with quadrupole, octupole, etc. polarisabilities. The isotropic $C_6$ dispersion coefficients in the weighted exchange-hole approximation are readily obtained by insertion of Eq. (14) evaluated for the two monomers $A$ and $B$ into Eq. (16).

Isotropic polarisabilities were calculated using Eq. (14) with Hartree-Fock (HF) and density-functional theory (DFT) orbitals and orbital eigenvalues, respectively. In case of DFT a hybrid functional termed HCTH(0.7x) containing a 30% exact exchange admixture was used, see section II D for details. Since the occupied orbital energies are quite different in both cases, the mean unoccupied orbital energies $\overline{\rho}$ used in the response function in Eq. (9) were chosen differently in both cases. For this a hand-optimisation of the value of $\overline{\rho}$ for the molecules from table I has been made, such that the resulting polarisabilities have the least deviation to the experimental reference values from the last column of table I. The result of this optimisation yielded $\overline{\rho} = 0.3$ in case of HF and $\overline{\rho} = 0.4$ in case of HCTH(0.7x), indicating that the HCTH(0.7x) eigenvalues generally lie higher than corresponding orbital energies from HF. Note that it was found that the optimal value of $\overline{\rho}$ showed not a large dependency on the orbitals, i.e., for hybrid functionals with the same amount of exact exchange the optimal value of $\overline{\rho}$ was very similar. The results for the static polarisabilities are shown in table I. It can be observed that both, for HF and HCTH(0.7x) there is a fairly good agreement with the reference polarisabilities. The HCTH(0.7x) polarisabilities tend to be larger on average than the HF polarisabilities and are slightly more accurate with a deviation of 11.6% to the reference values compared to an average deviation of 14.2% in case of HF.

Using the optimised mean values of $\overline{\rho}$, isotropic $C_6$ dispersion coefficients were calculated using Eq. (16) for the molecules of the first column of table II. A comparison of the frequency dependence of the respective polarisabilities with those from time-dependent Hartree-Fock (TDHF) polarisabilities showed that the decrease of the polarisabilities from Eq. (14) for larger imaginary frequencies is too slow compared to TDHF, yielding significantly larger dispersion coefficients. Therefore, similar to the method by Tang [95], a scaling factor is introduced in the $\overline{\rho}(i\omega)$ factors in the response function of Eq. (8) which is then given by

$$\overline{\rho}_s(i\omega) = \frac{4(\overline{\rho} - \varepsilon_i)}{(\overline{\rho} - \varepsilon_i)^2 + \mu \omega^2}$$

(17)

with $\mu$ having generally a value of larger than one to correct the frequency dependence of the weighted exchange-hole polarisabilities. As for the static dipole polarisabilities the value of $\mu$ was optimised both, for HF and HCTH(0.7x) to reproduce isotropic $C_6$ dispersion coefficients from dipole oscillator strength distributions (DOSD), see table II. The result of this optimisation was $\mu = 1.5$ in case of HF and $\mu = 1.95$ in case of HCTH(0.7x). The $C_6$ dispersion coefficients for HF and HCTH(0.7x) using these optimised values of $\mu$ are shown in table II. It can be seen that the HCTH(0.7x) values are a bit lower on average than the HF values and the mean percentual deviation of the HCTH(0.7x) dispersion coefficients to the DOSD reference values of the last column of table II is a bit larger (13.8%) than with HF (10.5%). Notable cases where both, the HF and HCTH(0.7x) dispersion coefficients have a larger deviation to the corresponding DOSD dispersion coefficient are H$_2$ where the $C_6$ value is strongly underestimated and CO$_2$ for which a significant overestimation of the $C_6$ value is found, see table II. Note that in both cases the same is true also for the static dipole polarisabilities, see table I.

Figure 1 shows the frequency dependence (at imaginary frequencies) of the weighted exchange-hole polarisabilities from Eq. (14) calculated with the HCTH(0.7x) functional in comparison with dynamic TDHF polarisabilities. As can be seen in case of the H$_2$O and CO molecule, figures 1a and 1b, the TDHF polarisabilities are slightly overestimated at smaller values of $\omega$ while for larger frequencies the TDHF polarisabilities are underestimated. Thus, when calculating $C_6$ coefficients from the weighted exchange-hole (WXhole) polarisabilities one can expect some error cancellation if the integral in Eq. (16) is evaluated. In case of the C$_2$H$_2$ molecule, see figure 1c, the static WXhole polarisability underestimates the TDHF value but starting from $\omega = 0.2$ is fairly close to the TDHF curve.

C. Localised polarisabilities from the weighted exchange-hole approximation

In order to obtain localised polarisabilities from Eq. (13) the total molecular volume is partitioned using a superposition of atomic densities similar to the scheme used in Refs. [54, 96, 97]:

$$\int dr \rightarrow \int dr \sum_n w_n(r) = \int dr \sum_n \rho_n(r)$$

(18)

where $\rho_n(r)$ corresponds to the free spherical density of atom $n$ and $\rho^{\text{total}}(r) = \sum_n \rho_n(r)$ so that the sum of the individual weight functions $w_n(r)$ yields $\sum_n w_n(r) = 1$. In this work the atomic densities are approximated by spherical Slater densities determined using Salter’s rules, see Ref. [98]. The insertion of Eq. (18) into Eq. (13) yields (compare Refs. [99–102] for related distribution schemes):

$$\alpha_{\alpha\beta}(\omega) = \int dr_1 \sum_n w_n(r_1) \int dr_2 \hat{r}_{1}^{\alpha} \hat{r}_{2}^{\beta} \chi(r_1, r_2, \omega)$$

$$\alpha_{\alpha\beta} \in \{x, y, z\}$$

(19)

so that one may write

$$\alpha_{\alpha\beta}(\omega) = \sum_n \alpha^{n}_{\alpha\beta}(\omega)$$

(20)
\[ \alpha_n^\alpha(\omega) = \int dr_1 w_n(r_1) r_1^\alpha \int dr_2 r_2^\beta \chi(r_1, r_2, \omega) \] \tag{21}

which can be identified as the contribution of site \( n \) (usually referring to an atom within the molecule) to the total polarisability. However, while now Eq. (20) yields an exact decomposition of the total polarisability into atomic terms, this decomposition is unfortunately not unique. This can be understood if one considers the dipolar charge distribution

\[ d^\beta(r_1, \omega) = \int dr_2 r_2^\beta \chi(r_1, r_2, \omega) \] \tag{22}

According to Eq. (12) this charge distribution has a charge equal to zero and thus its dipole moment is origin independent as it should be and yields the total polarisability:

\[ \int dr_1 r_1^\alpha d^\beta(r_1, \omega) = \alpha_{\alpha\beta}(\omega) \] \tag{23}

This, however, does not in general hold for the atomic dipolar charges defined implicitly in Eq. (21), that is

\[ \int dr_1 w_n(r_1) d^\beta(r_1, \omega) \neq 0 \] \tag{24}

and therefore the corresponding atomic dipole polarisabilities are not origin independent. It has been observed that the decomposition according to Eqs. (20)-(21) can quite strongly depend on the choice of the origin (see also Ref. [103]). Because of this, in order to obtain a reasonable and unique partitioning of the molecular polarisability into atomic ones the unwanted charges from Eq. (24) have to be removed. Such localisation schemes have, e.g., been developed by LeSuer and Stone [104, 105] or Wheatley and Lillestolen [106, 107]. In this work the method by Wheatley and Lillestolen [106, 107] is adopted. For this the origin for coordinate \( r_1^\alpha \) in Eq. (21) is set to the respective atomic coordinates \( r_\alpha^m \), i.e. \( R_\alpha^m = r_\alpha^m - r_\alpha^n \) so that the atomic polarisabilities decompose into a dipole-dipole and a charge-dipole term [96, 97, 101]:

\[ \alpha_{\alpha\beta}^n(\omega) = \int dr_1 w_n(r_1) R_\alpha^m d^\beta(r_1, \omega) + r_\alpha^n \int dr_1 w_n(r_1) d^\beta(r_1, \omega) \] \tag{25}

The second term in Eq. (25) is also termed as charge-flow [105] or charge delocalisation term [96] as it quantifies the sum of charge contributions that are erroneously assigned to atom \( n \). Following Wheatley and Lillestolen one can solve a system of coupled differential equations to correctly distribute these charge-flow contributions, generally starting from:

\[ \Delta_n = \sum_m \Delta_{n\rightarrow m} - \Delta_{m\rightarrow n} \] \tag{26}

with \( \Delta_n \) being the required change of charge in the region of atom \( n \) and \( \Delta_{n\rightarrow m} \) being the charges that are erroneously assigned to different centres. Obviously, in order to preserve symmetry, \( \Delta_{n\rightarrow m} = -\Delta_{m\rightarrow n} \). The method requires a ‘rate constant’ as input that defines the connectivities of the atoms within the molecule. While in their first work [106] Wheatley et al. simply defined covalently bound atoms as connected, they extended this approach by measuring the charge densities at the \( mn \) midpoint \((r_n + r_m)/2\) between two atoms, see Ref. [107] for details. With this method the localisation procedure could also be applied to molecular systems that are not simply connected. I will discuss this point in more detail in section II D. As a result of the method of Wheatley and Lillestolen one obtains an antisymmetric matrix containing the individual terms \( \Delta_{n\rightarrow m} \):

\[ D^\alpha = \begin{pmatrix} 0 & \Delta_{1\rightarrow 2}^\alpha & \cdots \\ -\Delta^\alpha_{1\rightarrow 2} & 0 & \\ \vdots & \ddots & 0 \end{pmatrix} \] \tag{27}

and \( \alpha \) here denoting the cartesian component. The charge-dipole contribution to be assigned to site \( n \) can then be calculated as

\[ q_{\alpha\beta}^n(\omega) = \sum_m \frac{\Delta_{\alpha\beta}^{m\rightarrow n}}{\sum_k |D_{\alpha\beta}^{m\rightarrow n}|} \int dr_1 w((r_1) d^\beta(r_1, \omega) \] \tag{28}

where \( \sum r_1^\beta \int dr_1 w(r_1) d^\beta(r_1, \omega) \) is the total charge-flow and \( \sum_{\alpha\beta} |D_{\alpha\beta}^{m\rightarrow n}| \) measures the contribution that should be assigned to site \( n \). With this result localised polarisabilities are then given by

\[ \alpha_{\alpha\beta}^n(\omega) = \int dr_1 w_n(r_1) R_\alpha^m d^\beta(r_1, \omega) + q_{\alpha\beta}^n(\omega) \] \tag{29}

and the corresponding localised isotropic polarisabilities are

\[ \tau_{\alpha\alpha}^n(\omega) = \frac{1}{3} \sum_\alpha \alpha_{\alpha\alpha}^n(\omega) \] \tag{30}

Table III shows localised isotropic polarisabilities obtained from Eq. (29) for some small molecules in comparison to localised coupled Hartree-Fock (CHF) polarisabilities from Lillestolen et al. [106] (at \( \omega = 0 \)). It can be seen that for those molecules where the total polarisabilities from WXhole and CHF are close to each other, namely CO, C2H2 and C2H4, the percentual contributions of the atomic polarisabilities to the total polarisability are quite similar. In contrast to this, for H2O and CO2 the absolute values for the localised polarisabilities from WXhole and CHF deviate much more from each other. In case of CO2 one even finds that the WXhole polarisability for carbon is almost twice as large than the corresponding CHF value, see table III. In fact, the localised polarisabilities for carbon for the molecules considered seem to be less dependent on the bonding partners in the WXhole case.
10. Intermolecular interactions

than for CHF: they range between 7.46 a.u. (CO$_2$) to 8.61 a.u. (C$_2$H$_2$) compared to 3.97 a.u. (CO$_2$) to 9.46 a.u. (C$_2$H$_2$) in case of CHF. This probably is related to deficiencies of the underlying single-particle response function that does not describe any coupling effects.

D. Correlation energies from the localised weighted exchange-hole polarisabilities

Using the localised isotropic polarisabilities from Eq. (30) the long-range correlation energy between two molecules A and B can be calculated as

$$E_{c}^{(2)}(A-B) = -rac{3}{π} \sum_{n \in A} \sum_{m \in B} \frac{1}{R_{nm}^{6}} \int_{0}^{∞} dω \, ρ^n(ω) |\nabla ρ^n(ω)| (ω)$$

(31)

which is, in contrast to the nonexpanded dispersion energy expression from Eq. (3), valid only, however, if the two monomers have a large distance from each other, that is, if the distances $R_{nm}$ between two atoms $n$ and $m$ are larger than typical intramolecular bond distances within the molecule. At shorter distances the correlation contribution from Eq. (31) has to be properly damped. This is true also, because the aim is here to combine Eq. (31) with density-functional theory to account for the short-range interaction contributions as is done in common DFT+D methods. Standard (hybrid-)DFT methods are able to describe intermolecular correlation energies if the monomers are closer to each other. Thus Eq. (31) has to be damped for short distances $R_{nm}$ using

$$E_{c}^{(2)}(A-B) = -rac{3}{π} \sum_{n \in A} \sum_{m \in B} \frac{f_{\text{damp}}(R_{nm})}{R_{nm}^{6}} \int_{0}^{∞} dω \, ρ^n(ω) |\nabla ρ^n(ω)| (ω)$$

(32)

with

$$f_{\text{damp}}(R_{nm}) = \begin{cases} 0 & \text{if } R_{nm} \to 0 \\ 1 & \text{if } R_{nm} \to ∞ \end{cases}$$

In this work the following form of the damping function is used

$$f_{\text{damp}}(R_{nm}) = \left(\frac{1}{2} \left( \text{erf} \left[ p_1 (R_{nm} + p_2) \right] + \text{erf} \left[ p_1 (R_{nm} - p_2) \right] \right) \right)^p$$

(33)

including the parameters $p_1$, $p_2$ and $p_3$ to be determined. Note that this form for the damping function is based on the two-error function used by Dutoi and Head-Gordon for calculating attenuated two-electron integrals [108].

Since the form of the damping function will depend on the type of density functional used to calculate the short-range contributions to the interaction energy, the problem of combining Eq. (32) with supermolecular DFT interaction energies will now briefly be discussed. Studying the interaction potentials of rare gas dimers from some common density functionals it has been found by a number of groups that some functionals yield some attractive interactions in these dimers while others do not [109, 110]. Functionals that fall into the first type of category are, e.g., PBE (Perdew-Burke-Ernzerhof) [111], PW91 (Perdew-Wang) [112] and TPSS (Tao-Perdew-Staroverov-Scuseria) [18], and functionals that fall in the second group of functionals are, e.g., BLYP (Becke-Lee-Yang-Parr) [113, 114] and B3LYP (Becke’s 3-parameter hybrid density functional) [13, 14]. Thus one finds that apparently those functionals that obey the Lieb-Oxford bound [115], namely PBE, PW91 and TPSS, provide also more accurate interaction energies for van-der-Waals systems. However, if Eq. (32), which is negative definite, is to be combined with supermolecular DFT interaction energies, it would be desirable that the corresponding functional would not mimic dispersion interactions, otherwise there would be some double-counting of electron correlation effects in the mid-range region of the interaction potentials. One possibility to solve this problem would be to use so-called short-range density functionals [21, 36, 38, 116, 117] which are used in this work to calculate the two-electron integrals [108].

The general form of the HCTH functional is given by the following equations [118, 119]

$$E_{xc}^{\text{HCTH}} = E_{xc}^{\text{HCTH}} + E_{xc}^{\text{HCTH}}$$

(34)

$$E_{xc}^{\text{HCTH}} = \sum_{σ} \int dρ \, ε_{\text{LSDA}}(ρσ) g_{σω}(s_{σ}^2)$$

(35)

$$g_{σω} = \sum_{i=0}^{M} c_{σω,i} u_{σω,i}$$

(36)

$$u_{σω} = γ_{σω} s_{σ}^2 (1 + γ_{σω} s_{σ}^2)^{-1} \quad γ_{σω} = 0.004$$

(37)

$$E_{xc}^{\text{HCTH}} = \sum_{σ} E_{xc}^{\text{HCTH}}$$

(38)

$$E_{xc}^{\text{HCTH}} = \int dρ \, ε_{\text{LSDA}}(ρσ) g_{σω}(s_{σ}^2)$$

(39)

$$g_{σω} = \sum_{i=0}^{M} c_{σω,i} u_{σω,i}$$

(40)

$$u_{σω} = γ_{σω} s_{σ}^2 (1 + γ_{σω} s_{σ}^2)^{-1} \quad γ_{σω} = 0.2$$

(41)

$$E_{xc}^{\text{HCTH}} = \int dρ \, ε_{\text{LSDA}}(ρσ) g_{σω}(s_{σ}^2)$$

(42)

$$g_{σω} = \sum_{i=0}^{M} c_{σω,i} u_{σω,i}$$

(43)

$$u_{σω} = γ_{σω} s_{σ}^2 (1 + γ_{σω} s_{σ}^2)^{-1} \quad γ_{σω} = 0.0064$$

(44)

$$s_{σ}^2 = \frac{1}{2} \left( s_{σ}^2 + s_{σ}^3 \right)$$

(45)

with $ε_{\text{LSDA}}$ and $ε_{\text{LSDA}}^{\text{sigma}}$ corresponding to the local spin-
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density approximation exchange- and correlation functional kernels. In the HCTH functional the number of terms in Eqns. (36), (40) and (43) is set to $M = 4$ leading to 15 parameters altogether. The HCTH functional is chosen in this work since it does not obey the Lieb-Oxford bound [119] and is therefore a more suitable functional for the current purpose than other functionals, see above. Moreover, the form of the functional yields a good flexibility which is advantageous for adapting the functional to the long-range correlation term of Eq. (32).

Instead of using extensive fitting procedures in order to derive the parameters from Eqns. (33), (36), (40) and (43), the following strategy has been used: the parameters $p_1$ and $p_2$ were fixed to values of $p_1 = 2.0$ and $p_3 = 4.0$ while parameter $p_2$ has been set to $p_2 = s_{vdW}(R_{vdW}^{c} + R_{vdW}^{m})$ where $s_{vdW}$ is a scaling parameter and $R_{vdW}^{c}$ and $R_{vdW}^{m}$ are the van-der-Waals radii of atoms $n$ and $m$. The latter were taken from Ref. [120] and are determined by calculating the repulsive walls in the interaction energy curve for the interactions of the respective element with various probes using relativistic CCSD(T) calculations. Then the interaction energies of several small dimers in their equilibrium structure were calculated using supermolecular DFT with the HCTH functional using several parametrisations as implemented in the Molpro [121] program package, namely HCTH93 [118], HCTH120 and HCTH147 [119]. It was found that, for the cases considered, the HCTH147 functional almost always underestimated the binding energy compared to CCSD(T) reference values. The addition of the undamped dispersion interaction energies calculated by Eq. (31), however, lead to interaction energies too large in comparison with the reference values. Because of this the interaction energies from the HCTH functional in the HCTH147 parametrisation were made more repulsive in the following way: firstly the functional has been turned into a hybrid functional, termed as HCTH(0.7x) in this work, using a 30% admixture of exact exchange:

$$E_{xc}^{HCTH(0.7x)} = a_x E_x^{HCTH} + (1-a_x) E_x^{mol} + E_c^{HCTH}$$

(47)

with the nonlocal exact-exchange functional given by $E_x^{mol} = - \sum \langle \phi_{ij}|\phi_{ij} \rangle$. Secondly, it was found that particularly the squared contribution $u_{a\sigma}^2$ to the enhancement factor of Eq. (36) lead to a considerable decrease of the interaction energy for the test cases considered. The original value of $c_{x\sigma}^2 = 5.5721$ from the HCTH147 functional [119] has therefore been modified such that the combined DFT+Disp interaction energies match corresponding CCSD(T) interaction energies. This hand-optimisation lead to a value of $c_{x\sigma} = 6.0$. Finally, the scaling parameter $s_{vdW}$ used to calculate the parameter $p_2$ of the damping function in Eq. (33), see above, has been determined by studying the equilibrium region of the potential energy curves of the (C2H4)2 and C2H4-C2H2 dimers, see section III B. It was found that a value of $s_{vdW} = 0.6$ yielded the best agreement with CCSD(T) reference interaction energies for these two systems in the close minimum region.

The total interaction energy of a dimer $AB$ has been calculated by adding the damped dispersion interaction energy of Eq. (32) to the supermolecular DFT interaction energy

$$E_{int}^{WXhole} = E^{HCTH(0.7x)}(AB) - E^{HCTH(0.7x)}(A - B)$$

(48)

where $E^{HCTH(0.7x)}$ denotes the total energy obtained with the HCTH(0.7x) functional from Eq. (47) and the acronym ‘WXhole’ (weighted exchange hole) will be used for the whole method for convenience in the following. All parameters defining Eq. (48) are compiled in table IV.

It has to be noted that in Eq. (IV) the long-range correlation contribution $E_x^{(2)}(A - B)$ is calculated in a perturbative way, that is, using solely frequency-dependent polarisabilities of the monomers $A$ and $B$. There exist also two other possibilities to calculate this contribution. Firstly, one could use the supermolecular method for the long-range correlation energy as well, by calculating the term $E_x^{(2)}(AB)$ for the dimer system and subtract therefrom the monomer contributions $E_x^{(2)}(A, B)$. Secondly, defining the monomer regions within the dimer using some cutoff criteria, the term $E_x^{(2)}$ could also be calculated using the localised polarisabilities calculated for the atoms within the dimer. While for standard DFT+D all three approaches are identical, since the atomic dispersion coefficients in these methods are the same for the atoms within the monomers and the supermolecule, this is not the case in the present approach. This is so, because firstly the molecular orbitals and eigenvalues of the dimer are different from the set of monomer orbitals and eigenvalues. Actually this change of the electronic structure through a perturbing electric field of a neighbouring molecule presents a relaxation effect that is missing in standard force-field descriptions of the dispersion interaction energy. Secondly, however, the localisation scheme by Wheatley and Lillestolen used in this work depends on a connection matrix for the system that defines to which neighbouring atoms the unwanted charge-contributions should be assigned to, see Refs. [106, 107]. It has been found that all three ways to calculate $E_x^{(2)}(A - B)$ described above give practically the same result if the monomers are far apart from each other while in case of smaller monomer distances signif-
significant differences were observed in some cases. As the calculation of the long-range correlation energy within the dimer, more precisely, the interaction contribution to this energy, will depend quite strongly on the choice of the connection matrix, in this work the perturbative way to calculate $E^{(2)}_c(A - B)$ is prevered over the other two options. These will be investigated in more detail in another work [122].

III. RESULTS

Intermolecular interaction energies were calculated for various benchmark sets (see the following subsections) using the method described in section II.D that will be termed as WXhole method in the following. In all cases the the aug-cc-pVTZ basis set [123] was used which was found to yield results fairly close to the basis set limit. In fact, it was found that already the aug-cc-pVDZ basis set [123] turned out to be sufficiently large in most cases to obtain converged results. Notable exceptions to this were the σ-stack bound benzene dimer (section III.A) where a relative change of the interaction energy of ~6.7% was observed and the stacked indole-benzene dimer (section III.A) where a relative change of ~3.5% was observed upon increase of the basis set from aug-cc-pVDZ to aug-cc-pVTZ. The threshold for molecular integration grids in the DFT calculations and the calculation of the localised polarisabilities was set to a value of $10^{-8}$ that adapts the integration grid such that the numerical integration over the Slater-Dirac exchange energy kernel does not differ by more than this value from the corresponding analytical integral for each respective molecule. This value turned out to be sufficiently accurate. The frequency integration in Eq. (32) was done numerical using a 10-point Gauss-Legendre quadrature [124]. For the adenine-thymine base pair calculations (section III.A) density fitting was used to approximate the Coulomb- and (exact-)exchange matrices employing the corresponding cc-pVTZ-JKFit auxiliary basis sets by Weigend [125] augmented with one additional diffuse function by building the progression ratio $\epsilon_1^2/\epsilon_2$ where $\epsilon_1$ was the most-diffuse exponent already present and $\epsilon_2$ the next most diffuse one if both existed, or $\epsilon_1/2.5$ if only one exponent existed beforehand (implemented by Gerald Knizia in the Molpro basis set library [121]). All calculations were counterpoise corrected with the scheme by Boys and Bernardi [126] to reduce the basis set superposition error.

In case of the potential energy curves for the $(C_2H_4)_2$, C$_2$H$_4$-C$_2$H$_2$ and C$_2$(CHO)$_2$ dimers explicitly correlated second-order Møller-Plesset (MP2) and coupled-cluster singles doubles (with and without perturbative triples) (CCSD/CCSD(T)) calculations were performed as reference [127–129]. Core electrons were not correlated. The aug-cc-pVDZ basis set was employed for these calculations. Since the use of this basis set in explicitly correlated calculations generally gives results smaller than corresponding basis set extrapolated values, the F12a model was used for the coupled-cluster calculations as this is known to yield results slightly overestimating the complete basis set limit results if large basis sets are used. Moreover, the triples correction was calculated without using F12 terms and therefore has been scaled by the ratio $E^{MP2-F12}/E^{MP2}$ as proposed and tested in [129] with $E^{c-F12}$, $E^{c-MP2}$ being the correlation energies of MP2-F12 and MP2, respectively. The CABS (complementary auxiliary basis set) singles correction was included in the reference energy as proposed in Refs. [127, 128].

All calculations were performed using the Molpro quantum chemistry package [121].

A. S22 dimer systems

The S22 database of intermolecular complexes, developed by Hobza and co-workers [130], comprises hydrogen-bridged systems (lines 1-6 in table V), dispersion dominated systems (lines 7-14 in table V) and mixed type systems, i.e., systems in which the electrostatic and dispersion interactions have an equal weight (lines 15-22 in table V). The geometries for the dimers can be found in Refs. [130, 131]. The basis-set extrapolated MP2 and CCSD(T) results shown in table V are taken from Ref. [132] and slightly deviate from the original values due to better extrapolation schemes in some cases, see Ref. [132] for more details.

Table V shows the interaction energies for the S22 complexes calculated with the WXhole method compared to extrapolated MP2 and CCSD(T) results. It can be observed that for most of the hydrogen-bridged systems the MP2 values are closer to the CCSD(T) results than the interaction energies from WXhole. Only in case of 2-Pyridoxine-2-Aminopyridine that forms a double O-H/N-H hydrogen-bond the interaction energy from WXhole is clearly closer to the CCSD(T) value than the MP2 interaction energy. In total, the mean absolute error of the WXhole method for the hydrogen-bridged systems is not much larger than with MP2 and amounts to 0.22 kcal/mol only, see upper panel in figure 2. In case of the dispersion dominated complexes, see group in the middle in table V, it is known that MP2 in most cases crucially overestimates the CCSD(T) interaction energies due to an improper description of the dispersion interaction energy on an uncoupled Hartree-Fock level, see Refs. [89, 90, 133]. In contrast to this, the average percentual deviation of WXhole to CCSD(T) for the dispersion dominated group is much smaller than with MP2, see table V and lower panel of figure 2. However, it can be observed that in some cases the WXhole method strongly underestimates the CCSD(T) reference interaction energies, namely the Bz-CH$_4$ and the stacked Bz$_2$ (benzene) dimer, see table V. In case of the stacked Bz dimer this will be investigated more in detail in section III.C. For the mixed-type complexes again the WXhole method performs clearly better than MP2 and has an average abso-
lute error of 0.2 kcal/mol only to the CCSD(T) values.

As a consequence the total performance of the WX-
hole method for the S22 complexes is much better than
with MP2 if the CCSD(T) method is taken as reference,
see figure 2. However, the S22 database comprises only
dimers in their equilibrium structure and is therefore not
sufficient to analyse the quality of a method to reproduce
potential energy surfaces. Thus, in the following, the per-
formance of the WXhole method will also be tested for
non-equilibrium geometries for some dimer systems.

B. Potential energy curves for \( (\text{C}_2\text{H}_4)_2 \) and
\( \text{C}_2\text{H}_4\text{-C}_2\text{H}_2 \)

The interaction energies for the \( (\text{C}_2\text{H}_4)_2 \) and \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_2 \) dimers were calculated at non-equilibrium struc-
tures by decreasing and increasing the distance of the
centres of mass in both cases relative to to their equi-
lbrium structures from the S22 database. The resulting
potential energy curves for WXhole and explicitly corre-
lated methods are shown in figures 3 and 4. In case of
\( \text{C}_2\text{H}_4\text{-C}_2\text{H}_2 \) all methods have their minimum at about the
same distance, see figure 3, while for \( (\text{C}_2\text{H}_4)_2 \) the mini-
um of the potential energy curve of WXhole is slightly
displaced by 0.1 Å to a larger monomer distance com-
pared to MP2 and CCSD(T). It can be seen that for
\( (\text{C}_2\text{H}_4)_2 \) the well depths of MP2, CCSD(T) and WXhole are
very close to each other while in case of \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_2 \) both
MP2 and WXhole overestimate the binding energy
from CCSD(T) by about 0.15 kcal/mol. Compared to
this, the CCSD method underestimates the CCSD(T)
interaction energy at the equilibrium both, in case of the
\( (\text{C}_2\text{H}_4)_2 \) and the \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_2 \) dimer, see figures 3 and
4. In the asymptotic ranges \( (R_{AB} > 3 \text{ Å}) \) all methods show
very small deviations from each other. In sum-
mary, the interaction energy potentials of WXhole for
the \( (\text{C}_2\text{H}_4)_2 \) and \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_2 \) dimers agree well with the
MP2 and CCSD(T) potentials.

C. S66 dimer systems

Recently, Hobza \textit{et al.} have developed a more extensive
database, termed as S66, comprising 66 dimer struc-
tures altogether [134]. While the S66 database itself, as the S22
database, contains only equilibrium structures optimised
on the MP2 level, they extended this database further by
determining 2 structures with a smaller and 5 structures
with a larger distance of the monomers by scaling the
intermolecular distances in the optimised structure using
values of 0.9, 0.95, 1.05, 1.10, 1.25, 1.5 and 2.0, resulting
in 8 structures for a given dimer system altogether in
each case (the corresponding extended database termed
as S66×8). Please refer to Ref. [134] for more details.

Here I have chosen the following subset of the S66×8
database for studying the performance of WXhole:
\( \text{C}_2\text{H}_2\text{-H}_2\text{O} \) (E), \( \text{CH}_3\text{NH}_2\text{-H}_2\text{O} \) (E), \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_12 \) (D), Bz-
\( \text{C}_2\text{H}_2 \) (M), Bz2 (D) (which is identical to the correspond-
ing parallel displaced structure from the S22 database,
but with a slightly different geometry, see Ref. [134])
and \( \text{(pyridine)}_2 \) (M). The acronyms in parenthesis stand
for E: electrostatics-dominated, D: dispersion-dominated
and M: mixed, measured by the ratios of the dispersion
over the electrostatic interaction energies obtained from
DFT-SAPT [62, 63] calculations.

The corresponding interaction energy curves for MP2,
CCSD(T) and WXhole are shown in figures 5a-5f. It can
be seen that in case of the dispersion dominated com-
plexes, namely \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_12 \) and Bz2, as well as the elec-
rostatics dominated \( \text{CH}_3\text{NH}_2\text{-H}_2\text{O} \) dimer, the WXhole
method tends to overestimate the equilibrium distance
from CCSD(T). As a result, the true binding energy from
the WXhole method is lower than if it would be calcu-
lated at the equilibrium structures of the S66 database.
In case of Bz2 the actual minimum for WXhole lies about
-0.5 kcal/mol lower than at the minimum structure of
the S66 database. As a consequence, the binding energy
of WXhole for the \( \pi-\pi \) stacked Bz2 dimer is much closer
than to the extrapolated CCSD(T) reference result than the
first estimate for the S22 database, see table VI. As can
be seen in figure 5c, also the minimum of the CCSD(T)
curve is somewhat displaced to the right compared to the
minimum at the scaling factor of 1.0 that refers to the
minimum distance yield by the MP2 method, see Ref.
[134].

For the two electrostatic bound complexes \( \text{C}_2\text{H}_2\text{-H}_2\text{O} \)
(figure 5a), and \( \text{CH}_3\text{NH}_2\text{-H}_2\text{O} \) (figure 5b), one can ob-
cer that the MP2 curves are very close to the CCSD(T)
to interaction curves, as expected, while WXhole in case
of \( \text{C}_2\text{H}_2\text{-H}_2\text{O} \) overestimates the CCSD(T) curve and in case of
\( \text{CH}_3\text{NH}_2\text{-H}_2\text{O} \) the WXhole curve lies slightly above the
CCSD(T) curve. For the Bz-Cz-Hz and the Bz2 dimers
(figures 5d and 5e) the WXhole interaction energy curves
are much closer to the CCSD(T) reference curves than
the MP2 curves which show a strong overbinding com-
pared to CCSD(T). Note that the Bz-Cz-Hz dimer has a
T-shaped structure and is therefore comparable to the
\( \text{CH-}\pi \) bound Bz2 structure from the S22 database,
see table V. In Ref. [135] it was argued that the \( \text{CH-}\pi \)
bound Bz2 structure from the S22 data base actually
should be categorised as dispersion bound complex, since
the ratio of the dispersion interaction energy over the
total sum of all polarisation terms up to second order of
the intermolecular perturbation theory expansion ex-
ceds a value of 0.7 [135]. In case of \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_12 \) (figure
5c) and \( \text{(pyridine)}_2 \) (figure 5f) the deviations of the MP2
and WXhole interaction curves to the CCSD(T) curves
are similar: for the \( \text{C}_2\text{H}_4\text{-C}_2\text{H}_12 \) dimer the MP2 curve
somewhat overbinds and the WXhole curve somewhat
underbinds while for the \( \text{(pyridine)}_2 \) dimer both, MP2
and WXhole slightly overbind compared to the CCSD(T)
interaction energy curve. In all six dimers considered the
long-range behaviour of the potential energy curves look
similar to each other.

In table VI the binding energies for the six dimers
calculated with MP2, SCS-MP2 (spin-component scaled MP2 [136]), CCSD, CCSD(T) and WXhole are shown. Note that in case of WXhole the corresponding values were obtained from a cubic splines interpolation of the close minimum regions of the interaction curves using solely the energy data from the geometries of the S66×8 database and have therefore a smaller precision than the reference values from Ref. [134] shown in the table. As can be seen, both SCS-MP2 and CCSD improve the MP2 interaction energies on average for the six dimers, but the improvement is not large, see statistical errors displayed in the last two lines of table VI. In contrast to this, the WXhole method yields the most balanced description for the binding energies as the deviations from the CCSD(T) reference values are similar for the electrostatics-dominated and the dispersion-dominated complexes. In total, the mean absolute error and the average percentual errors to CCSD(T) for the binding energy of WXhole is clearly smaller than with the other methods from table VI.

D. C_{2}(CHO)_{2} dimer

In order to test the performance of the WXhole method to predict interaction energies for a dimer system where both, electrostatic interactions and dispersion interactions occur depending on the respective positions of the monomers, the rotation of one monomer in the C_{2}(CHO)_{2} dimer along the axis connecting the bond centres of the C-C triple bonds is considered, see figure 6. The monomer geometries were not explicitly optimised, but sensible default values for the respective distances and angles were used, see figure 6. Then the in-plane structure (φ = 0°, left hand-side of figure 6) and perpendicular structure (φ = 90°, right hand-side of figure 6) was roughly optimised by varying the distance of the two monomers such that the MP2 interaction energies in the cc-pVDZ basis set yielded a minimum. The result of this optimisation was R = 4.5 Å for φ = 0° and R = 3.8 Å for φ = 90° with R denoting the distance of the bond centres of the C-C triple bonds, see figure 6. As can be seen in figure 6, the in-plane structure corresponds to a double O-H hydrogen bridged structure while the perpendicular geometry is a π−π stacking geometry. The interaction energies were then also calculated along the path from the in-plane structure to the perpendicular structure by rotating one monomer about the axis connecting the C-C triple bond centres and varying the distance by R = 4.5 − 0.7 · φπ Å.

The resulting interaction energy curves for WXhole and explicitly correlated perturbation theory and coupled-cluster methods is shown in figure 7. As can be seen, both for the hydrogen bridged structure and the π−π stacking structure the WXhole interaction energy is larger on magnitude than the corresponding CCSD(T) interaction energy. In contrast to this the SCS-MP2 and CCSD interaction energies underestimate the CCSD(T) reference curve. For MP2 one can observe the well known trend that MP2 gives interaction energies close to the CCSD(T) ones for the hydrogen bridged structure while it deviates more from CCSD(T) for the π−π stacking structure, see figure 7. Contrary to this the SCS-MP2 interaction energy curve deviates more in case of the hydrogen bridged geometry and gets closer to the CCSD(T) interaction energy curve for larger angles when the dimer turns into the π-stacking geometry. While figure 7 shows that the WXhole method certainly is not more accurate than MP2 if one measures the absolute deviation to CCSD(T), as it only gets better than MP2 for angles φ > 80°, another criteria of a method is the balanced description of both, electrostatic and dispersion bound configurations. Clearly, in this respect the CCSD and WXhole methods are better than MP2 and SCS-MP2, since the interaction energy curves for CCSD and WXhole are more parallel to the CCSD(T) reference curve than those from MP2 and SCS-MP2, see figure 7. The minimal and maximal deviations of the CCSD interaction energy curve from CCSD(T) are +0.34 and +0.51 kcal/mol for the given range while for WXhole one finds −0.42 and −0.25 kcal/mol as the minimal and maximal deviation from CCSD(T). In contrast to this, the corresponding range of deviation from CCSD(T) for MP2 is +0.13 and −0.38 kcal/mol and for SCS-MP2 +0.74 and +0.29 kcal/mol, respectively.

It can be observed in figure 7 that all methods yield a minimum at an angle of about φ = 8° that indicates a local or possibly global minimum structure in which both, the hydrogen bridge and the π−π interaction contribute to the stabilisation in the system, the latter, however, to a much lesser extent.

IV. CONCLUSION

The exchange-hole model of the response function from Ref. [81] has been refined by replacing the constant mean excitation energy with occupied orbital energy shifts that more accurately model the structure of the response function at resonance frequencies. The response function obtained in this way contains a nonlocal contribution that is similar to the exchange-hole density, but contains weight factors stemming from the occupied orbital energy shifts. Because of this the new approach is termed as weighted exchange-hole’ (WXhole) method in this work. Two parameters in the response function were introduced, one standing for the average energy of an unoccupied state and another one improving the frequency dependence of the response function, see Eq. (17). Both were individually optimised for Hartree-Fock and a hybrid density functional with 30% exact exchange admixture, termed as HCTH(0.7x), to reproduce static dipole-dipole polarisabilities and isotropic C_{6} dispersion coefficients. Considering the crude approximations underlying the WXhole model, the agreement of calculated polarisabilities and dispersion coefficients with accurate reference results was
fairly good. Both, for Hartree-Fock and HCTH(0.7x) the average absolute deviations to corresponding reference results for a number of small molecules was found to be about $10 - 14\%$ only.

The scheme by Wheatley and Lillestølen [106, 107] was used to obtain localised polarisabilities from the frequency-dependent WXhole polarisabilities. These were used as input to calculate damped long-range correlation energies which were combined with density functional theory to obtain total intermolecular interaction energies for a number of complexes. For this, a new hybrid density functional has been developed, termed as HCTH(0.7x). The comparison of intermolecular interaction energies obtained by this method with interaction energies from high-level basis set extrapolated ab-initio results showed a quite good performance. In fact, it was found that the WXhole method (in combination with the HCTH(0.7x) functional) is clearly more accurate on average than MP2 or CCSD if compared to CCSD(T) interaction energies as a reference. Moreover, the method is much more efficient than ab-initio wave function methods as it requires only occupied orbitals and orbital energies as input and can thus be applied also to fairly large systems.

On the other hand, of course, the WXhole method is more expensive than common DFT+D methods including damped atom-atom dispersion contributions. Also the computation of gradients within the WXhole model would be more involved than with standard DFT+D approaches, see Ref. [137] for a corresponding implementation of gradients for the exchange-hole model of Becke and Johnson. However, in the current approach the long-range correlation energy is directly related to the (approximate) response functions and therefore will depend on the chemical environment in contrast to standard force-field expressions for the dispersion energy. In fact, the method described in this work could easily be extended to open-shell and/or non-zero charge cases (the latter, however, requiring a modification of the localisation scheme) that constitute a problem in standard DFT+D methods. Moreover, while in this work only the leading order $-C_6/R_{AB}^6$ term of the asymptotic form of the dispersion energy is considered, the use of higher order polarisabilities give easy access also to higher order interaction terms. The approach used in this work also easily permits to calculate three- and higher-body long-range interactions simply by the generalisation of Eq. (31).

The long-range correlation term to the DFT energy in this work was calculated as a post Kohn-Sham contribution, i.e., using Kohn-Sham orbitals and eigenvalues. I believe, however, that this modification would only be marginal, as the change in the Kohn-Sham potential occurs only in the long-range region. Thus it would not or only slightly affect, e.g., molecular properties calculated from the Kohn-Sham orbitals. The long-range correlation correction does, however, contribute to thermodynamical properties calculated from DFT energy differences. It is known from common DFT+D methods that actually the dispersion interaction contribution appears to lead even to improvements over standard DFT functionals for the prediction of, e.g., reaction barriers [12, 52]. It will be tested in a forthcoming work whether this is true also for the WXhole method described in this work.

ACKNOWLEDGMENTS

The author gratefully acknowledges the funding of the German Research Council (DFG), which, within the framework of its ’Excellence Initiative’, supports the Cluster of Excellence ’Engineering of Advanced Materials’ (www.eam.uni-erlangen.de) at the University of Erlangen-Nuremberg.
TABLES

Table I: Isotropic dipole polarisabilities $\alpha(\omega = 0)$ (in a.u.) calculated by Eq. (14) using orbitals and orbital energies from Hartree-Fock (HF) theory and density-functional theory with the HCTH(0.7x) functional (see section II D). The molecular geometries were taken from Refs. [81, 131] and the aug-cc-pVTZ basis set has been used. The experimental values from the last column are compiled from Refs. [131, 138, 139]. The last line contains the average absolute deviations to the reference values in $\%$.

<table>
<thead>
<tr>
<th>System</th>
<th>HF</th>
<th>HCTH(0.7x)</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.30</td>
<td>1.47</td>
<td>1.379</td>
</tr>
<tr>
<td>Ne</td>
<td>3.42</td>
<td>3.98</td>
<td>2.669</td>
</tr>
<tr>
<td>Ar</td>
<td>11.67</td>
<td>12.11</td>
<td>11.08</td>
</tr>
<tr>
<td>H$_2$</td>
<td>3.84</td>
<td>3.97</td>
<td>5.428</td>
</tr>
<tr>
<td>HF</td>
<td>5.94</td>
<td>6.72</td>
<td>5.606</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>9.13</td>
<td>10.00</td>
<td>9.642</td>
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<tr>
<td>NH$_3$</td>
<td>12.52</td>
<td>13.32</td>
<td>14.56</td>
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<tr>
<td>CH$_4$</td>
<td>14.65</td>
<td>15.27</td>
<td>17.27</td>
</tr>
<tr>
<td>N$_2$</td>
<td>12.64</td>
<td>13.16</td>
<td>11.54</td>
</tr>
<tr>
<td>HCN</td>
<td>16.71</td>
<td>17.19</td>
<td>17.5</td>
</tr>
<tr>
<td>CO</td>
<td>12.34</td>
<td>13.11</td>
<td>13.18</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>17.95</td>
<td>19.75</td>
<td>16.92</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
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<td>21.54</td>
<td>23.53</td>
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<td>C$_2$H$_4$</td>
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<td>24.88</td>
<td>28.26</td>
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<tr>
<td>C$_2$H$_6$</td>
<td>25.97</td>
<td>27.17</td>
<td>28.52</td>
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<tr>
<td>C$_3$H$_8$</td>
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<td>39.38</td>
<td>39.96</td>
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<tr>
<td>C$_6$H$_6$</td>
<td>66.08</td>
<td>66.09</td>
<td>69.5</td>
</tr>
</tbody>
</table>

$|\Delta|$ [%] | 14.2 | 11.6 |
### Table II: Isotropic $C_6(A - A)$ dispersion coefficients (in a.u.) calculated with Eq. (16) using orbitals and orbital energies from Hartree-Fock (HF) theory and density-functional theory with the HCTH(0.7x) functional (see section II.D). The molecular geometries were taken from Refs. [81, 131] and the aug-cc-pVTZ basis set has been used. The DOSD (dipole oscillator strength distribution) values from the last column are compiled from Refs. [54, 140–143]. The last line contains the average absolute deviations to the reference values in %.

<table>
<thead>
<tr>
<th>system</th>
<th>HF</th>
<th>HCTH(0.7x)</th>
<th>DOSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.26</td>
<td>1.27</td>
<td>1.458</td>
</tr>
<tr>
<td>Ne</td>
<td>8.42</td>
<td>8.82</td>
<td>6.383</td>
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<tr>
<td>Ar</td>
<td>75.32</td>
<td>68.43</td>
<td>64.30</td>
</tr>
<tr>
<td>H$_2$</td>
<td>8.10</td>
<td>7.31</td>
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</tr>
<tr>
<td>HF</td>
<td>21.67</td>
<td>22.17</td>
<td>19.04</td>
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<tr>
<td>H$_2$O</td>
<td>46.15</td>
<td>45.55</td>
<td>45.37</td>
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<td>NH$_3$</td>
<td>81.48</td>
<td>77.54</td>
<td>89.08</td>
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<td>103.9</td>
<td>129.6</td>
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<td>N$_2$</td>
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<td>85.37</td>
<td>73.43</td>
</tr>
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<td>HCN</td>
<td>147.0</td>
<td>133.5</td>
<td>135.0</td>
</tr>
<tr>
<td>CO</td>
<td>87.9</td>
<td>83.28</td>
<td>81.31</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>185.9</td>
<td>186.8</td>
<td>157.8</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>230.3</td>
<td>190.7</td>
<td>204.1</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>293.2</td>
<td>265.1</td>
<td>300.5</td>
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<tr>
<td>C$_2$H$_6$</td>
<td>344.7</td>
<td>322.2</td>
<td>381.8</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>714.1</td>
<td>671.3</td>
<td>768.1</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$</td>
<td>2045.5</td>
<td>1818.0</td>
<td>1723.0</td>
</tr>
<tr>
<td>[A]</td>
<td>10.5</td>
<td>13.8</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table IV: Parameters used in the WXhole functional of Eq. (48) defined by Eqs. (34)-(46), (17) and (32)-(33). Parameter $c_{nl}^\alpha\beta$ defines the amount of admixture of exact exchange in the hybrid HCTH(0.7x) functional. The parameter $p_2$ of the damping function of Eq. (33) is given by $p_2 = s_{vdW}(R_{vdW}^m + R_{vdW}^m)$ with the atomic van-der-Waals radii $R_{vdW}$ taken from Ref. [120].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HCTH(0.7x)</th>
<th>response function</th>
<th>damping function</th>
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<tr>
<td>$c_{2s,0}$</td>
<td>0.763175</td>
<td>$\mu$</td>
<td>$s_{vdW}$</td>
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<tr>
<td>$c_{2s,1}$</td>
<td>-0.55944</td>
<td></td>
<td>2.0</td>
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<tr>
<td>$c_{2s,2}$</td>
<td>4.2</td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>$c_{2s,3}$</td>
<td>-4.10732</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>$c_{2s,4}$</td>
<td>2.13178</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{2s,5}$</td>
<td>0.3</td>
<td></td>
<td></td>
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<tr>
<td>$c_{2s,6}$</td>
<td>0.562580</td>
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<td></td>
</tr>
<tr>
<td>$c_{2s,7}$</td>
<td>-0.0171</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{2s,8}$</td>
<td>-1.3064</td>
<td></td>
<td></td>
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<tr>
<td>$c_{2s,9}$</td>
<td>1.0575</td>
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<tr>
<td>$c_{2s,10}$</td>
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<tr>
<td>$c_{2s,11}$</td>
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<td>$c_{2s,12}$</td>
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<td>$c_{2s,13}$</td>
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<tr>
<td>$c_{2s,14}$</td>
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</tr>
<tr>
<td>$c_{2s,15}$</td>
<td>-20.428</td>
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</tbody>
</table>

### Table V: Intermolecular interaction energies for the S22 complexes (in kcal/mol).

<table>
<thead>
<tr>
<th>Dimer</th>
<th>MP2/cbs CCSD(T)/cbs WXhole</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_3$)$_2$ (C$_2$H$_4$)</td>
<td>-3.16</td>
</tr>
<tr>
<td>(H$_2$O)$_2$ (C$_2$H$_2$)</td>
<td>-4.98</td>
</tr>
<tr>
<td>(HCOOH)$_2$ (C$_2$H$_4$)</td>
<td>-18.57</td>
</tr>
<tr>
<td>Uracil-Uracil (C$_2$H$_4$)</td>
<td>-20.41</td>
</tr>
<tr>
<td>2-Pyridine-2-Aminopyridine</td>
<td>-17.37</td>
</tr>
<tr>
<td>AT (WC)</td>
<td>-16.54</td>
</tr>
<tr>
<td>(CH$_3$)$_2$ (D$_2$O)</td>
<td>-0.49</td>
</tr>
<tr>
<td>(C$_2$H$_4$)$_2$ (D$_2$O)</td>
<td>-1.58</td>
</tr>
<tr>
<td>Bz-CH$_4$ (C$_4$)</td>
<td>-1.81</td>
</tr>
<tr>
<td>Bz-Bz (C$_2$H$_4$)</td>
<td>-4.96</td>
</tr>
<tr>
<td>Pyrazine-Pyrazine (C$_s$)</td>
<td>-6.91</td>
</tr>
<tr>
<td>Uracil-Uracil (C$_2$H$_4$)</td>
<td>-11.10</td>
</tr>
<tr>
<td>Indole-Bz (stacked)</td>
<td>-8.09</td>
</tr>
<tr>
<td>AT (stacked)</td>
<td>-14.83</td>
</tr>
<tr>
<td>C$_2$H$_4$-C$_2$H$_2$ (C$_2$H$_4$)</td>
<td>-1.67</td>
</tr>
<tr>
<td>Bz-H$_2$O (C$_s$)</td>
<td>-3.54</td>
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<tr>
<td>Bz-NH$_3$ (C$_s$)</td>
<td>-2.66</td>
</tr>
<tr>
<td>Bz-HCN (C$_s$)</td>
<td>-5.16</td>
</tr>
<tr>
<td>Bz-Bz (C$_2$H$_4$)</td>
<td>-3.63</td>
</tr>
<tr>
<td>Indole-Bz (T-shaped)</td>
<td>-6.98</td>
</tr>
<tr>
<td>Phenole-Phenole</td>
<td>-7.76</td>
</tr>
</tbody>
</table>
Table VI: Binding energies for a subset of 6 dimers from the S66 database (in kcal/mol). The first column contains the reference number for the respective dimer used in the S66 database. The last two lines show the mean absolute errors (in kcal/mol) and the average absolute percentual errors to the CCSD(T)/cbs reference values.

<table>
<thead>
<tr>
<th>ref. nr</th>
<th>dimer</th>
<th>MP2/cbs</th>
<th>SCS-MP2/cbs</th>
<th>CCSD/cbs</th>
<th>CCSD(T)/cbs</th>
<th>WXhole</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>CH$_3$NH$_2$H$_2$O</td>
<td>-7.084</td>
<td>-6.391</td>
<td>-6.595</td>
<td>-6.908</td>
<td>-6.68</td>
</tr>
<tr>
<td>24</td>
<td>Bz$_2$ (π-π)</td>
<td>-4.703</td>
<td>-2.905</td>
<td>-1.762</td>
<td>-2.822</td>
<td>-2.23</td>
</tr>
<tr>
<td>44</td>
<td>C$_2$H$_4$C$_5$H$_2$</td>
<td>-2.151</td>
<td>-1.280</td>
<td>-1.524</td>
<td>-2.005</td>
<td>-1.85</td>
</tr>
<tr>
<td>50</td>
<td>Bz-C$_2$H$_2$ (CH-π)</td>
<td>-3.463</td>
<td>-2.648</td>
<td>-2.493</td>
<td>-2.867</td>
<td>-2.94</td>
</tr>
<tr>
<td>58</td>
<td>Pyridine$_2$ (CH-N)</td>
<td>-4.367</td>
<td>-3.576</td>
<td>-3.688</td>
<td>-4.146</td>
<td>-4.47</td>
</tr>
<tr>
<td>59</td>
<td>C$_2$H$_2$H$_2$O</td>
<td>-2.873</td>
<td>-2.553</td>
<td>-2.731</td>
<td>-2.850</td>
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</tr>
<tr>
<td>mae</td>
<td>0.50</td>
<td>0.40</td>
<td>0.47</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Δ</td>
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<td>17.2</td>
<td>13.1</td>
<td>15.7</td>
<td>8.8</td>
</tr>
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</table>
Figure 1: Frequency-dependent polarisabilities from time-dependent Hartree-Fock (TDHF) and the weighted exchange-hole approximation (WXhole) of Eq. (14) using the HCTH(0.7x) xc functional (in a.u.). The aug-cc-pVTZ basis set was used.
Figure 2: Mean absolute errors (mae) and mean absolute percentual errors ($|\Delta|$) of MP2 and WXhole to the CCSD(T) reference interaction energies for the S22 complexes.
10. Intermolecular interactions

Figure 3: \( \text{C}_2\text{H}_4-\text{C}_2\text{H}_2 \): interaction energy potentials.

Figure 4: \( \text{C}_2\text{H}_4-\text{C}_2\text{H}_4 \): interaction energy potentials.
10. Intermolecular interactions

Figure 5: Interaction energy curves for six dimers from the S66×8 database.
Figure 6: $C_2(CHO)_2$ dimer: path along which the interaction energy was calculated. The monomer geometries are given by: C-H: $1.11 \text{ Å}$, C-O: $1.21 \text{ Å}$, C-CH: $1.4 \text{ Å}$, C-CC: $1.21 \text{ Å}$, $\angle$(H-C-O): $120.42^\circ$, $\angle$(C-C-C): $180^\circ$. At $\phi = 0^\circ$ the two monomers are in plane with the oxygens arranged in a trans configuration while at $\phi = 90^\circ$ the planes containing the monomers are perpendicular to each other. The distance $R$ of the bond centres of the C-C triple bond is $4.5 \text{ Å}$ at $\phi = 0^\circ$ and $3.8 \text{ Å}$ at $\phi = 90^\circ$. For angles $\phi$ between $0^\circ$ and $90^\circ$ the distance was chosen as $R = 4.5 - 0.7 \cdot \frac{\phi}{90^\circ} \text{ Å}$.

Figure 7: Interaction energy curves of the $C_2(CHO)_2$ dimer. The angle $\phi$ refers to the rotation about the axis connecting the bond centres of the C-C triple bonds, see figure 6.
11. Exact-exchange density functional theory

11.1. Efficient exact exchange approximations in density functional theory

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**volume:** 123

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**Key words:**

- exact exchange
- Local Hartree-Fock
- density fitting
- Becke-Roussel exchange hole model
- Slater potential
E. Exchange approximations in density-functional theory

I. INTRODUCTION

In Kohn-Sham (KS) density-functional theory (DFT) a real interacting many-particle system is described by a set of noninteracting pseudoparticles which move in a local potential. If this local potential were known, the exact density and correspondingly all ground-state properties of the real many-particle system could be obtained. However, one component of this local Kohn-Sham potential, namely, the exchange-correlation (xc) potential, is in general unknown and can only be approximated in practical calculations. Today a large number of approximations to the xc functional and thus the xc potentials are used in quantum chemistry, most of them based on generalized gradient approximations (GGA’s). Due to the computational advantages of these methods they have become very popular in quantum chemistry applications.

However, it has been found that one can often improve the description of various properties by introducing a certain amount of nonlocal exact exchange via the adiabatic connection. One reason for the success of these so-called hybrid functionals may be the partial removal of the Coulomb self-interaction error of the approximate GGA exchange functionals. Unfortunately, on the other hand, the total replacement of the GGA exchange functional with exact exchange from Hartree-Fock theory leads to a delocalized xc hole if combined with a local correlation functional. Therefore a mixing of about 20% exact exchange is often used in hybrid functionals. This can be seen as a kind of compromise between accounting for the self-interaction error and the proper description of the xc hole.

Despite the in general satisfactory performance of hybrid GGA’s, the development of DFT methods which converge to exact DFT via defined extensions as in wave-function methods needs new approaches. One natural strategy is to separate the xc functional into exchange and correlation, since, for exchange, the exact functional can easily be derived. A possible way to proceed would be to generalize the conventional KS method to nonlocal potentials as in the Hartree-Fock Kohn-Sham (HF/KS) method. In this method the local Kohn-Sham exchange potential is replaced by the nonlocal exchange potential from Hartree-Fock (HF) theory. However, in its conventional form, the nonlocal HF potential, if acting on a virtual orbital, describes the interaction with \( N \) instead of \( N-1 \) electrons. This usually leads to diffuse unoccupied orbitals and has important consequences for the calculation of response properties and excitation energies.

A natural approach to include local exact exchange in DFT calculations is the optimized effective potential (OEP) method, also denoted as exact exchange (EXX) approach if correlation effects are neglected. In this method a local potential is varied such that it yields orbitals that form a determinant that minimizes the Hartree-Fock energy expectation value. One can argue that the potentials obtained in this way are the best local approximations to the corresponding nonlocal potentials. In the case of molecules one usually uses an expansion of the local potentials in terms of an auxiliary basis set with linear coefficients to determine. Numerical solutions then involve an inversion of the static Kohn-Sham response matrix which itself is given in the auxiliary basis set. However, because the expansion can never be complete, the static Kohn-Sham response matrix involves near singularities which have to be taken into account when inverting it. While this can be remedied by different expansions of the local potential, one still has a strong dependency of the quality of the obtained local potentials on the choice of the auxiliary basis set.

Among other approaches a more direct derivation of the local exact exchange potential can be obtained with the local Hartree-Fock (LHF) method by starting from the assumption that the occupied HF and exchange-only KS orbitals are identical. Via subtraction of the Kohn-Sham equa-
tions from the Hartree-Fock equations one then can obtain a direct expression for the local exchange potential given as a sum of two components, namely, the Slater potential\(^\text{\[12\]}\) and a correction term:

\[
v_s(r) = v_S(r) + v_{\text{cor}}(r),\]

(1)

where the Slater potential \(v_S\) can be written as the negative electrostatic potential integral over the Fermi hole density \(\rho_N\):

\[
v_S(r) = -\int \frac{\rho_N(r')}{|r - r'|} \, dr'.
\]

and

\[
v_{\text{cor}}(r) = \frac{2}{\rho(r)} \sum_{ij} \phi_i(r) \phi_j(r) \int \frac{\hat{\nabla} \phi_i(r') \phi_j(r')}{|r - r'|} \, dr'.
\]

(2)

where \(\phi_i(r)\) denote occupied orbitals, \(\rho(r)\) is the electronic density, and \(\hat{\nabla} \phi_i\) is the nonlocal Hartree-Fock potential. We note that without loss of generality the formulas presented in this work are given for the closed-shell case and for real-valued orbitals. The correction potential \(v_{\text{cor}}\) describes the responsiveness of the exchange screening due to density variations\(^\text{\[13\]}\). It possesses a characteristic atomic step structure\(^\text{\[14\]}\) and has been denoted as response potential in Ref. 15. Since due to the assumption of the equality between the HF- and the exchange-only KS determinants the LHF method is an approximation to the exact exchange Kohn-Sham scheme, the corresponding correction term is not identical with the potential arising due to the response of the exact exchange hole to density variations. But it can be argued that because of the closeness between the HF- and LHF-orbitals the differences between the correction potential and the response potential are rather small.\(^\text{\[11\]}\) A more detailed analysis between various exact exchange approaches has been made in Ref. 16. Here it has been shown that the LHF and OEP methods show notable differences in the prediction of isotropic nuclear-shielding constants which highlights the differences between the exchange potentials in the core region. In this work it will be shown that the LHF method gives electric molecular properties which are rather close to those of Hartree-Fock and so the use of LHF as an exact exchange treatment in DFT is supported.

As the calculation of the correction potential [Eq. (3)] involves the differences of the matrix elements over the local and the nonlocal exchange potentials, the LHF method requires an iterative solution starting from a first guess of the local exchange potential. Alternatively an approximate exact exchange potential can be obtained by direct insertion of Hartree-Fock orbitals into the expressions for the local exchange potential. This method has been termed as transformation local Hartree-Fock (TLHF) method in Ref. 11.

The advantage of the LHF method over the OEP approaches is that it involves no additional auxiliary basis set, so that the quality of the obtained potentials is only limited by the truncation of the atomic-orbital (AO) basis sets which have been employed. The quality of the potential, especially in the asymptotic region, is of crucial importance for the description of the virtual orbitals and thus for the calculation of excitation energies or response properties in subsequent time-dependent DFT calculations. However, the generation of the LHF potential is rather costly, mainly due to the expensive electrostatic potential integrals at each grid point, needed for the construction of the Slater potential. One approach to reduce the computational costs of one LHF cycle, introduced in Ref. 11, is to employ the resolution of the identity (RI) in the AO basis set, leading to an overall scaling of the method which is not much higher than in standard hybrid DFT calculations. However, the AO basis sets usually are not optimal for RI schemes so that one has to use extremely large even tempered basis sets in the calculations. As this is not feasible anymore for all but the smallest systems, in Ref. 11 also a hybrid approach is used in which the RI in the AO basis set is only used in the core regions of a molecule while in the outer regions the Slater potentials are calculated in the standard manner. This can be done since the numerical problems of the RI ansatz are usually small in the near-nuclei regions. But this scheme now demands a splicing of two potentials in the intermediate region. Moreover, not knowing the "exact" Slater potential, it cannot be measured how accurate the RI approximation in different regions of space is, so that the choice of the splice region is more or less empirical (here and in the following the term exact denotes that the Slater potential is exact apart from errors due to basis set truncations).

In this work an alternative method will be investigated in which the Slater potential is generated via density fitting\(^\text{\[17\]}\) (DF) of the corresponding electrostatic potentials. While introducing an additional auxiliary basis set, the expensive generation of electrostatic potentials over products of two AO basis functions at each grid point is reduced to the calculation of electrostatic potentials over only one auxiliary function for each grid point. The advantage of this ansatz is that, compared to the RI approach of Ref. 11, the quality of the obtained potential can be adjusted by the choice of the auxiliary basis set only, and is independent of the AO basis set used. It will be shown that the density-fitted Slater potentials are rather insensitive due to the choice of the fitting basis sets. Moreover, apart from special asymptotic descriptions of the molecular orbitals,\(^\text{\[18\]}\) no corrections in the asymptotic region are necessary, since the approach always yields a correct Coulombic \(-1/r\) decay of the potential. Thus approximate Slater potentials can efficiently be obtained as continuous functions over the whole range of space.

As the Slater potential can be described as the electrostatic potential over the exchange hole, it will also be investigated how well it can be reproduced by a simple generalized gradient approximation of it, namely, the Becke-Roussel (BR) model.\(^\text{\[19\]}\) It is shown that the BR Slater potential closely resembles the exact one in the core region and the asymptotic region, but deviates from it in the bonding regions of the CO and ethyne molecules. Nevertheless the total exchange potentials obtained from the BR model with an energy-optimized parameter as replacement of the exact Slater potential in a TLHF scheme yields energies and molecular properties which are close to the exact TLHF values.
Though this scheme, other than similar approaches to model the OEP potential, still requires quantities from a previous HF calculation, the results are encouraging in the sense that simple models of the exchange hole can approach to the same accuracy as exact exchange treatments. For this method we will use the acronym BR-TLHF in the following.

It will further be analyzed how well the first-order molecular electric properties of the LHF, TLHF, and BR-TLHF approaches agree with those from the HF method. Note that here and in the following the acronym TLHF is used for the scheme in which the local exchange potential is calculated from Hartree-Fock orbitals as input, as described in Ref. 11. However, in Ref. 11 the orbitals are obtained by just one diagonalization step, whereas here, this potential is used in a subsequent KS calculation, thus relaxing the Coulomb contribution to the Kohn-Sham potential. It is shown that the differences between the molecular properties from the LHF and TLHF approaches are always rather small, thus justifying the use of the one-step transformation approach.

II. THEORETICAL METHODS

A. Density fitting for the Slater potential

The time-consuming step for the calculation of the Slater potential \( V_{\text{el}}(r) \) is the generation of the electrostatic potential integrals over products \( \phi_i(r)\phi_j(r) \) in Eq. (2). As the orbitals usually are expanded in a set of \( N \) atomic-orbital basis functions \( \chi_i \), the electrostatic potential integrals can be calculated as

\[
V_{\text{el}}^{ij}(r) = \sum_{\mu\nu} c_{\mu\nu}^{ij} \int \frac{\chi_\mu(r') \chi_\nu(r')}{|r' - r|} \, dr'.
\]

The generation of \( V_{\text{el}}^{ij}(r) \) therefore scales as \( N(N+1)/2 \times N_{\text{grid}} \) where \( N_{\text{grid}} \) is the number points of a numerical quadrature grid. As the \( V_{\text{el}}^{ij} \) are needed for all occupied pairs \( ij \) one can see that also two transformations are necessary which have a scaling of \( n_{\text{oec}} \times N^2 \times N_{\text{grid}} \) thus being an \( N^3 \) step, where \( N \) is a measure of the size of the molecular system.

Density fitting of the \( V_{\text{el}}^{ij} \) potential is straightforward. For this we write the exchange integral as

\[
(ij|ij) = \int \phi_i(r)\phi_j(r) V_{\text{el}}^{ij}(r) \, dr
\]

\[
= \sum_{AB} (ij|A)(A|B)^{-1}(B|ij)
\]

\[
= \sum_A \langle ij|A \rangle d^{ij}_A,
\]

where \( \langle ij|A \rangle \) is a three-index Coulomb integral over two occupied orbitals and one auxiliary basis function and \( (A|B) \) is a two-indexed Coulomb integral (Coulomb norm fitting). The \( d^{ij}_A \) are the exchange fitting coefficients which occur in standard DF implementations of Hartree-Fock theory. Alternatively one can also use the overlap norm to express the exchange integral as

\[
(ij|ij) = \sum_{AB} \langle ij|A \rangle \langle A|B \rangle^{-1} \langle B|ij \rangle
\]

\[
= \sum_A \langle ij|A \rangle \tilde{d}^{ij}_A(B|ij),
\]

with \( \langle \rangle \) denoting an overlap integral. Employing the Coulomb norm the electrostatic potentials from Eq. (4) can be written as

\[
v_{\text{el}}^{ij}(r) = \sum_{A} d^{ij}_A \int \frac{f_A(r')}{|r' - r|} \, dr',
\]

and in the case of the overlap norm,

\[
v_{\text{el}}^{ij}(r) = \sum_{A} \tilde{d}^{ij}_A f_A(r),
\]

where \( f_A(r) \) is an auxiliary basis function. The overall cost to calculate \( v_{\text{el}}^{ij} \) via DF still scales as \( N^3 \) due to the computation of the fitting functions, which is a \( n_{\text{aux}} \times N^2 \times N_{\text{grid}} \) step [see Eq. (6)], and the final transformations in Eqs. (10) and (11), scaling both as \( n_{\text{oec}}(n_{\text{oec}}+1)/2 \times n_{\text{aux}} \times n_{\text{grid}} \) as they are required for each occupied pair \( ij \). Nevertheless the prefactor is greatly reduced because \( n_{\text{aux}} \ll n_{\text{grid}} \) and because the prefactor for either Eq. (10) or Eq. (11) is considerably lower than for Eq. (4). While the overlap-norm fitting appears to be more computationally attractive, in practice it has been found to require very large auxiliary basis sets. This can be ascribed to the fact that in the case of the overlap norm errors in the fitted densities lead to proportional errors in the final integrals. In this work therefore only the Coulomb-norm fitting [Eq. (10)] has been used.

Even if the Coulomb norm is used, it is possible to avoid the evaluation of most of the Coulomb potentials of Eq. (10), through the use of the Poisson ‘trick’.

11. Exact-exchange density functional theory

The exchange integral as

\[
(ij|ij) = \sum_{AB} \langle ij|A \rangle (A|B)^{-1} \langle B|ij \rangle
\]

\[
= \sum_B \tilde{d}^{ij}_B (B|ij),
\]

with \( \langle \rangle \) denoting an overlap integral. Employing the Coulomb norm the electrostatic potentials from Eq. (4) can be written as

\[
v_{\text{el}}^{ij}(r) = \sum_{A} d^{ij}_A \int \frac{f_A(r')}{|r' - r|} \, dr',
\]

and in the case of the overlap norm,

\[
v_{\text{el}}^{ij}(r) = \sum_{A} \tilde{d}^{ij}_A f_A(r),
\]

where \( f_A(r) \) is an auxiliary basis function. The overall cost to calculate \( v_{\text{el}}^{ij} \) via DF still scales as \( N^3 \) due to the computation of the fitting functions, which is a \( n_{\text{aux}} \times N^2 \times n_{\text{grid}} \) step [see Eq. (6)], and the final transformations in Eqs. (10) and (11), scaling both as \( n_{\text{grid}}(n_{\text{grid}}+1)/2 \times n_{\text{aux}} \times n_{\text{grid}} \) as they are required for each occupied pair \( ij \). Nevertheless the prefactor is greatly reduced because \( n_{\text{aux}} \ll n_{\text{grid}} \) and because the prefactor for either Eq. (10) or Eq. (11) is considerably lower than for Eq. (4). While the overlap-norm fitting appears to be more computationally attractive, in practice it has been found to require very large auxiliary basis sets. This can be ascribed to the fact that in the case of the overlap norm errors in the fitted densities lead to proportional errors in the final integrals. In this work therefore only the Coulomb-norm fitting [Eq. (10)] has been used.

Even if the Coulomb norm is used, it is possible to avoid the evaluation of most of the Coulomb potentials of Eq. (10), through the use of the Poisson ‘trick’. This approach has previously been used in low-scaling DFT (Ref. 27) and in Hartree-Fock and MP2 theories. The key equation, which is obtained by insertion of the Poisson equation into the expression for the Coulomb potential, is given as

\[
\int \frac{\hat{P}f(r')}{|r' - r|} \, dr' = f(r),
\]

where \( \hat{P} = -(4\pi)^{-1} \nabla^2 \). Equation (12) holds for any \( f(r) \) which decreases faster than \( r^{-1} \) as \( r \to \infty \). Instead of expanding the occupied orbital product densities in a set of Gaussian functions one can then use an expansion in Poisson functions \( \hat{P}f_A' \)

\[
\rho_A(r) = \phi_A(r)\phi_A(r) = \sum_{A} \tilde{d}^{ij}_A f_A(r).
\]

Insertion into Eq. (4) gives
function expansion alone cannot describe a density with an expansion of Eq. 1

B. The Becke-Roussel model of the exchange hole

From Eq. (2) it can be seen that the Slater potential can be expressed as the electrostatic potential of the exchange hole density \( \rho_X \), which in its exact form is given as

\[
\rho_X(\mathbf{r}, \mathbf{r'}) = 2 \sum_{i,j} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_i(\mathbf{r'}) \phi_j(\mathbf{r'}) \frac{|\rho_i(\mathbf{r}, \mathbf{r'})|^2}{\rho(\mathbf{r})}.
\]

Therefore, if an accurate model of the exchange hole can be derived, one can also deduce an accurate approximation for the Slater potential. One such attractive model is the BR model since, other than conventional descriptions of the exchange hole, it does not start with the uniform electron gas as the prototypical system, but has been derived from the well-known form of the exchange hole for a hydrogenic atom. We do not repeat the whole derivation here, but note that the BR model depends on two parameters which are fixed by the normalization condition of the exchange hole:

\[
\int \rho_X(\mathbf{r}, \mathbf{r'}) d\mathbf{r'} = 1,
\]

and the adjustment of the first two coefficients of the Taylor expansion around the reference point \( \mathbf{r} \) to the one for the exact spherically averaged exchange hole:

\[
v_{\text{BR}}(\mathbf{r}) = \frac{1}{6} \left( \nabla^2 \rho_\sigma - 2 \gamma \left( \frac{\nabla^2 \rho_\sigma}{4 \rho_\sigma} \right) \right) s^2 + \ldots,
\]

where the argument \((\mathbf{r}, s)\) denotes a spherical average on a shell of radius \( s \) about the reference point \( \mathbf{r} \) and \( \tau_\sigma = \sum_i \frac{|\nabla \phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \) is the kinetic-energy density. In Ref. 19 an additional parameter \( \gamma \) has been introduced in Eq. (18) which is one in the exact expansion but is found to be an attractive parameter in order to adjust the model to the uniform electron-gas case, for which it is set to 0.80. Graphical analyses of the exchange hole of the uniform electron gas in Ref. 19 show that the change of \( \gamma \) from 1.0 to 0.8 only has a slight effect on the shape of the hole function. It also has to be noted that an adjustment of \( \gamma \) has no effect on hydrogenic or closed shell two-electron systems, since in these cases the term in the inner brackets in Eq. (18) can be shown to vanish.

The Slater potential, obtained via Eq. (2), has the correct asymptotic form for the BR model,

\[
\lim_{r \to \infty} v_{\text{BR}}(\mathbf{r}) = \lim_{r \to \infty} \left[ - \frac{1}{r^2} \right] = \frac{1}{r}.
\]

Moreover, graphical comparisons for the rare-gas atoms He, Ne, and Ar show that the BR-Slater potential also accurately reproduces the exact one in the near-nuclei and intershell regions.

### III. COMPUTATIONAL DETAILS

The Hartree-Fock and Kohn-Sham calculations have been performed for the four atoms He, Ne, Ar, and Be as well as for a selection of molecules consisting of H\(_2\), HF, BH, N\(_2\), CO, BeO, HCN, ethyne, H\(_2\)O, NH\(_3\), CH\(_4\), benzene, and the three DNA bases adenine, thymine, and cytosine. The geometries of the molecules are compiled in Table I. All molecules have been oriented such that the origin is the center of mass and the axes are the inertia tensor eigenvectors with the \( z \) axis as the main symmetry axis.

The augmented triple zeta basis set of Kendall et al. has been used in each case. For beryllium the cc-pVTZ basis
set of Dunning has been augmented by one diffuse function for every angular momentum employing a geometrical factor of 2.0 in the even tempered expansion. In the case of benzene and the three DNA bases the Coulomb and exchange matrices have been calculated using density fitting. For this the cc-pVQZ JK-Fit basis set of Weigend has been used. For the density fitting of the Slater potential [Eq. (10)] a truncated cc-pVQZ JK-Fit basis set has been used: one in which the cc-pVQZ JK-Fit standard basis set is truncated after the g functions (“auxbasis1”) and a smaller subset in which the truncation is made after the f functions (“auxbasis2”). For Be and the rare-gas atoms He, Ne, and Ar no JK-Fit standard basis sets are available, so that here the aug-cc-pVQZ MP2-Fit (auxbasis1) and the aug-cc-pVTZ MP2-Fit (auxbasis2) basis sets by Weigend et al. have been employed, respectively.

In the case of the Poisson fitting method [Eqs. (13)–(15)] we use the even tempered auxiliary basis sets optimized for cc-pVQZ (Ref. 28) where available. For Be, BeO, and the rare-gas atoms the respective aug-cc-pVQZ MP2-Fit basis sets have been used for the Poisson functions and the uncontracted STO-3G basis sets for the Gaussian auxiliary functions.

All calculations have been performed using the MOLPRO quantum chemistry package. The LHF method by Della Sala and Göring and the density-fitting variant described in Sec. II A have been implemented in the developers version of MOLPRO. Sufficiently fine integration grids have been used throughout. The errors coming from the numerical quadrature are estimated to lie below the microhartree range and therefore do not affect the results presented in this work.

The TLHF method used in this work differs from that of Ref. 11 in the way that after the transformation step from the nonlocal to the local exchange potential this local exchange potential is used in a subsequent self-consistent field (SCF) calculation in order to obtain the molecular orbitals.

IV. RESULTS AND DISCUSSION

A. Timings for the density-fitting TLHF method

Total timings for the generation of the Slater potential [Eq. (2) with Eqs. (4), (10), and (14)] are shown in Table II for benzene and the three DNA bases. For the density-fitting TLHF scheme (DF-TLHF) two auxiliary basis sets as described in Sec. III have been tested. We note here that in the case of the smaller molecules and the medium-sized basis sets used in this work the performance improvements for the DF scheme cannot be measured so well due to the overhead for the density fitting. Typically we achieved speedups with factors of 3 and more in these cases. For benzene and the three DNA bases, however, for which the total timings are naturally much higher due to the larger number of grid points, the DF-TLHF scheme is 3.6–5.4 times faster than TLHF using auxbasis1. We note here that quadrature grids of about 10^5 points have been used for benzene, adenine, thymine, and cytosine, respectively. Using the smaller auxiliary basis set auxbasis2 in DF-TLHF the timings for the construction of the Slater potential are usually one-half of those for TLHF for the medium-sized molecules while for benzene and the DNA bases the speedups now have factors ranging from 4.8 to 7.6. In Secs. IV C and IV D it will be investigated how much the reduction of auxiliary basis functions in DF-TLHF affects the accuracy of energies and molecular properties.

In the last column of Table II the timings for the Poisson fitting variant of Eqs. (13)–(15) are given. It can be seen that in all cases the timings are below those for the Coulomb-fitting scheme employing the smaller fitting basis set auxbasis2. We have observed that for the smaller molecules the use of the Poisson fitting can remarkably reduce the computational effort even of the Coulomb fitting variant. For the DNA bases the timings are only slightly lower than for the auxbasis2 calculations. We note that for larger systems the assembly steps in Eqs. (10) and (14), which require equal computational efforts in both cases, become dominant. As for the Coulomb-fitting calculations we find an approximately linear dependence of computational time with respect to the size of the Poisson basis sets.

B. Local Hartree-Fock scheme with an energy-adjusted Becke-Roussel-Slater potential

The local Hartree-Fock method has been implemented by replacing the exact Slater potential with the BR model potential (see Sec. II B). In a first attempt the standard BR model with a value of 1.0 [Eq. (18)] has been applied. However, while giving reasonable descriptions of the molecular properties for some of the smaller systems, this choice completely failed to give a potential which reproduces molecular properties for the DNA bases. By varying the value, violating, however, the reproduction of the second coefficient of the Taylor expansion of the exact exchange hole [Eq. (18)], it has been found that in most of the cases the description of molecular properties improved with values of in between 1.1 and 1.2. We did not succeed, however, in finding a universal value of which gave potentials which satisfactorily reproduced the molecular properties from the standard TLHF method for all molecules. Therefore the value of has been individually adjusted in order to reproduce the exchange energies from HF calculations. The exchange energy can be calculated from the Slater potential via

\[ E_x = \frac{1}{2} \int \rho(r) v_x(r) dr. \]  

Since the TLHF method itself can be seen as a post-HF method which needs HF orbitals as input, this approach does
not lead to higher computational costs. Moreover it has been found that the dependency of the exchange energies on $\gamma$ are nearly perfectly linear throughout, so that optimal values could be efficiently found using linear interpolations. In this way optimized values are shown in Table III. It can be seen that for most systems the optimal $\gamma$ lies in between 1.1 and 1.2. However, for a group of molecules, namely, N$_2$, CO, BeO, HCN, ethyne and ethyne the optimized values are beyond 1.2. The two extreme cases are the atoms Ar and Be with $\gamma$ values of 0.96 and 1.41, respectively.

It is clear that the choice of parametrizing the BR model in this way will lead to a lack of extensivity in the case of weakly bound molecular complexes. One possible remedy would be to divide the molecular volume into different fragment regions with individual optimized values for $\gamma$. Such a scheme would be applicable without numerical problems because the $\gamma$ values only affect the potential in the bulk regions while the asymptotic part is relatively insensitive to the choice of $\gamma$ (see below). Note that similar suggestions have also been made in the context of asymptotic correction schemes for $xc$ potentials.\[3.4\]

In Figs. 1–4 the BR-Slater potentials for $\gamma=1$ (BR(1.0)) and for optimized values of $\gamma$ (BR(opt)) are compared with the exact Slater potentials for Ne, H$_2$O, CO, and ethyne. Also shown are the corresponding Slater potentials from the Becke88 exchange functional.\[3.5\] The Becke88 Slater potential has been used in the GLLB model of the exchange potential.\[3.6\] In Fig. 1 it can be seen that both the BR(1.0) and the BR(opt) potential is in very good agreement with the exact one. They both go to a value of about $-10$ a.u. for $r \to 0$ as the exact potential and they both possess the correct $-1/r$ asymptotic behavior. Also the slight peak at about $0.4a_0$ is correctly reproduced. These findings are in agreement with those from Ref. 19. In Fig. (4b) of Ref. 19 and in Fig. 1 of this work one can observe that the BR(1.0) model slightly underestimates the exact Slater potential in the region of about $0.4a_0-0.5a_0$. This has the effect that the exchange energy calculated via Eq. (20) underestimates the exact exchange energy by an amount of $-0.08$ a.u. When using the energy-optimized BR Slater potential in the TLHF scheme the $\langle r^2 \rangle$ expectation value changes from 9.29 to 9.37 a.u. which is close to the exact value of 9.40 a.u. The B88 Slater potential for Ne, also shown in Fig. 1, also has the correct asymptotic behavior of $-1/r$, but one can see that in the range of $1.5a_0-3.0a_0$ the shape of the exact potential is slightly overestimated. Furthermore a sharp negative peak occurs near the nucleus, as has been found in Ref. 36. In the region of $0.4a_0-0.8a_0$ the B88 Slater potential strongly underestimates the exact Slater potential.

The same behavior for the BR and the B88 Slater potential models can also be observed in the case of the H$_2$O molecule, shown in Fig. 2. In the case of CO and ethyne (Figs. 3 and 4) the Slater potential is shown also in the bonding regions of the C–O, the C–C, and the C–H bond, respectively. While B88 yields a Slater potential which is too attractive in these regions, the BR model is too repulsive in the corresponding regions. While in the case of the CO molecule

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**TABLE III. Optimized $\gamma$ values for the Becke-Roussel-Slater potential approximation.**

<table>
<thead>
<tr>
<th>System</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1.1127</td>
</tr>
<tr>
<td>Ar</td>
<td>0.9601</td>
</tr>
<tr>
<td>Be</td>
<td>1.4125</td>
</tr>
<tr>
<td>HF</td>
<td>1.1569</td>
</tr>
<tr>
<td>BH</td>
<td>1.1686</td>
</tr>
<tr>
<td>N$_2$</td>
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</tr>
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<td>CO</td>
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</tr>
<tr>
<td>BeO</td>
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</tr>
<tr>
<td>HCN</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>1.1554</td>
</tr>
<tr>
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<tr>
<td>Cytosine</td>
<td>1.1550</td>
</tr>
</tbody>
</table>

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**FIG. 1.** Comparison of the “exact” Slater potential with GGA approximations to it for the neon atom.

**FIG. 2.** Comparison of the “exact” Slater potential with GGA approximations to it for the H$_2$O molecule along the $z$ axis. The oxygen atom is positioned at $-0.124a_0$. 

---

11. Exact-exchange density functional theory
the differences in the potential between BR(1.0) and BR(opt) again appear to be very small, the change from \( \gamma = 1.0 \) to the optimized value of 1.21 has a dramatic effect on the molecular properties, e.g., the dipole moment changes from \(-0.72\) to \(-0.12\) a.u. This again leads to a better correspondence with the TLHF method for which a dipole moment of \(-0.08\) a.u. has been found. The same also holds for the ethyne molecule where the \(zz\) component of the quadrupole moment changes from \(4.80\) to \(5.40\) a.u. compared to the TLHF value of \(5.49\) a.u. Both the B88 and the BR Slater potentials fail to correctly describe the behavior of the exact Slater potential at the hydrogen site of ethyne in Fig. 4 which is rather smooth in this region. In contrast to this the B88 potential possesses a slightly negative peak at the position of the hydrogen atom. The BR potential, on the other hand, starts to oscillate somewhat in the corresponding region.

![Graph](image1)

**Fig. 3.** Comparison of the “exact” Slater potential with GGA approximations to it for the CO molecule along the molecular axis. The carbon atom is positioned at \(-1.218a_0\) and the oxygen atom at \(0.914a_0\), respectively.

![Graph](image2)

**Fig. 4.** Comparison of the “exact” Slater potential with GGA approximations to it for the ethyne molecule along the molecular axis. The carbon atoms are positioned at \(\pm 1.136a_0\) and the hydrogen atoms at \(\pm 3.143a_0\), respectively.

### C. Energies from the density-fitting TLHF and the BR-TLHF schemes

In Table IV the total, exchange, and highest-occupied molecular-orbital (HOMO) energies from DF-TLHF and the BR(opt)-TLHF approaches are compared with those from HF and the standard LHF and TLHF methods.

The LHF method, which can be regarded as an approximate optimized effective potential method, always gives total energies that are higher than those from HF. This can be explained with the further constraint of a local potential in the solution of the Euler-Langrange equations. The only exceptions are He and the \(H_2\) molecule where the HF exchange potential is simply \(-\frac{1}{2}\) times the Coulomb potential and thus exactly local. In Table IV one can see, however, that the differences are small. For the smaller systems they are in the millihartree range and for benzene and the DNA bases in the 10 mhartree range. In the case of the exchange energies, on the other hand, the deviations to HF are about one order larger than those for the total energies. In a sense these deviations also indicate how much the orbitals from HF and LHF differ, since the calculation of the exchange energy via Eqs. (2) and (20) should give the HF exchange energy if the orbitals used in Eq. (2) are HF ones. The exchange energies from the TLHF method thus are equal to the HF exchange energies in the given numerical precision, as can be seen in Table IV. In contrast to this the total energies are always lower than those from HF. This can happen because other than in the case of the LHF method, the local exchange potential is not variationally optimized in the TLHF approach. It can be seen from Table IV that the absolute deviations from the total HF energies of the TLHF method are typically twice as large as those from LHF. Both, in the case of LHF and TLHF the HOMO eigenvalues of the HF method are reproduced to within millihartree accuracy.

The individual deviations from the HF energies for the Coulomb-fitting DF-TLHF method, both for the larger auxiliary basis set auxbasis1 and the smaller auxiliary basis set auxbasis2, are nearly identical to those from the standard TLHF approach. The only exception is the Ar atom for which also the two DF-TLHF schemes have slightly different energies. The reason for this might be that the use of the MP2-Fit basis set as auxiliary basis (see Sec. III) is nonoptimal in this case. Nevertheless one can see that the use of the larger auxiliary basis auxbasis1 gives deviations which are closer to those of TLHF, as expected. In the case of the Poisson-fitting DF-TLHF approach the errors are essentially the same as those for the Coulomb fitting. This shows that both fitting strategies lead to equal accuracies of the potential. In summary, the values for the DF-TLHF method clearly demonstrate that the density fitting of the Slater potential very accurately reproduces the exact Slater potentials from the TLHF method (see also Sec. IV D).

For the BR(opt) model the deviations to the HF exchange energies are naturally zero, with exception of He and \(H_2\) (see Sec. IV B). Here the deviations to HF are \(-0.013\) and \(-0.001\) hartree, and thus relatively small. By comparing the total energies from the BR model with the HF values, one again observes that in nearly all cases the HF energies are...
TABLE IV. Total, exchange, and HOMO energies for HF and deviations from it (in a.u.).

<table>
<thead>
<tr>
<th>System</th>
<th>HF</th>
<th>LHF</th>
<th>TLHF</th>
<th>DF-TLHF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>auxbasis1</td>
<td>auxbasis2</td>
<td>Poisson</td>
<td>BR(opt.)</td>
</tr>
<tr>
<td>He total exchange</td>
<td>−2.861 18</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>HOMO</td>
<td>−1.025 45</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>Ne</td>
<td>−9.197 90</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>Ar</td>
<td>−128.533 27</td>
<td>0.001</td>
<td>−0.007</td>
<td>−0.006</td>
</tr>
<tr>
<td>Be</td>
<td>−12.102 24</td>
<td>0.013</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>H2</td>
<td>−12.858 90</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>BH</td>
<td>−14.572 88</td>
<td>0.002</td>
<td>−0.002</td>
<td>−0.002</td>
</tr>
<tr>
<td>N2</td>
<td>−14.763 35</td>
<td>0.002</td>
<td>−0.012</td>
<td>−0.006</td>
</tr>
<tr>
<td>CO</td>
<td>−30.183 27</td>
<td>0.025</td>
<td>0.0</td>
<td>0.010</td>
</tr>
<tr>
<td>BeO</td>
<td>−30.444 37</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>HCN</td>
<td>−113.303 00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>H2O</td>
<td>−106.841 00</td>
<td>0.000</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>NH3</td>
<td>−112.781 45</td>
<td>0.006</td>
<td>−0.019</td>
<td>−0.019</td>
</tr>
<tr>
<td>CH4</td>
<td>−13.327 36</td>
<td>0.042</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>Benzene</td>
<td>−92.909 11</td>
<td>0.005</td>
<td>−0.016</td>
<td>−0.016</td>
</tr>
</tbody>
</table>
overestimated on magnitude. The deviations are often similar to those for TLHF and in some cases they are even smaller, for example, for the DNA bases. The HOMO energies for the BR(opt)/H2O model, however, do not as well agree with the HF or TLHF values, but one can see that the error nearly always lies in the range of a few millihartrees.

D. Molecular properties from the density-fitting TLHF and the BR-TLHF schemes

Table V compiles the dipole, quadrupole, and radial $r^2$ moments for the different systems. Note that for the dipole and quadrupole moments only the components along the main axis of inertia are given.

<table>
<thead>
<tr>
<th>System</th>
<th>HF</th>
<th>LHF</th>
<th>TLHF</th>
<th>DF-TLHF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\langle r^2 \rangle$</td>
<td>$\langle Q_{zz} \rangle$</td>
<td>$\langle Q_{zz} \rangle$</td>
<td>$\langle r^2 \rangle$</td>
</tr>
<tr>
<td>He</td>
<td>2.374</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>Ne</td>
<td>9.405</td>
<td>−0.003</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Ar</td>
<td>26.069</td>
<td>0.014</td>
<td>0.061</td>
<td>0.111</td>
</tr>
<tr>
<td>Be</td>
<td>17.322</td>
<td>0.024</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>CH4</td>
<td>18.736</td>
<td>−0.024</td>
<td>−0.024</td>
<td>−0.024</td>
</tr>
<tr>
<td>H2</td>
<td>0.499</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>HN2</td>
<td>−0.926</td>
<td>−0.006</td>
<td>0.061</td>
<td>0.061</td>
</tr>
<tr>
<td>Ethyne</td>
<td>5.462</td>
<td>0.016</td>
<td>0.031</td>
<td>0.031</td>
</tr>
<tr>
<td>Benzene</td>
<td>−6.574</td>
<td>0.029</td>
<td>0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>HF</td>
<td>−0.757</td>
<td>−0.003</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>BH</td>
<td>0.686</td>
<td>−0.006</td>
<td>−0.015</td>
<td>−0.015</td>
</tr>
<tr>
<td>CO</td>
<td>−0.105</td>
<td>0.036</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>BeO</td>
<td>−2.957</td>
<td>−0.068</td>
<td>−0.048</td>
<td>−0.048</td>
</tr>
<tr>
<td>HCN</td>
<td>1.296</td>
<td>−0.008</td>
<td>−0.019</td>
<td>−0.019</td>
</tr>
<tr>
<td>H2O</td>
<td>0.780</td>
<td>−0.003</td>
<td>−0.014</td>
<td>−0.013</td>
</tr>
<tr>
<td>NH3</td>
<td>−0.636</td>
<td>−0.050</td>
<td>−0.031</td>
<td>−0.031</td>
</tr>
<tr>
<td>Adenine</td>
<td>−2.141</td>
<td>−0.064</td>
<td>−0.042</td>
<td>−0.042</td>
</tr>
<tr>
<td>Thymine</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Cytosine</td>
<td>−0.246</td>
<td>−0.001</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>−6.744</td>
<td>0.003</td>
<td>−0.077</td>
<td>−0.079</td>
</tr>
<tr>
<td></td>
<td>120.494</td>
<td>−0.058</td>
<td>−0.283</td>
<td>−0.283</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>2.442</td>
<td>−0.206</td>
<td>−0.286</td>
<td>−0.287</td>
</tr>
<tr>
<td></td>
<td>122.474</td>
<td>−0.430</td>
<td>−0.709</td>
<td>−0.708</td>
</tr>
<tr>
<td></td>
<td>−0.252</td>
<td>0.004</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>−4.507</td>
<td>−0.233</td>
<td>−0.259</td>
<td>−0.260</td>
</tr>
<tr>
<td></td>
<td>99.663</td>
<td>−0.494</td>
<td>−0.679</td>
<td>−0.680</td>
</tr>
</tbody>
</table>

The absolute deviations for LHF and TLHF in Table V show that in nearly all cases both methods accurately recover the molecular properties from HF. The only somewhat larger deviations are found for the quadrupole and $r^2$ moments for benzene and the three DNA bases. While for benzene and adenine the quadrupole moments are rather close to the HF values, in the case of thymine and cytosine the deviations are of the order of about −0.25 a.u. for LHF and TLHF. The HF $r^2$ moments are for all four molecules underestimated by LHF and TLHF. However, while the total deviations are relatively large, the relative deviations from the HF values are below 1% in each case. If one compares the deviations from...
LHF and TLHF among each other, one can see that their total magnitude is often very similar. This again shows that the occupied HF and LHF orbitals are rather identical.

The total deviations for DF-TLHF, shown in Table V, to the HF molecular properties are very close to those of the standard TLHF approach. Thus the conclusion from Sec. III, that the density-fitted Slater potentials reproduce the exact one, is confirmed. Again, in the case of the Coulomb fitting, the total values do not change very much when using the smaller auxiliary basis set auxbasis2. It can therefore be stated that the DF-TLHF method is not very sensitive concerning the choice of the basis set. One exception, however, is again found for the Ar atom where the absolute deviation to the HF r² value is nearly twice as large for the smaller auxbasis2 than for auxbasis1. This can once more be ascribed to the nonoptimal MP2-Fit auxiliary basis set in this case. The same is also true for the Poisson-fitting DF-TLHF for which the r² value of Ar is underestimated by 0.2 a.u. compared to HF. Altogether it can be observed that the errors of the Poisson-fitting approach are of similar small magnitude as those of the Coulomb-fitting approach.

For the BR(opt)-TLHF model the total deviations to the HF molecular properties are given in the last column of Table V. In nearly all of the cases the magnitudes of the values are not much larger than those for the standard TLHF method and in some cases the molecular properties from BR(opt) are even closer to the HF ones than those of TLHF, e.g., in the case of the dipole moment of BH or for the quadrupole moment of cytosine. It can thus be concluded that the BR(opt) model gives Slater potentials which are close to the exact potentials (see Sec. IV B). However, with only a few exceptions, one can see that the r² moments are systematically overestimated by the BR(opt) model. It has been found that this behavior is connected with the choice of the γ value of the BR model. In Figs. 1–4 it can be seen that the potentials for BR(opt) are always slightly above the BR(1.0) potentials in the regions near to the nuclei [note that the optimal values of γ are always greater than 1 in these cases (see Table III)]. With this effect the electron density is lowered in these regions and as a consequence shifted into the outer ranges. Therefore the increase of γ in the BR model leads to an increase of the radial r² moments. This can be best observed for the Be atom, where the optimal γ value of 1.4125 is by far larger than for all other systems studied in this work. In Table V one can see that with this value the r² moment of Be is strongly overestimated. In contrast to this the r² moment of the Ar atom is very well described by the BR(opt) potential, for which the optimal γ value has been found to be slightly below 1.0. In summary it can be stated but, that in most of the cases, the deviations of the BR(opt) r²-moments to the HF ones are below 2%.

In Table VI the deviations from unity of the overlap of the Slater determinants from the exact exchange approximations with the Hartree-Fock determinant (values are in units of 10⁻⁴)

<table>
<thead>
<tr>
<th>System</th>
<th>LHF</th>
<th>TLHF</th>
<th>DF-TLHF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>auxbasis1</td>
</tr>
<tr>
<td>He</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ne</td>
<td>0.33</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Ar</td>
<td>0.57</td>
<td>0.54</td>
<td>0.51</td>
</tr>
<tr>
<td>Be</td>
<td>0.53</td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td>H₂</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>HF</td>
<td>1.59</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>BH</td>
<td>4.33</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>N₂</td>
<td>8.40</td>
<td>7.74</td>
<td>7.74</td>
</tr>
<tr>
<td>CO</td>
<td>10.34</td>
<td>8.71</td>
<td>8.72</td>
</tr>
<tr>
<td>BeO</td>
<td>5.68</td>
<td>5.44</td>
<td>5.45</td>
</tr>
<tr>
<td>HCN</td>
<td>8.15</td>
<td>7.28</td>
<td>7.29</td>
</tr>
<tr>
<td>Ethyne</td>
<td>5.30</td>
<td>4.72</td>
<td>4.72</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.79</td>
<td>2.31</td>
<td>2.31</td>
</tr>
<tr>
<td>NH₃</td>
<td>4.58</td>
<td>3.46</td>
<td>3.46</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.97</td>
<td>5.59</td>
<td>5.59</td>
</tr>
<tr>
<td>Benzene</td>
<td>33.83</td>
<td>30.14</td>
<td>30.16</td>
</tr>
<tr>
<td>Adenine</td>
<td>107.59</td>
<td>91.83</td>
<td>91.88</td>
</tr>
<tr>
<td>Thymine</td>
<td>118.30</td>
<td>100.79</td>
<td>100.81</td>
</tr>
<tr>
<td>Cytosine</td>
<td>101.85</td>
<td>86.37</td>
<td>86.41</td>
</tr>
</tbody>
</table>
significantly larger than those for the LHF and TLHF schemes. Moreover in the case of larger molecular systems the determinantal overlaps can no longer be used as a measure for the equality of two determinants, as has been explained in Ref. 11.

V. SUMMARY

In this work two approximations to the local Hartree-Fock (LHF) method by Della Sala and Görling have been investigated: one in which the Slater potential is computed via density fitting and one in which the Slater potential is obtained from the Becke-Roussel model of the exchange hole.19

The density-fitting transformation local Hartree-Fock approach, termed as DF-TLHF, has been shown to accurately reproduce energies and molecular properties of the conventional approach. Two different density-fitting variants of the Slater potential have been investigated: one employing conventional Gaussian functions as the expansion basis, and one using the Poisson trick.27 While both approaches still possess a nominal N scaling with respect to the molecular size as the conventional computation of the Slater potential, the very large prefactor due to the computation of electrostatic potential integrals in the AO basis set on the molecular grid in the latter case is significantly reduced. For the Coulomb-fitting variant two different auxiliary basis sets have been employed for the density fitting of the Slater potential, one larger and one somewhat smaller basis set. The overall accuracy of DF-TLHF has been found to be rather insensitive to the choice of the auxiliary basis and thus this approach can much more reliably be used than basis set expansions of the exchange potential in related optimized effective potential (OEP) methods.7 Total timings of the computation of the Slater potential for the TLHF and the DF-TLHF approaches show that in the case of larger molecular systems speedups with factors of up to 8 and more can be gained by using density fitting. In order to make this method feasible for even larger molecules local fitting techniques as described in Refs. 28 and 37 could be applied.

The TLHF scheme using the Becke-Roussel model for the Slater potential has been shown to give energies and molecular properties which are relatively close to the standard TLHF values if one parameter of the model is optimized such that the exchange energies from Hartee-Fock are retained. It has been demonstrated that though the BR Slater potentials show some deviations from the “exact” Slater potentials in the bonding regions, their overall shape is in much better agreement with the exact potential than is the B88 model potential.53 One drawback is but the fact that the individual adjustment of the BR parameter will lead to a lack of size extensivity. We have pointed out that this could be solved by a partitioning of the molecular volume into different regions. However, such a scheme certainly limits the applicability of this approach for very large molecular systems. While the aim in this work was to reproduce the corresponding exact Slater potentials as close as possible, it would be interesting to investigate how the BR model performs when the BR parameter is optimized to reproduce the exchange energies of a range of molecules. Moreover, if combined with approximations of the response part of the exchange potential,36 the previous HF calculation could be avoided at all. In summary, despite the nonunique parameter in the BR-TLHF approach and though it still requires information from a previous HF calculation, the results in this work suggest that even better pure density-functional approximations of the Slater potential and thereby the exchange potential can be found in the future.

ACKNOWLEDGMENTS

We would like to thank Petr Jurecka for providing us with the geometries for the DNA bases. This work has been supported by the Danish Natural Research Council. F.R.M. thanks the Royal Society for financial support.

33 H.-J. Werner and P. J. Knowles, MOLPRO, version 2002.9, a package of ab initio programs, with contributions by J. Almlöf, R. D. Amos, A. Berning et al., 2005, see http://www/molpro.net.

11. Exact-exchange density functional theory
11.2. Relation between exchange-only optimized potential and Kohn-Sham methods with finite basis sets; solution of a paradox

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year: 2008
volume: 128
pages: 104104
Key words:
- exact exchange
- optimised effective potential method
- numerical instability
- finite basis sets
- silicon
Relation between exchange-only optimized potential and Kohn–Sham methods with finite basis sets, and effect of linearly dependent products of orbital basis functions

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Recently, Staroverov, Scuseria, and Davidson [J. Chem. Phys. \textbf{124}, 141103 (2006)] presented examples of exchange-only optimized effective potential (xOEP) calculations that yield exactly the Hartree–Fock (HF) total energy. Here, building on their work, arguments showing under which conditions xOEP methods, with finite basis sets, do or do not yield the HF ground state energy but a higher one, are given. While the orbital products of a complete basis are linearly dependent, the HF ground state energy can only be obtained via a finite basis set xOEP scheme in the case that all products of occupied and unoccupied orbitals emerging from the employed orbital basis set are linearly independent of each other. Further, exchange potentials leading to the HF ground state energy likely exhibit unphysical oscillations and do not represent a Kohn–Sham (KS) exchange potential as a functional derivative of the exchange energy. These findings appear to explain the seemingly paradoxical results of Staroverov et al. that certain finite basis set xOEP calculations lead to the HF ground state energy despite the fact that within a real space (or complete basis) representation, the xOEP ground state energy is always higher than the HF energy. Moreover, independent of whether or not the occupied and unoccupied orbital products are linearly dependent, it is shown that finite basis set xOEP methods only represent exact exchange-only (EXX) KS methods, i.e., proper density-functional methods, if the orbital basis set and the auxiliary basis set representing the exchange potential are balanced to each other, i.e., if the orbital basis is comprehensive enough for a given auxiliary basis. Otherwise xOEP methods do not represent EXX KS methods and yield unphysical exchange potentials. The question whether a xOEP method properly represents a KS method with an exchange potential that is a functional derivative of the exchange energy is related to the problem of the definition of local multiplicative operators in finite basis representations. Plane wave calculations for bulk silicon illustrate the findings of this work. © 2008 American Institute of Physics. [DOI: 10.1063/1.2826366]

\textbf{1. INTRODUCTION}

In a recent stimulating article with important implications for the use of finite basis sets, Staroverov, Scuseria, and Davidson\textsuperscript{1} presented an exchange-only optimized effective potential (xOEP) scheme that yields, for given finite Gaussian orbital basis sets, ground state energies that surprisingly equal exactly the ground state Hartree–Fock (HF) energies for these basis sets. Moreover, their xOEP scheme yields not only one, but an infinite number of exchange potentials and each of the latter leads to the corresponding ground state HF energy if used as the exchange potential in the corresponding exchange-only Kohn–Sham (KS) Hamiltonian operator. On the other hand, it is known that in a complete basis set limit, which corresponds to a complete real space representation of all quantities, the xOEP method is identical\textsuperscript{2} to the exact exchange-only Kohn–Sham method and yields ground state energies that always lie above\textsuperscript{3} the corresponding ground state HF energy. Moreover, due to the Hohenberg–Kohn theorem, the real space xOEP exchange potential is unique up to an additive constant. Staroverov \textit{et al.} then stated: “Our conclusions may appear paradoxical. For any finite basis set, no matter how large, there exist infinitely many xOEPs that deliver exactly the ground-state HF energy in that basis, however close it may be to the HF limit. Nonetheless, in the complete basis set limit, the xOEP is unique and $E(\text{xOEP})$ is above $E(\text{HF})$.” [Here $E(\text{xOEP})$ and $E(\text{HF})$ denote the xOEP and HF total energies, respectively, that are denoted $E^{\text{xOEP}}$ and $E^{\text{HF}}$ in our work.] Furthermore they stated: “The nonuniqueness of OEPs in a finite basis set raises doubt about their usefulness in practical applications.” Consistent with the results of Staroverov \textit{et al.} we here first show, by different means including a constrained-search one, that the above statement of theirs, that it is always possible to construct optimized effective potentials that deliver exactly the ground state HF energy, holds if the products of the orbital basis functions, or at least the products of the

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corresponding occupied and unoccupied HF orbitals from a given orbital basis set, form a linearly independent set. Otherwise, if the products of occupied and unoccupied HF orbitals are linear dependent then we show that xOEP schemes, in general, do not deliver exactly the corresponding ground state HF energies. Note that Staroverov et al. employed basis sets of contracted even-tempered primitive Gaussian functions that are formally, i.e., with respect to an infinite computational accuracy, as well as effectively, i.e., with respect to the actual computational accuracy, linearly independent, and that for those basis sets the above statement of theirs, regarding the equality of the xOEP and HF energy, indeed applies. (Note also that they anticipate our results, to some extent, in that they also concern themselves with linear dependencies. However, our focus is entirely on just orbital basis products by themselves, and this orientation is crucial for our analysis.)

Secondly, we show that in order to get a physically meaningful KS exchange potential as a functional derivative of the exchange energy with respect to the electron density, an xOEP scheme has to be set up in a way that it represents a KS method. For instance, in order to adequately describe the virtual orbitals, the orbital basis has to be comprehensive enough for the given auxiliary basis. If xOEP schemes are set up thusly then they are of great usefulness in practice as demonstrated, e.g., by numerically stable plane wave xOEP procedures for solids and, very recently, by a numerically stable Gaussian basis set approach for molecules.

It will turn out to be important in this context to distinguish between OEP and KS methods and, in particular, between xOEP and exchange-only KS methods. In order to clarify this distinction we first concentrate on real space representations that correspond to the limit of complete basis sets and that are the representations used in the original derivations and formulations of OEP (Refs. 10 and 11) and KS methods. OEP methods are characterized by the fact that the orbitals are eigenstates of a one-particle Schrödinger equation with an optimized effective potential that is a local multiplicative potential. Subsequently also the OEP exchange potential is a local multiplicative exchange potential. This distinguishes OEP methods from the HF method that contains a nonlocal exchange potential. Within KS methods the orbitals are eigenstates of a one-particle Schrödinger equation with a KS effective potential defined as the functional derivative of the noninteracting kinetic energy, i.e., the kinetic energy of the occupied KS orbitals, with respect to the electron density. The KS exchange potential is given as the functional derivative of the KS exchange energy with respect to the electron density. Because functional derivatives with respect to the electron density are local functions the KS effective potential as well as the KS exchange potential, by definition, are local multiplicative potentials. In a real space representation the OEP method is a KS method and the term xOEP method can be used synonymously to the term exchange-only KS method. Moreover the Hohenberg--Kohn theorem applies and all KS and OEP potentials are unique up to an additive constant.

For a representation within a finite orbital basis set the problem arises that, given the basis set representation of a potential, i.e., given the corresponding matrix representing the potential, it is not possible to distinguish between local multiplicative and nonlocal operators. Thus it is not clear a priori how to properly define OEP or KS methods. The definition for OEP methods adopted by Staroverov et al. in Ref. 1 and also in this work is to define OEP methods as methods with an optimized effective potential that is represented in the orbital basis by a matrix containing matrix elements obtained as real space integrals of orbital basis functions with a local multiplicative potential. Note, however, that a matrix obtained in this way may be identical to matrix representations of a nonlocal operator and that different local multiplicative potentials may have the same matrix representation, i.e., the Hohenberg–Kohn theorem no longer holds. As a consequence xOEP methods can yield the HF energy and can do so for more than one effective potential if products of orbital basis functions or, at least, products of occupied times unoccupied orbitals are linearly independent. This leads to the seemingly paradoxical finding of Staroverov et al.

Proper basis set KS methods must be set up in a way that they yield unique KS effective and exchange potentials that converge toward the corresponding potentials of a real space representation. Finite basis set OEP methods, however, do not always obey this criterion and thus are not always KS methods. In particular, finite basis set xOEP methods do not always represent exchange-only KS methods. This means that within finite basis set representations the terms OEP and xOEP method are more general than the terms KS and exchange-only KS method, respectively. Only certain special basis set OEP or xOEP methods that are set up properly as described below represent KS or exchange-only KS methods and are physically meaningful. Other basis set OEP or xOEP methods may be technically correct OEP methods but they do not represent physically meaningful methods. This is one explanation for the seemingly paradoxical finding of Staroverov et al. that for finite basis sets their xOEP calculations always yielded the HF total energy and that the corresponding xOEP exchange potentials do not need to be unique, while in a real space representation the xOEP total energy lies above the HF one and the xOEP exchange potential is unique, up to an additive constant: For finite orbital basis sets with linearly independent products of orbital basis functions, the requirements to yield a total energy that is higher than the corresponding HF total energy and a unique exchange potential only would hold true for exchange-only KS methods. However, the basis set xOEP calculations of Staroverov et al. do not represent exchange-only KS calculations and thus are allowed to yield the HF total energy and more than one exchange potential. In Appendix B we give a derivation of basis set xOEP methods that completely avoids any real space representations and demonstrates that basis set xOEP methods are not necessarily exchange-only Kohn–Sham methods.

An understanding of the apparent energy paradox utilizes the constrained-search approach, where we shall analyze the energetics during the transition from the finite to the complete basis situation. We shall see how, perhaps counterintuitively, the addition of orbital basis functions to an xOEP calculation can actually raise (not lower) the xOEP energy.
because of the onset of orbital pair linear dependencies! Also, an alternative simple proof of the result of Ref. 1 is presented in Sec. II A that employs the fact that only one single Slater determinant yields any electron density within an orbital basis when orbital products are linearly independent.

II. RELATION OF xOEP AND HF ENERGIES WITHIN FINITE BASIS SET METHODS

We start by briefly reconsidering the xOEP approach of Staroverov et al.\(^1\) that showed that xOEP methods may yield the HF total energy for certain choices of basis sets. The relevant Hamiltonian operators are the HF Hamiltonian operator, i.e., the Fock operator,

\[
\hat{H}^{\text{HF}} = -\frac{1}{2} \nabla^2 + v_{\text{ex}}(\mathbf{r}) + v_{\text{HF}}(\mathbf{r}) + \hat{v}_{\text{NL}}^{\text{aux}}.
\]

(1)

and the xOEP Hamiltonian operator

\[
\hat{H}^{\text{xOEP}} = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) = -\frac{1}{2} \nabla^2 + v_{\text{ex}}(\mathbf{r}) + v_{\text{HF}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}).
\]

(2)

Atomic units are used throughout. In Eqs. (1) and (2), \(v_{\text{ext}}(\mathbf{r})\) denotes the external potential, usually the electrostatic potential of the nuclei, \(v_{\text{HF}}(\mathbf{r})\) is the Hartree potential, i.e., the Coulomb potential of the electron density, \(v_{\text{ext}}(\mathbf{r})\) is the local multiplicative xOEP exchange potential, \(v_{\text{ext}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})\) is the effective xOEP potential, and \(\hat{v}_{\text{NL}}^{\text{aux}}\) is the non-local exchange operator with the kernel

\[
\hat{v}_{\text{NL}}^{\text{aux}}(\mathbf{r}, \mathbf{r}') = \frac{\rho(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.
\]

(3)

Here \(\rho(\mathbf{r}, \mathbf{r}')\) designates the first-order density matrix. In the HF-Hamiltonian operator of Eq. (1) the first-order density matrix occurring in the nonlocal exchange operator of Eq. (3) equals the HF first-order density matrix \(\rho^{\text{HF}}(\mathbf{r}, \mathbf{r}')\) and the nonlocal exchange operator subsequently equals the HF exchange operator. For simplicity we consider closed shell systems with non-degenerate ground states. In this case, orbitals, first-order density matrices, and basis functions all can be chosen to be real valued.

Next we introduce an orbital basis set \(\{\chi_i\}\) of dimension \(N\). The representations of the HF and xOEP Hamiltonian operators in this basis set are

\[
\hat{H}^{\text{HF}} = \hat{T} + \hat{V}_H + \hat{V}_x^{\text{NL}} + \hat{V}_{\text{ext}}
\]

(4)

and

\[
\hat{H}^{\text{xOEP}} = \hat{T} + \hat{V}_x = \hat{T} + \hat{V}_H + \hat{V}_X + \hat{V}_{\text{ext}},
\]

(5)

respectively. The matrices \(\hat{T}, \hat{V}_H, \hat{V}_X, \hat{V}_{\text{ext}}\), and \(\hat{V}_x\) are defined by the corresponding matrix elements \(T_{\mu\nu} = \langle \chi_\mu | T | \chi_\nu \rangle\), \(V_{H\mu\nu} = \langle \chi_\mu | v_H | \chi_\nu \rangle\), \(V_{\text{ext},\mu\nu} = \langle \chi_\mu | v_{\text{ext}} | \chi_\nu \rangle\), \(V_{X,\mu\nu} = \langle \chi_\mu | v_X | \chi_\nu \rangle\), and \(V_{\text{ext},\mu\nu} = \langle \chi_\mu | v_{\text{ext}} | \chi_\nu \rangle\), respectively, and by \(V_x = \hat{V}_H + \hat{V}_X + \hat{V}_{\text{ext}}\). Because the orbital basis functions are real valued all matrices are symmetric.

Now we expand the xOEP exchange potential in an auxiliary basis set \(\{\phi_p\}\) of dimension \(M^{\text{aux}}\), i.e.,

\[
v_x(\mathbf{r}) = \sum_{p=1}^{M^{\text{aux}}} c_p \phi_p(\mathbf{r}).
\]

(6)

The auxiliary basis set, of course, shall be chosen such that its basis functions are linearly independent. The crucial question arising now is how many and what types of matrices \(V_x\) representing the xOEP exchange potential can be constructed for a given auxiliary basis set \(\{\phi_p\}\). This question was answered in Ref. 12. First we consider the case when the \(M = (1/2)N(N+1)\) different products \(\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})\) of orbital basis functions are linearly independent. In this case, if \(M^{\text{aux}} = M\) and the auxiliary basis functions span the same space as the products of the orbital basis functions, then any symmetric matrix \(V_x\) can be constructed in a unique way by determining appropriate expansion coefficients \(c_p\) for the exchange potential. The reason is that the determination of the \(M^{\text{aux}} = M\) expansion coefficients \(c_p\) for the construction of the \(M = M^{\text{aux}}\) different matrix elements of the symmetric matrix \(V_x\) leads to a linear system of equations

\[
A_c = y
\]

(7)

dimension \(M \times M^{\text{aux}}\) with

\[
A_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle / \rho_{\mu\nu}
\]

(8)

and

\[
y_{\mu\nu} = V_{x,\mu\nu}
\]

(9)

for the coefficients \(c_p\) that is nonsingular and thus has a unique solution.\(^{12}\) In Eq. (7), \(A\) is an \(M \times M^{\text{aux}}\) matrix that contains the overlap matrix elements \(\langle \chi_\mu | \chi_\nu \rangle / \rho_{\mu\nu}\). The first index of \(A\), i.e., \(\mu\nu\), is a superindex referring to products of orbital basis functions, while the second index \(k\) refers to auxiliary basis functions. The vector \(c\) collects the expansion coefficients of Eq. (6) for the exchange potential and the right-hand side \(y\), a vector with superindices \(\mu\nu\), contains the \(M = N(N+1)/2\) independent elements of an arbitrarily chosen matrix \(V_x\). If we choose \(V_x\) to be equal to the matrix representation of an arbitrary nonlocal operator with respect to the orbital basis set then Eqs. (6) and (7) define a local potential with the same matrix representation. This demonstrates that a distinction of local multiplicative and nonlocal operators is not clearly possible for orbital basis sets with linearly independent products of orbital basis functions.

If \(M^{\text{aux}} > M\) and the space spanned by the auxiliary functions contains the space spanned by the products of orbital functions then\(^{12}\) an infinite number of sets of coefficients \(c_p\) lead to any given symmetric matrix \(V_x\). The real space xOEP exchange potentials \(v_x(\mathbf{r})\) corresponding according to Eq. (6) to these sets of coefficients \(c_p\) are all different but all represent local multiplicative potentials. Next we construct xOEP Hamiltonian operators [Eq. (2)] by adding these different xOEP exchange potentials to always the same external and Hartree potential. The resulting effective xOEP potentials in real space, i.e., the \(v_x(\mathbf{r})\) are all different. Nevertheless the resulting basis set representations \(\hat{H}^{\text{xOEP}}\) of the corresponding xOEP Hamiltonian operators are all identical because the basis set representations \(V_x\) of the different exchange potentials \(v_x(\mathbf{r})\), by construction, are all identical. As a conse-
sequence the xOEP orbitals resulting from diagonalizing the xOEP Hamiltonian matrix $H_{\text{xOEP}}$ and subsequently also the resulting ground state electron densities are identical in all cases. We thus have a situation where different local multiplicative xOEP potentials $v_i(r)$ lead to the same ground state electron density. This seems to constitute a violation of the Hohenberg–Kohn theorem. Indeed it was shown in Ref. 13 and discussed in Ref. 12 that the Hohenberg–Kohn theorem does not hold for finite orbital basis sets in its original formulation, i.e., that different local potentials, e.g., local potentials obtained by different linear combinations of auxiliary basis functions, must lead to different ground state wave functions and thus different ground state electron densities.

We will come back to this point later on. Finally, if $M_{\text{aux}} < M$ then not all symmetric matrices $V_i$ can be constructed from a local xOEP exchange potential given by an expansion [Eq. (6)].

In their xOEP approach Staroverov et al.\textsuperscript{1} can expand the xOEP exchange potential in $M_{\text{aux}} = M$ auxiliary basis functions and determine the coefficients such that the resulting matrix $V_i$ exactly equals the HF exchange matrix $V_i^{\text{NL}}$. If additionally the xOEP Hartree potential is set equal to the HF one then the resulting HF and xOEP Hamiltonian operators are identical. Subsequently also the HF and xOEP orbitals, the ground state electron densities, and the ground state energies are identical. Because the HF and the xOEP electron densities turn out to be identical, the Coulomb potential of this density can equally well be considered as a HF or a xOEP Hartree potential. It follows immediately that the local exchange potential constructed in this way is the xOEP exchange potential: The HF total energy is the lowest total energy any Slater determinant can yield. Thus if a local multiplicative potential leads to this total energy, it is clearly the optimized effective potential defined as the potential that yields the lowest total energy achievable by any local multiplicative potential. The xOEP ground state energy resulting from this construction equals the corresponding HF energy. Moreover by enlarging the number of auxiliary basis functions, resulting in $M_{\text{aux}} > M$, not only one optimized exchange potential leading to the HF energy but infinitely many can be constructed.

Staroverov et al. obtained the HF energy in their xOEP scheme even if the number of auxiliary functions only equaled the product $M_{\text{aux}}$ of occupied and virtual orbitals.\textsuperscript{1} Indeed this case constitutes the first and most important version of their approach that is also of greatest interest for its practical implementations. In this case a similarity transformation of the HF and the xOEP Hamiltonian matrices and their constituents is carried out in order to obtain representations of all matrices with respect to the HF orbitals. Then it is sufficient to choose the expansion coefficients of the xOEP exchange potential such that only the occupied-virtual block of the xOEP exchange matrix equals that of the HF exchange matrix. The resulting xOEP Hamiltonian matrix then may differ from the HF Hamiltonian matrix in the occupied-occupied and the virtual-virtual block, but this merely leads to unitary transformations of the occupied and virtual orbitals among themselves and thus does not change the ground state energy or the electron density.

For a finite basis set situation it is straightforward to show that the occupied-virtual block of the exchange matrix equals that of the HF exchange matrix if the products of occupied and unoccupied orbitals are linearly independent and if the xOEP equation

$$
4 \sum_i \sum_a \phi_i(r) \phi_a(r) \frac{\langle \phi_i | v_i | \phi_a \rangle}{E_i - E_a} = 4 \sum_i \sum_a \phi_i(r) \phi_a(r) \frac{\langle \phi_i | V_i^{\text{NL}} | \phi_a \rangle}{E_i - E_a}
$$

is obeyed pointwise. Equation (10) represents the xOEP equation that was originally derived to determine the exact real space xOEP exchange potential\textsuperscript{10,11} for a full infinite set of orbitals resulting in a real space representation. In Eq. (10) $\phi_i$ and $\phi_a$ denote occupied and unoccupied xOEP orbitals, respectively, with eigenvalues $E_i$ and $E_a$, where, of course, the unoccupied orbitals form an infinite set. Both sides of Eq. (10) are linear combinations of products $\phi_i(r) \phi_a(r)$ of occupied and unoccupied xOEP orbitals with coefficients $\langle \phi_i | v_i | \phi_a \rangle/(E_i - E_a)$ and $\langle \phi_i | V_i^{\text{NL}} | \phi_a \rangle/(E_i - E_a)$, respectively. Now let us consider the special case of a finite basis OEP calculation, where the orbitals and the local exchange potential $v_i$ are made to satisfy Eq. (10). Then, if the products $\phi_i(r) \phi_a(r)$ are linearly independent then the two linear combinations can only be identical if the coefficients multiplying the products are all identical. This, however, requires that $\langle \phi_i | v_i | \phi_a \rangle = \langle \phi_i | V_i^{\text{NL}} | \phi_a \rangle$, i.e., that the occupied-virtual block of the xOEP exchange matrix equals that of the corresponding exchange matrix of a nonlocal exchange operator of the form of the HF exchange operator. Replacement of the xOEP exchange matrix by the matrix of the nonlocal exchange operator thus again leads only to a unitary transformation of the occupied and virtual orbitals among themselves. Therefore the corresponding xOEP determinant would be interpreted as the HF determinant. In the constrained-search analysis to follow, we shall consider the general finite basis OEP situation, where Eq. (10) is not necessarily satisfied pointwise. [In any case, it is interesting that for the real space situation Eq. (10) implies directly that the occupied-virtual products are linearly dependent because for the real space situation the xOEP energy differs from the HF energy.]

Next we consider the crucial point what happens if the products of orbital basis functions $\phi_i(r) \phi_a(r)$ are linearly dependent. To that end we refer to the equation

$$\tilde{A} c = \tilde{y},$$

which is a matrix equation of the form of Eq. (7), however, of different dimensions, $M_{\text{occ}} \times M_{\text{aux}}$ instead of $M \times M_{\text{aux}}$ (with $M_{\text{occ}}$ denoting the number of occupied times unoccupied orbitals) and with matrix elements given by

$$\tilde{A}_{i,\mu} = \langle \phi_i | f_{\mu} \rangle$$

and

$$\tilde{y}_{\mu i} = \langle \phi_i | g_{\mu i}^{\text{NL}} \rangle.$$  

If Eq. (11) can be solved then the exchange potential is determined such that the occupied-virtual block of the ex-
change matrix equals that of the HF exchange matrix. However, if the products \( \phi_i \phi_a \) of occupied times unoccupied orbitals are linearly dependent then the rows of the matrix \( \mathbf{A} \) of Eq. (11) are linearly dependent, thus the rank of the matrix \( \mathbf{A} \) is lower than \( M^{\text{NL}} \), and as consequence Eq. (11), in general, has no solution.

For a further argument, observe that for linear dependent products \( \phi_i(r) \phi_a(r) \) of occupied times unoccupied orbitals, there exists at least one linear combination of such products that equals zero

\[
0 = \sum_{ia} a_{ia} \phi_i(r) \phi_a(r). \tag{14}
\]

In Eq. (14) the \( a_{ia} \) denote the coefficients of that linear combination. The corresponding sum of matrix elements of \( \mathbf{V}_k \) also equals zero, i.e.,

\[
0 = \int \text{d}r \sum_{ia} a_{ia} \phi_i(r) \phi_a(r) = \sum_{ia} a_{ia} \langle \phi_i | \psi_k | \phi_a \rangle \tag{15}
\]

for any choice of expansion coefficients \( c_p \) in Eq. (6) because the product of any local function and thus of any xOEP exchange potential \( \psi_k(r) \) with the sum [Eq. (14)] equals zero. The products \( \phi_i(r) \phi_a(r') \) for two different arguments \( r \) and \( r' \), on the other hand, are always linearly independent because the occupied orbitals \( \{ \phi_i \} \), as well as the unoccupied orbitals \( \{ \phi_a \} \), are linearly independent among each other. Therefore the linear combination \( \sum_{ia} a_{ia} \phi_i(r) \phi_a(r') \) cannot be identical to zero for all values of the arguments \( r \) and \( r' \), and it would also be expected that the integral of this linear combination with \( \rho^{\text{HF}}(r, r')/|r-r'| \), i.e., with the kernel of the nonlocal HF exchange operator, in general, is not equal to zero, i.e., in general,

\[
0 \neq \sum_{ia} a_{ia} \langle \phi_i | \psi^{\text{HF}}_k | \phi_a \rangle. \tag{16}
\]

Comparison of Eqs. (15) and (16) implies that, in general, the exchange matrices \( \mathbf{V}_k \) and \( \mathbf{V}_k^{\text{NL}} \) are different no matter how the expansion coefficients \( c_p \) of the xOEP exchange potential, Eq. (6), are chosen. This suggests that, in general, neither the xOEP scheme of Ref. 1 nor any other leads to an xOEP Hamiltonian operator that equals the HF Hamiltonian operator if the orbital basis products are linearly dependent. If we consider the first basic version of Ref. 1’s xOEP scheme that refers only to the occupied-virtual block of the xOEP and HF exchange matrices, then by completely analogous arguments it follows that this scheme only works if the products of occupied and unoccupied HF orbitals are linearly independent. However, if the products of occupied and unoccupied HF orbitals are linearly dependent then, in general, it is not possible to obtain the HF ground state energy via an xOEP scheme.

We realize the fact that \( 0 \neq \sum_{ia} a_{ia} \phi_i(r) \phi_a(r') \) does not necessarily dictate with certainty the shown integrated Eq. (16). Partly with this in mind, we now elucidate the entire energy situation from a constrained-search perspective. We shall then discuss the question of how products of basis functions can be linearly dependent.

A. Constrained-search analysis

In this section, complete freedom in the xOEP potentials is assumed. We start with an alternative proof that the xOEP ground state energy \( E^{\text{xOEP}} \) must equal the HF ground state energy \( E^{\text{HF}} \) in their common finite orbital basis, when there is no linear dependence in the products of orbital basis functions. To accomplish this we appeal to the work of Harriman.\textsuperscript{13} He showed that only one first-order density matrix may yield any density generated by a given finite orbital basis whose basis products form a linearly independent set. This means that since an idempotent first-order density matrix uniquely fixes a corresponding single Slater determinant, it follows that only one single determinant, constructed from a given finite orbital basis whose products are linearly independent, may yield a density that is constructed from this same basis. Consequently, with use of a common finite orbital basis set, the xOEP single determinant must equal the HF single determinant if there exists at least one local potential such that its ground state density is the same as the Hartree–Fock density. That means it is only required that the HF density is noninteracting \( \rho \) representable with respect to the orbital basis set. That at least one such local potential exists when the basis products are linearly independent, as discussed above, follows from Ref. 12 and was shown in practice by Staroverov \textit{et al.}\textsuperscript{1}

What happens when the products are not linear independent? Due to the idempotency property of the first-order density matrix for a single determinant, a density generated from a given finite orbital basis could still generate a unique determinant if the basis products are linearly dependent, provided that this linear dependency is mild enough as in the sense of Refs. 13 and 16. However, by Sec. II in Ref. 16, if the number of linearly independent products in the orbital basis becomes smaller than the number of occupied times unoccupied orbitals, the “critical number” or “critical point,” then the situation changes dramatically in that more than one single determinant will yield the same density from the given basis set. In other words, the number of linearly independent products must remain at least as large as the critical number for a density to be generated by a unique determinant in the basis. Otherwise, we do not have the equality \( E^{\text{xOEP}} = E^{\text{HF}} \). Instead, we have the inequality \( E^{\text{xOEP}} > E^{\text{HF}} \), which arises from the following contradiction.

Assume that the xOEP determinant \( \Phi^{\text{xOEP}} \) equals the HF determinant \( \Phi^{\text{HF}} \) through respective optimizations in their common finite orbital basis set. Then it follows that their densities must be the same. But, from a constrained-search analysis,\textsuperscript{13} the xOEP determinant \( \Phi^{\text{xOEP}} \) would yield this HF density and minimize, within this common basis, just the expectation value \( \langle \Phi | \hat{T} | \Phi \rangle \) of the kinetic energy, while the HF determinant \( \Phi^{\text{HF}} \) yields this HF density and minimizes, within the common basis, the expectation value \( \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle \) of the kinetic energy plus the electron-electron repulsion energy. Here \( \hat{T} \) denotes the many-electron kinetic energy operator, \( \hat{V}_{ee} \) the corresponding electron-electron repulsion operator, and \( \Phi \) Slater determinants that yield the HF density. (Equivalently, the xOEP determinant would yield the
HF density and minimize \((\Phi|\hat{H} - \hat{V}_{\text{ext}}|\Phi)\) while the HF determinant yields this HF density and of course minimizes \((\Phi|\hat{H}|\Phi)\). Here \(\hat{H}\) denotes the many-electron Hamiltonian operator.) Because the Slater determinants \(\Phi^{\text{OEP}}\) and \(\Phi^{\text{HF}}\) would minimize different expectation values, i.e., \((\Phi|\hat{T}|\Phi)\) and \((\Phi|\hat{T} + \hat{V}_{\text{ext}}|\Phi)\), respectively, the two determinants would be different, in general, leading to a contradiction of the initial assumption that the two determinants are the same, and the inequality \(E^{\text{OEP}} > E^{\text{HF}}\) thus follows for this common finite orbital basis case. However, there is only one possible determinant \(\Phi\) that yields the HF density from a given finite basis when the basis products are linearly independent or the extent of linear dependency is weak. In this case both minimizations yield this one Slater determinant simply because both minimization only run over one Slater determinant. Thus there is no contradiction and the finite basis set conclusion of Staroverov et al. follows in that the equality \(E^{\text{OEP}} = E^{\text{HF}}\) applies. Hence we are now able to provide a resolution of the xOEP energy paradox\(^1\) from a constrained-search perspective: For a finite basis set case, no matter how large the basis, \(E^{\text{OEP}}\) equals \(E^{\text{HF}}\) provided that the orbital basis products form a linearly independent set or if the number of linearly independent basis products remains at least as large as the critical number. However, in going from any starting finite basis set to the complete basis set limit, \(E^{\text{OEP}}\) becomes greater than \(E^{\text{HF}}\) along the way because as more and more basis orbitals are added to the finite basis set, the onset of sufficient linear dependency eventually occurs when the number of linearly independent orbital basis products falls below the critical number. (See Appendix A for a proof that the products of a complete basis are linearly dependent.)

We have provided an explanation for what might very well seem counterintuitive to the reader without knowledge of the analysis provided here. As one keeps adding more and more orbital basis functions, both \(E^{\text{HF}}\) and \(E^{\text{OEP}}\), at first, decrease and continually remain equal to each other. Eventually in the addition of orbital basis functions, however, \(E^{\text{HF}}\) and \(E^{\text{OEP}}\) start to differ from each other and \(E^{\text{OEP}}\) keeps decreasing, while the behavior of \(E^{\text{OEP}}\) depends on the chosen orbital basis set and it might actually be that \(E^{\text{OEP}}\) rises! The latter behavior, for example, occurs if the exact HF orbitals as they correspond to a real space representation are themselves chosen as the basis set. If the basis set is restricted to the occupied HF orbitals, \(E^{\text{HF}}\) and \(E^{\text{OEP}}\) are of course equal. If unoccupied HF orbitals are added to the basis set, \(E^{\text{HF}}\) remains unchanged. In contrast, eventually \(E^{\text{OEP}}\) raises. The cause, of course, is the eventual appearance of sufficient linear dependence.

Note that numerical illustration of the above finite basis constrained-search analysis appeared in Ref. 12 where, for a common density, it was found that the \(\Phi\) that minimizes \((\Phi|\hat{T} + \hat{V}_{\text{ext}}|\Phi)\) was different than the \(\Phi\) that minimized \((\Phi|\hat{H}|\Phi)\). In effect, sufficient linear dependency was achieved. Consequently, an OEP calculation with their basis would not have achieved the HF energy.

### B. Creation of linear dependence

Next we consider how products of orbital basis functions become linearly dependent. As example we consider a plane wave basis set corresponding to a unit cell defined by the three linearly independent lattice vectors \(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\). The plane waves representing the orbital basis set \(\{\chi_0\}\) then are given by

\[
\chi_0(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}}
\]

with

\[
\mathbf{G} = \ell \mathbf{b}_1 + m \mathbf{b}_2 + n \mathbf{b}_3
\]

and

\[
\ell, m, n \in \mathbb{Z}
\]

and

\[
|\mathbf{G}| \leq \mathbf{G}_{\text{cut}}
\]

In Eq. (18), \(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\) denote three reciprocal lattice vectors defined by the conditions \(a_\ell \cdot b_n = 2\pi \delta_{\ell m}\) for \(\ell, m = 1, 2, 3\). By \(\mathbb{Z}\) the space of all integer numbers is denoted, \(\mathbf{G}_{\text{cut}}\) denotes the cutoff that determines the size of the plane wave basis set, and \(\Omega\) stands for the crystal volume. We have assumed before that basis functions are real valued. This is not the case for plane waves. However, we can always obtain a real valued basis set by linearly combining all pairs of plane waves with wave vectors \(\mathbf{G}\) and \(-\mathbf{G}\) to real-valued basis functions. This real-valued basis set and the original complex-valued plane wave basis set are related by a unitary transformation that does not change any of the arguments of this paper. All arguments therefore are also valid for the complex-valued plane wave basis sets considered here and below. The number \(M\) of basis functions roughly equals \((4\pi/3)\mathbf{G}_{\text{cut}}^3\sqrt{V/8\pi^3})\) with \(V\) denoting the unit cell volume. The exact value of \(M\) depends on whether reciprocal lattice vectors \(\mathbf{G}\) that lie in the immediate vicinity of the surface of the sphere with radius \(\mathbf{G}_{\text{cut}}\) have lengths that are slightly larger or slightly smaller than \(\mathbf{G}_{\text{cut}}\). The relation

\[
\chi_0(\mathbf{r})^\ast \chi_0(\mathbf{r'}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r'}} = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r'}} = \frac{1}{\sqrt{\Omega}} \chi_0(\mathbf{G}+\mathbf{G'})^\ast(\mathbf{r})
\]

shows that the products of plane waves of the orbital basis set are again plane waves of the same type with reciprocal lattice vectors \(\mathbf{G} + \mathbf{G}'\) that obey the relation \(\mathbf{G} + \mathbf{G}' = \pm 2\mathbf{G}_{\text{cut}}\). Due to the latter relation the number of different products \(\chi_0^\ast \chi_0\) is about eight times as large as the number \(N\) of orbital basis functions, i.e., equals about \(8N\). If \(N > 8\) then \(8N < N^2\). In this case the number \(8N\) of different products of orbital basis functions is smaller than the number \(N^2\) of products of orbital functions. Thus some products of orbital functions are equal and thus linearly dependent. For realistic systems the number of plane wave basis functions is much larger than \(8\). In a plane wave framework therefore xOEP and HF methods, in general, lead to different ground state energies with \(E^{\text{OEP}} > E^{\text{HF}}\). Results from plane wave xOEP
III. RELATION OF xOEP AND EXCHANGE-ONLY KS METHODS

In this section we show that the xOEP approach of Staroverov et al.4 does not correspond to an exact exchange KS method and does not yield a KS exchange potential, irrespective of whether or not the products of basis functions of the chosen orbital basis set are linearly independent. To this end we consider the xOEP or exact exchange (EXX) equation written in a form that slightly differs from that of Eq. (10),

\[
\int dr' X_s(r, r') v_s(r') = 4 \sum \sum \phi_i(r) \phi_a(r) \frac{(\phi_i | v^{NL}_s | \phi_a)}{E_i - E_a}.
\]  

(21)

The response function \( X_s \) in Eq. (21) is given by

\[
X_s(r, r') = 4 \sum \sum \phi_i(r) \phi_a(r) \phi_i(r') \phi_a(r').
\]

(22)

Equation (21) can be derived in completely different ways, see, e.g., Ref. 18. First, following Refs. 10 and 11, one can consider the expression of the HF total energy and search for those orbitals that minimize this energy under the constraint that the orbitals are eigenstates of a Schrödinger equation with an Hamiltonian operator of the form

\[
\hat{H}^{\text{OEP}} = -\frac{1}{2} \nabla^2 + v^{\text{OEP}}(r).
\]

(23)

The search for these orbitals is tantamount to searching the optimal effective potential \( v^{\text{OEP}} \), therefore the name optimized effective potential method. The optimized effective potential \( v^{\text{OEP}} \) can always be expressed as

\[
v^{\text{OEP}}(r) = v^{\text{Coul}}(r) + v^{\text{HF}}(r) + v_s(r),
\]

(24)

with the Hartree potential given as the Coulomb potential of the electron density generated by the orbitals. As shown in Refs. 10 and 11 the optimized effective potential \( v^{\text{OEP}} \) is obtained if the exchange potential \( v_s \) of Eq. (24) obeys the OEP or EXX equation [Eq. (21)]. The above derivation shall be denoted as the OEP derivation of the xOEP or EXX equation.

Alternatively the xOEP or EXX equation [Eq. (21)] can be derived within an exact exchange-only KS framework;18,20 this derivation shall be denoted KS derivation. The Hamiltonian operator \( \hat{H}^{\text{KS}} \) of the exact exchange-only KS equation is given by Eq. (2) with the effective KS potential,

\[
v_s(r) = v^{\text{Coul}}(r) + v^{\text{HF}}(r) + v_s(r).
\]

(25)

The KS exchange potential in Eq. (25) is defined as the functional derivative of the exchange energy

\[
E_s = -\sum \sum \int dr \int dr' \frac{\phi_i(r') \phi_i(r) \phi_a(r)}{|r - r'|}.
\]

(26)

with respect to the electron density \( \rho \), i.e., as

\[
v_s(r) = \frac{\delta E_s}{\delta \rho(r)}.
\]

(27)

Following Refs. 19 and 20 we now exploit that according to the Hohenberg–Kohn theorem there exists a one-to-one mapping between effective potentials \( v_s \) and resulting electron densities \( \rho \). Therefore all quantities that are functions of the electron density, here, in particular, the exchange energy, can be simultaneously considered as functionals of the effective potential \( v_s \). Taking the functional derivative \( \delta E_s / \delta v_s(r) \) of the exchange energy with respect to the effective potential \( v_s \), in two different ways with the help of the chain rule yields

\[
\int dr' \frac{\delta E_s}{\delta \rho(r')} \frac{\delta \rho(r')}{\delta v_s(r')} = \sum \int dr \frac{\delta E_s}{\delta \rho(r)} \frac{\delta \rho(r)}{\delta v_s(r')}.
\]

(28)

The functional derivative \( \delta \rho(r) / \delta v_s(r) \) equals the response function [Eq. (22)] and the right-hand side of Eq. (28) equals the right-hand side of the xOEP or EXX equation [Eq. (21)]. Furthermore the response function \( X_s \) is symmetric in its arguments for real valued orbitals. Therefore Eq. (28) is identical to the OEP or EXX equation [Eq. (21)]. This shows that the exchange potentials arising in the xOEP and the exact exchange-only KS schemes and subsequently the xOEP and the exact exchange-only KS schemes itself are identical. Another derivation of the xOEP or EXX equation, again within the KS framework, invokes perturbation theory and exploits the requirement that the first-order correction of the KS density due to the electron-electron interaction, has to vanish.20 Thus the xOEP or EXX equation can be derived in different ways within a KS framework.18 A crucial point, however, is that all derivations within a KS framework rely on real space representations in the sense that a local multiplicative exchange potential, i.e., a potential given in real space, is required and that the exchange potential is defined in real space as functional derivative of the KS exchange potential \( \delta E_s / \delta \rho(r) \). Thus the above conclusion that the xOEP and the exact exchange-only KS schemes are equivalent holds only in real space, i.e., if all quantities are represented in real space. Calculations, however, are usually carried out in basis sets, and we will show next that in this case an xOEP and an exact exchange-only KS scheme, in general, are not equivalent.

The xOEP or EXX equation [Eq. (21)] turns into the matrix equation

\[
X_s \mathbf{c} = \mathbf{t}
\]

(29)

for the coefficient vector \( \mathbf{c} \) determining the exchange potential according to Eq. (6) with matrix and vector elements

\[
X_{spq} = \sum \sum \frac{\langle \phi_i | f_p | \phi_a \rangle \langle \phi_a | f_q | \phi_i \rangle}{E_i - E_s}
\]

(30)

and

\[
t_p = \sum \sum \frac{\langle \phi_i | f_p | \phi_a \rangle \langle \phi_a | v^{\text{NL}}_s | \phi_i \rangle}{E_i - E_a}
\]

(31)

if an auxiliary basis set \( \{ f_p \} \) is introduced to represent the response function, the exchange potential, and the right-hand
side of the EXX equation [Eq. (21)]. For simplicity we assume at this point that the auxiliary basis set is an orthonormal basis set. This is actually the case for plane wave basis sets but not for Gaussian basis sets. However, without changing the following arguments we can assume that we have orthonormalized any auxiliary Gaussian basis set.

As long as the orbitals are represented in real space there is an infinite number of them and the summations over unoccupied orbitals in the response function [Eq. (22)] and the right-hand side of the xOEP or EXX equation [Eq. (21)] remains infinite and complete. For simplicity we assume that the considered electron system is either periodic and thus exhibits periodic boundary conditions or, in case of a finite system, is enclosed in a large but finite box with an infinite external potential outside the box. Then the number of orbitals is infinite but countable. As long as all the infinitely many orbitals are taken into account in the summation over unoccupied orbitals, the basis set representation of the exchange potential resulting from the basis set xOEP or EXX equation [Eq. (29)] becomes the more accurate the larger the auxiliary basis set and converges against the real space representation of the exchange potential and can be interpreted both as exact exchange-only KS or xOEP exchange potential.

This changes dramatically if the orbitals are represented in a finite orbital basis set. Then, provided a reasonable orbital basis set is chosen, the occupied and the energetically low unoccupied orbitals are well represented. Most of the energetically higher unoccupied orbitals, however, are not represented at all simply because a finite orbital basis set cannot give rise to an infinite number of unoccupied orbitals. Moreover, the energetically higher orbitals arising in a finite orbital basis set are quite poor representations of true unoccupied orbitals. Let us now concentrate on the representation of the response function. The integrals \( \langle \phi_a | f_p | \phi_i \rangle \) occurring in the matrix elements [Eq. (30)] of the response function contain the three functions \( \phi_a, \phi_i \) and \( f_p \). The occupied orbitals \( \phi_i \) have few nodes and thus are relatively smooth functions. The energetically low lying unoccupied orbitals still are relatively smooth, the higher ones, however, with an increasing number of nodes and with increasing kinetic energy become more and more rapidly oscillating. For smooth auxiliary basis functions \( f_p \) the integrals \( \langle \phi_a | f_p | \phi_i \rangle \) approach zero if they contain an energetically high unoccupied orbital \( \phi_a \) because the product of the smooth functions \( f_p \) and \( \phi_i \) again is a smooth function and the integral of this smooth product with a rapidly oscillating unoccupied orbital \( \phi_a \) is zero due to the fact that any integral of a smooth with a rapidly oscillating function vanishes. This means that for matrix elements \( X_{a,pq} \) of the response function with two sufficiently smooth functions \( f_p \) and \( f_q \) the summation over unoccupied orbitals in Eq. (30) can be restricted to unoccupied orbitals \( \phi_a \) below a certain energy depending on the smoothness of the involved auxiliary basis functions \( f_p \) and \( f_q \). For sufficiently smooth functions \( f_p \) and \( f_q \) the contributing unoccupied orbitals \( \phi_a \) thus are well represented in a finite orbital basis set. Therefore the matrix elements \( X_{a,pq} \) of the response functions are correct for indices \( p \) and \( q \) referring to sufficiently smooth auxiliary basis functions.

For a more rapidly oscillating auxiliary basis function nonvanishing matrix elements \( \langle \phi_a | f_p | \phi_i \rangle \) with energetically high unoccupied orbitals \( \phi_a \) occur. The energetically high unoccupied orbitals \( \phi_a \), however, are poorly described in the finite orbital basis set and moreover there are too few of them. Therefore the matrix elements \( X_{a,pq} \) of the response functions turn out to be wrong if at least one index refers to a more rapidly oscillating auxiliary basis functions. Indeed, if an auxiliary function \( f_p \) oscillates much more rapidly than the energetically highest unoccupied orbitals \( \phi_a \) obtained for a given orbital basis set, then all matrix elements \( \langle \phi_a | f_p | \phi_i \rangle \) and thus all corresponding elements \( X_{a,pq} \) of the response function are erroneously zero. We note in passing that by similar arguments also the elements \( t_{pq} \) of the right-hand side of the matrix OEP equation [Eq. (29)] turn out to be corrupted if the index \( p \) refers to a too rapidly oscillating auxiliary basis function.

For a given auxiliary basis set, according to the above argument, a representation of the response function is correct only if the orbital basis set is balanced to the auxiliary basis set in the sense that it describes well unoccupied orbitals up to a sufficiently high energy. Otherwise an incorrect representation of the response function is obtained. The matrix representation of the response function like the response function itself is negative semidefinite. This is easily seen if a matrix element of the type \( \langle f | X | f \rangle \) for an arbitrary function \( f \) is considered. Such a matrix element is obtained by summing up the contributions occurring in the summation over occupied and unoccupied orbitals in Eq. (22). Each single contribution and thus also the complete sum is nonpositive. Therefore an insufficient orbital basis set leading to too few energetically high unoccupied orbitals results in eigenvalues of the response matrix that have a too small magnitude. Solutions of the matrix equation [Eq. (29)] are given by the product of the inverse of the response matrix with the right-hand side of the equation, i.e., by \( X^{-1} \). If \( X \) contains eigenvalues that are too small, then the corresponding eigenvectors contribute with a too large magnitude to the solution of Eq. (29). The eigenvectors with too small eigenvalues correspond to rapidly oscillatory functions. Therefore the resulting exchange potential exhibits rapidly oscillatory features. This is exactly what is observed in the xOEP scheme of Staroverov et al. If the response matrix even contains eigenvectors with eigenvalues that are erroneously zero, then an infinite number of solutions arise of the matrix equation [Eq. (29)] corresponding to an infinite number of exchange potentials, which yield, within the finite basis set, the same KS orbitals.

Therefore if the auxiliary and the orbital basis sets are chosen unbalanced, e.g., if one chooses a too small orbital basis set for a given auxiliary basis set or a too large auxiliary basis set for a given orbital basis set, then the resulting response matrix \( X \) is corrupted and no longer represents a proper representation of the response function in real space. In this case the xOEP scheme no longer represents an exact exchange KS scheme and the resulting exchange potential is unphysical and no longer represents the KS exchange potential. However, even in this case the xOEP scheme still is a proper optimized potential scheme in the sense that it yields a linear combination of auxiliary basis functions that results
in the lowest total energy for this orbital basis set that can be obtained if the exchange potential shall be a linear combination of the auxiliary basis functions. While the resulting exchange potential is unphysical and does not resemble the KS exchange potential, it obeys the above requirement of the xOEP scheme. The reason is that, as shown in Appendix B, the arguments used for the OEP derivation of the real space EXX or xOEP equation can also be used if orbital and auxiliary basis sets are introduced, whereas no analog to the KS derivation exists anymore in this case.

IV. EXAMPLES

We now illustrate the arguments of the previous two sections by specific examples. These examples also demonstrate that an auxiliary basis set that consists of all products of occupied and unoccupied orbitals is not balanced to the corresponding orbital basis set in the sense that a correct representation of the response function and a proper KS exchange potential cannot be obtained for such an auxiliary basis set. First, a system of electrons in a box with periodic boundary conditions and an external potential equal to a constant is considered. The box shall be defined by corresponding unit cell vectors \( \mathbf{a}_i \) with \( i = 1, 2, 3 \). If the box, i.e., the unit cell vectors, become infinitely large then the system turns into a homogeneous electron gas. The KS eigenstates \( \phi_k \) of such a system are determined by symmetry and are simple plane waves \( x_{\text{G}_k} \) as they are given in Eq. (17). All plane waves with \( G \) vectors of a length smaller than some given constant \( G_f \), i.e., with \( |G| \leq G_f \), represent occupied KS orbitals, all plane waves with \( |G| > G_f \) represent unoccupied KS orbitals. The maximal length \( G_f \) of the vectors \( G \) of the occupied orbitals determines the Fermi level. For the orbital basis set as well as for the auxiliary basis set we choose plane waves, \( x_{\text{G}_i} \) and \( f_{\text{G}_i} \), respectively, again as given in Eq. (17). Thus for the considered system the special case arises that each orbital basis function \( x_{\text{G}_i} \) represents a KS orbital \( \phi_k \). Obviously, the cutoff \( G_{\text{cut}} \) of the orbital basis set has to be chosen equal to or larger than \( G_f \).

The matrix representation \( X_{i,j} \) of the response function in the considered case is diagonal with diagonal elements,

\[
X_{\text{G}_{\text{G}'},\text{G}} = \sum_{|G'| \leq G_{\text{cut}}} \frac{\langle \phi_{G'} | f_G | \phi_{G'} \rangle}{(|G'|^2 - |G'|^2 + |G|^2)^{1/2}}
\]

\[
eq \frac{8}{\Omega} \sum_{|G'| \leq G_{\text{cut}}} \frac{1}{(|G'|^2 - |G'|^2 + |G|^2)^{1/2}}
\]  

(32)

The auxiliary basis set shall be characterized by the cutoff radius \( G_{\text{aux}} \), i.e., the auxiliary basis set shall consist of all plane waves \( f_G \) with \( 0 < |G| \leq G_{\text{aux}} \). Note that the auxiliary basis function with \( G = 0 \) that equals a constant function has to be excluded from the auxiliary basis set because the xOEP or EXX equation in agreement with the basic formalism determines the exchange potential only up to an additive constant. A constant function would be an eigenfunction of the response function with zero eigenvalue. Now three cases can be distinguished: (i) If \( G_{\text{cut}}^+ = G_{\text{cut}} - G_f \) then the corresponding matrix elements \( X_{\text{G}_{\text{G}'},\text{G}} \) of the response function are obtained with their correct value in a basis set calculation with an orbital basis set characterized by the cutoff radius \( G_{\text{cut}} \) because all unoccupied orbitals \( \phi_{G',G} \) occurring in the summation in Eq. (32) can be represented by the orbital basis set. (ii) If \( G_{\text{cut}}^+ = G_{\text{cut}} - G_f < |G| \leq G_{\text{cut}} + G_f \) then for the matrix elements \( X_{\text{G}_{\text{G}'},\text{G}} \) with \( G_{\text{cut}}^+ = G_{\text{cut}} - G_f < |G| \leq G_{\text{cut}} + G_f \) incorrect values are obtained because some of the unoccupied orbitals \( \phi_{G',G} \) occurring for these matrix elements in the sum in Eq. (32) cannot be represented in the orbital basis set and therefore are not taken into account. Because all terms in the sum in Eq. (32) have the same sign the magnitudes of the resulting matrix elements \( X_{\text{G}_{\text{G}'},\text{G}} \) are too small. (iii) If \( G_{\text{cut}}^+ = G_{\text{cut}} + G_f < |G| \leq G_{\text{aux}} \) then the resulting \( X_{\text{G}_{\text{G}'},\text{G}} \) not only contains elements with a too small magnitude but additionally all matrix elements \( X_{\text{G}_{\text{G}'},\text{G}} \) with \( G_{\text{cut}} + G_f < |G| \) are erroneously zero because all of the unoccupied orbitals \( \phi_{G',G} \) occurring in the summation in Eq. (32) cannot be represented in the orbital basis set and therefore are not taken into account.

If the auxiliary basis set is chosen to be the space spanned by all products of occupied and unoccupied orbitals, then it consists of all plane waves \( f_G \) with \( 0 < |G| \leq G_{\text{cut}} + G_f \), i.e., \( G_{\text{aux}} = G_{\text{cut}} + G_f \). Thus the auxiliary basis set is chosen according to the above case (ii). Therefore some of the resulting matrix elements \( X_{\text{G}_{\text{G}'},\text{G}} \) of the response function are incorrect. This demonstrates that an auxiliary basis set given by all products of occupied and unoccupied orbitals is not balanced with the corresponding orbital basis set.

The considered system is special in that the right-hand side of the xOEP or EXX matrix equation is zero due to the translational symmetry. Therefore also the resulting exchange potential is zero or more precisely equals an arbitrary constant. If the auxiliary basis set is chosen according to the above cases (i) and (ii), then a basis set calculation yields the correct exchange potential, i.e., zero or a constant. If the auxiliary basis set contains functions according to the above case (iii), however, then the xOEP or EXX matrix equation erroneously has an infinite number of solutions that equal a constant plus an arbitrary contribution of auxiliary basis functions with \( G_{\text{aux}} + G_f < |G| \). The reason why the correct exchange potential is obtained for an auxiliary basis set chosen according to the above case (ii) despite the fact that in this case the response function is already corrupted is that for the special system considered here, as mentioned above, the right-hand side of the xOEP or EXX matrix equation is zero. Therefore any values for the diagonal elements \( X_{\text{G}_{\text{G}'},\text{G}} \) that differ from zero lead to the correct result. However, in general, the right-hand side of the xOEP or EXX matrix equation is not equal to zero and then a response matrix with eigenvalues with erroneously too small magnitudes leads to a wrong exchange potential that exhibits too large contributions from those linear combinations of auxiliary basis functions that correspond to the too small eigenvalues of the response matrix. This is demonstrated in the following example.

We consider plane wave xOEP calculations for bulk silicon carried out with the method of Ref. 4. The integrable singularity occurring in HF and xOEP exchange energies in plane wave treatments of solids is taken into account according to Ref. 21. The lattice constant was set to the experimental value of 5.4307 Å. The set of used \( \mathbf{k} \)-points was chosen
as a uniform 4 $\times$ 4 $\times$ 4 mesh covering the first Brillouin zone. In all calculations, all unoccupied orbitals resulting for a given orbital basis set were taken into account for the construction of the response function and the right-hand side of the xOEP equation. EXX pseudopotentials\textsuperscript{22,23} with angular momenta $l=0,1,2$ and cutoff radii, in atomic units, of $r_{c,\text{Si}}=1.8$, $r_{c,\text{p}}=2.0$, and $r_{c,\text{H}}=2.0$ were employed. The pseudopotential with $l=1$ was chosen as local pseudopotential.

Figures 1 and 2 display xOEP exchange potentials along the silicon-silicon bond axis, i.e., the unit cell’s diagonal, for an auxiliary basis set cutoff $E_{\text{cut}}^{\text{aux}}=5.0$ a.u. and different orbital basis set cutoffs $E_{\text{cut}}$. The upper and lower panels differ in the energy scale. The curve for $E_{\text{cut}}=1.25$ a.u. is only displayed in the upper panel.

![FIG. 1. xOEP exchange potential along the silicon-silicon bond axis, i.e., the unit cell’s diagonal, for an auxiliary basis set cutoff $E_{\text{cut}}^{\text{aux}}=5.0$ a.u. and different orbital basis set cutoffs $E_{\text{cut}}$. The upper and lower panels differ in the energy scale. The curve for $E_{\text{cut}}=1.25$ a.u. is only displayed in the upper panel.](image1)

![FIG. 2. xOEP exchange potential along the silicon-silicon bond axis, i.e., the unit cell’s diagonal, for an auxiliary basis set cutoff $E_{\text{cut}}^{\text{aux}}=10.0$ a.u. and different orbital basis set cutoffs $E_{\text{cut}}$. The upper and lower panels differ in the energy scale. The curve for $E_{\text{cut}}=5.0$ a.u. is only displayed in the upper panel.](image2)

This demonstrates the point that the xOEP scheme only represents a KS scheme if the orbital basis set is balanced to the auxiliary basis set. In the case of a plane wave basis set this requires the energy cutoff $E_{\text{cut}}$ of the orbital basis set is about 1.5 times as large as the cutoff of the auxiliary basis set $E_{\text{cut}}^{\text{aux}}$, i.e., equals 7.5 ($G_{\text{cut}}=3.9$), then the exchange potential is converged. A further increase of $E_{\text{cut}}$ to $E_{\text{cut}}=10.0$ ($G_{\text{cut}}=4.5$) leads to an exchange potential that is indistinguishable from that for $E_{\text{cut}}=7.5$ ($G_{\text{cut}}=3.9$) on the scale of Fig. 1. This demonstrates the point that the xOEP scheme only represents a KS scheme if the orbital basis set is balanced to the auxiliary basis set. In the case of a plane wave basis set this requires the energy cutoff $E_{\text{cut}}$ of the orbital basis set is about 1.5 times as large as the cutoff of the auxiliary basis set $E_{\text{cut}}^{\text{aux}}$, i.e., equals 7.5 ($G_{\text{cut}}=3.9$), then the exchange potential is converged. A further increase of $E_{\text{cut}}$ to $E_{\text{cut}}=10.0$ ($G_{\text{cut}}=4.5$) leads to an exchange potential that is indistinguishable from that for $E_{\text{cut}}=7.5$ ($G_{\text{cut}}=3.9$) on the scale of Fig. 1. This demonstrates the point that the xOEP scheme only represents a KS scheme if the orbital basis set is balanced to the auxiliary basis set. In the case of a plane wave basis set this requires the energy cutoff $E_{\text{cut}}$ of the orbital basis set is about 1.5 times as large as the cutoff of the auxiliary basis set $E_{\text{cut}}^{\text{aux}}$, i.e., equals 7.5 ($G_{\text{cut}}=3.9$), then the exchange potential is converged. A further increase of $E_{\text{cut}}$ to $E_{\text{cut}}=10.0$ ($G_{\text{cut}}=4.5$) leads to an exchange potential that is indistinguishable from that for $E_{\text{cut}}=7.5$ ($G_{\text{cut}}=3.9$) on the scale of Fig. 1.

Table I lists for a number of orbital basis set cutoffs $E_{\text{cut}}$ exchange and ground state energies for series of auxiliary basis set cutoffs $E_{\text{cut}}^{\text{aux}}$. Table I shows that the ground state energies for a given $E_{\text{cut}}$ always decrease with increasing $E_{\text{cut}}$ even if the values of $E_{\text{cut}}$ are that large that the resulting exchange potential is unphysical. This demonstrates that the xOEP scheme remains well defined even if unbalanced basis sets are used. In this case, however, the xOEP scheme no
longer represents a KS method and the resulting exchange potential is unphysical and does not represent the KS exchange potential. Table I also lists the differences of the xOEP and HF ground state energies and shows that the xOEP energy does not converge to the HF energy. In the basis set xOEP methods only represent exchange-only methods, within practical use in those cases for which it does not represent an agreement with different operators, \( \langle \hat{T} + \hat{V}_e \rangle \) in HF and \( \langle \hat{T} \rangle \) in OEP, leads to the OEP energy being above the HF energy. In contrast, the different operator criterion has no effect when there is no orbital basis pair linear dependency because then only one wave function yields the density within the basis. It then follows that the two energies are the same.

Moreover, whether or not the products of occupied and unoccupied orbitals are linearly independent, we have shown that basis set xOEP methods only represent exchange-only (EXX) KS methods, i.e., proper density-functional methods, if the orbital basis set and the auxiliary basis set representing the exchange potential are balanced to each other, i.e., if the orbital basis set is comprehensive enough for a given auxiliary basis set. Otherwise xOEP schemes do not represent EXX KS methods. We have found that auxiliary basis sets that consist of all products of occupied and unoccupied orbitals are not balanced to the corresponding orbital basis set. The xOEP method, even in cases of unbalanced orbital and auxiliary basis sets, works properly in the sense that it determines among all exchange potentials that can be represented by the auxiliary basis set the one that yields the lowest ground state energy. However, in these cases the resulting exchange potential is unphysical and does not represent a KS exchange potential. Therefore the xOEP method is of little practical use in those cases for which it does not represent an EXX KS method. Remember that, at present, the main reason to carry out xOEP methods in most cases is to obtain a qualitatively correct KS one-particle spectrum, either for the purposes of interpretation or as input for other approaches such as time-dependent density-functional methods. However, the unphysical oscillations of the exchange-potential of xOEP schemes with unbalanced basis sets affect the unoccupied orbitals and eigenvalues. Another reason to carry out xOEP methods that represent EXX KS methods is that the latter may be combined with new, possibly orbital-dependent, correlation functionals to arrive at a new genera-

### Table I. xOEP exchange and ground state energies \( E_{\text{xOEP}} \) and \( E_{\text{HF}} \), respectively, and the difference \( E_{\text{xOEP}} - E_{\text{HF}} \) between HF and xOEP ground state energies for bulk silicon (per unit cell) for various combinations of orbital and auxiliary basis sets, characterized by energy cutoffs \( E_{\text{cut}} \) and \( M_{\text{aux}} \), respectively. \( N \) and \( M^{\text{aux}} \) denote the corresponding number of basis functions. All quantities are given in a.u.

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<th>( E_{\text{cut}}/N )</th>
<th>( E_{\text{aux}}^{\text{cut}} )</th>
<th>( M_{\text{aux}}^{\text{cut}} )</th>
<th>( E_{\text{xOEP}} )</th>
<th>( E_{\text{HF}} )</th>
<th>( E_{\text{xOEP}} - E_{\text{HF}} )</th>
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11. Exact-exchange density functional theory
tion of density-functional methods. Also in this case it is important that xOEP methods represent proper KS methods.

A balancing of auxiliary and orbital basis sets is straightforward for plane wave basis sets. In this case xOEP schemes are proper EXX KS methods if the energy cutoff for the orbital basis set is about 1.5 times as large as that of the auxiliary basis set. This as well as other results of this work was illustrated with plane wave calculations for bulk silicon. For Gaussian basis sets on the contrary, a proper generally applicable and reasonably simple balancing scheme of orbital and auxiliary basis sets for a long time could not be developed despite much efforts.\textsuperscript{24–29} Numerical grid methods, on the other hand, so far, could be applied only to atoms,\textsuperscript{41} and a few very small molecules.\textsuperscript{30} Therefore effective exact exchange-only methods like the KLL,\textsuperscript{31} the “localized Hartree–Fock,”\textsuperscript{32} the equivalent “common energy denominator approximation” method,\textsuperscript{33} and the closely related very recent method of Ref. 34 as well as OEP methods that add terms smoothing the exchange potential to the total energy expression\textsuperscript{35} are in use as numerically stable alternatives that yield results very close to those of full EXX KS methods. Very recently, however, a numerically stable OEP method based on Gaussian basis sets with an accompanying construction and balancing scheme for the involved auxiliary and orbital Gaussian basis sets was presented.\textsuperscript{9}

There are exact known stringent necessary constraints for a $v_s$ to be consistent with the KS functional derivative criterion. These constraints include the exchange potential identity involving the highest occupied KS orbital,\textsuperscript{36,31} the virial\textsuperscript{37} relation $E_v=-f_0(r)\cdot \nabla \psi_s(r)\,dr$, and $f_0(r)\nabla \rho(r)\,dr=0$, which arises simply from the requirement that $v_s$ is the functional derivative of some functional. These constraints alone would eliminate many $v_s$ potentials that do not satisfy the KS criterion.

**APPENDIX A: LINEAR DEPENDENCE OF PRODUCTS OF BASIS FUNCTIONS OF A COMPLETE BASIS**

Let $\{\phi_b(x)\}$ be a complete set of functions of a complex valued variable $x$ such that any arbitrary square integrable function can be written as a linear combination of the functions in the complete set. We show that the set $\{\phi_b(x)\phi_b(x)\}$ is linearly dependent.

Using our complete sets, an arbitrary function $f(x,y)$ of two complex valued variables $x$ and $y$ may be expanded in terms of $\{\phi_b(x)\}$ and $\{\phi_b(y)\}$,

$$f(x,y) = \sum_{b=1}^{\infty} \sum_{r=1}^{\infty} b_{b,r} \phi_b(x) \phi_b(y).$$  \hspace{1cm} (A1)

Set $y=x$ to get

$$f(x,x) = \sum_{b=1}^{\infty} \sum_{r=1}^{\infty} b_{b,r} \phi_b(x) \phi_b(x).$$  \hspace{1cm} (A2)

Now choose a function $f(x,x)$ and a $\phi_b(x)$ out of the set $\{\phi_b(x)\}$ such that (i) $\lim_{x\to\infty} f(x,x)/\phi_b(x)=0$ and (ii) at least one $b_{b,r} \neq 0$ when $b \neq n$ and $r \neq 0$. Since $f(x,x)/\phi_b(x)$ is just a function of $x$, we may expand it in terms of the $\{\phi_b(x)\}$,

$$\frac{f(x,x)}{\phi_b(x)} = \sum_{n=1}^{\infty} d_n \phi_n(x).$$  \hspace{1cm} (A3)

Solving for $f(x,x)$,

$$f(x,x) = \phi_b(x) \sum_{n=1}^{\infty} d_n \phi_n(x) = \sum_{n=1}^{\infty} d_n \phi_n(x) \phi_b(x)$$  \hspace{1cm} (A4)

and equating Eq. (A2) with Eq. (A4), we get

$$\sum_{n=1}^{\infty} d_n \phi_n(x) \phi_b(x) = \sum_{n=1}^{\infty} \sum_{r=1}^{\infty} b_{b,r} \phi_b(x) \phi_n(x),$$  \hspace{1cm} (A5)

or by setting $k=m$,

$$\sum_{n=1}^{\infty} d_n \phi_n(x) \phi_b(x) - \sum_{n=1}^{\infty} \sum_{r=1}^{\infty} b_{m,r} \phi_b(x) \phi_n(x) = 0,$$  \hspace{1cm} (A6)

or

$$(d_n - b_{m,n}) \phi_b(x) \phi_n(x) + \sum_{j \neq n} (d_j - b_{j,n} - b_{m,n}) \phi_b(x) \phi_j(x) = 0.$$  \hspace{1cm} (A7)

Equation (A7) is a linear combination of a subset of $\{\phi_b(x) \phi_b(x)\}$ broken up into disjoint components and equated to zero. If a subset of a set is linearly dependent, then the set must also be linearly dependent. We show such a case by contradiction: According to Eq. (A7), for the subset $\{\phi_b(x) \phi_b(x)\}$ (appearing in the equation) to be linearly independent, three conditions must be met:

1. $d_n = b_{n,n}$.
2. $d_j - b_{j,n} - b_{m,n} = 0 \ (\forall j \in \mathbb{N} \text{ with } j \neq n)$.
3. $b_{m,l} = 0 \ (\forall m \in \mathbb{N} \text{ with } m \neq n \text{ and } \ell \neq n)$.

But according to our condition on $f(x,x)$ there is at least one $b_{m,l} \neq 0$ with $m \neq n$ and $\ell \neq n$, which is a contradiction to number three of our linear independence criteria. Therefore $\{\phi_b(x) \phi_b(x)\}$ must be linearly dependent by contradiction, and therefore $\{\phi_b(x) \phi_b(x)\}$ for all $k,l \in \mathbb{N}$ is linearly dependent because $\{\phi_b(x) \phi_b(x)\}$ is linearly dependent.

One may take the result one step further to show with an induction argument that for any complete set such as $\{\phi_b(x)\}$ the set defined by $\{\phi_b(x) \phi_b(x) | N, i, p \in \mathbb{N}\}$ is complete and linearly dependent.

**APPENDIX B: DIRECT DERIVATION OF THE BASIS SET xOEP EQUATION**

If the orbitals and the exchange potential are represented by basis sets then the OEP derivation\textsuperscript{10,11} of the real space xOEP equation [Eq. (10)] can be adapted in such a way that it directly yields the basis set xOEP equation [Eq. (29)] without the need to invoke the real space xOEP equation [Eq. (10)]. In order to show this we consider a basis set representation $H^{xOEP} = T + V_x$ of a Hamiltonian as it is given in Eq. (5). The energetically lowest eigenvectors $u_i$ represent the
corresponding occupied orbitals, while the other eigenvectors \( u_a \) represent the unoccupied orbitals. Any matrix \( V_i \), representing an effective potential in the orbital basis set can be written as sum \( V_H + V_{le} + V_{ext} \) of the matrix \( V_{ext} \) representing the external potential, the matrix \( V_H \) representing the Coulomb potential resulting from the occupied orbitals, and a remainder \( V_i \) given by matrix elements \( V_{i,a,b} = \langle \chi_{a} | \sum_{\mu} \xi_{\mu}^{a} c_{\mu}^{a} | \chi_{b} \rangle \) that are determined by a linear combination of auxiliary basis functions \( f_p \), see Eq. (6). The derivative of the corresponding exchange-only total energy \( E^{\text{xOEP}} \) with respect to the coefficients \( c_p \) is given by

\[
\frac{dE^{\text{xOEP}}}{dc_p} = 4 \sum_{i} \sum_{a} \tilde{A}_{i,a,p} u_i [T + V_H + V_{\text{NL}} + V_{\text{ext}}] u_a \quad \text{for all indices } p
\]

with matrix elements \( \tilde{A}_{i,a,p} = \langle \phi_i \phi_a | f_p \rangle \) of Eq. (12). The matrix \( \tilde{A} \) is the one that also occurs in Eq. (11). For the second line of Eq. (B1) it is used that \( T_{au} = [e^S - V_i]_{uu} = [e^S - V_H - V_i - V_{\text{ext}}]_{uu} \), because the coefficient vectors \( u_i \) representing the orbitals solve the generalized eigenvalue problem \( [T + V_i]_{uu} = e \cdot S_{uu} \), with \( S \) being the overlap matrix with respect to the orbital basis set. Furthermore, it is used that \( u_i^T e \cdot S_{uu} u_a = 0 \) due to the orthonormality of the orbitals.

Next we consider the energy \( E^{\text{xOEP}} \) as function of the coefficients \( c_p \) and search the minimum of this function, i.e., the minimum of the energy \( E^{\text{xOEP}} \). At the minimum energy derivatives \( dE^{\text{xOEP}} / dc_p \) for all indices \( p \) have to be zero. This means that for each index \( p \) an equation

\[
4 \sum_{i} \sum_{a} \tilde{A}_{i,a,p} u_i^T V_{i,a} u_a \quad \text{for all indices } p
\]

holds. The set of equations [Eq. (B2)] is identical to the basis set xOEP equation [Eq. (29)] if it is used that the right-hand side of Eq. (B2) equals the elements \( t_{ip} \) of the vector \( t \) on the right-hand side of the basis set xOEP equation [Eq. (29)] and that the left side of Eq. (B2) equals the \( p \)th element of the product \( X_c \), i.e., the \( p \)th row of the left side of the basis set xOEP equation [Eq. (29)]. The latter follows because

\[
X_{i,a}^T V_{i,a} u_a = \sum_{p} \sum_{\mu} \mu_{\mu}^{a} V_{i,a}^{\mu} \mu_{\mu}^{a} = \sum_{p} \sum_{\mu} \mu_{\mu}^{a} \langle \chi_{a} | \sum_{\nu} \xi_{\nu}^{a} c_{\nu}^{a} | \chi_i \rangle \quad \text{with } \mu_{\mu}^{a} \quad \text{denoting the elements of } u_a \quad \text{and } u_i \quad \text{and the matrix elements } A_{\mu \nu a} \text{ given by Eq. (8)}
\]

and because the response matrix \( X_c \) of Eq. (29) can be written as \( X_c = 4 \tilde{A} X^{-1} \tilde{A} \) with the diagonal matrix \( \tilde{A} \) defined by the matrix elements \( \lambda_{i,a,b} = \delta_{i,a,b} (e_i - e_a) \).

17. See the constrained-search discussion in Ref. 3, which includes appropriate references on the approach in this context.
11.3. Numerically stable optimized effective potential method with balanced Gaussian basis sets

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- numerical instability
- finite basis sets
- balancing scheme
- exchange potential
Numerically stable optimized effective potential method with balanced Gaussian basis sets

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A solution to the long-standing problem of developing numerically stable optimized effective potential (OEP) methods based on Gaussian basis sets is presented by introducing an approach consisting of an exact exchange OEP method with an accompanying construction and balancing scheme for the involved auxiliary and orbital Gaussian basis sets that is numerically stable and that properly represents an exact exchange Kohn-Sham method. The method is a purely analytical method that does not require any numerical grid, scales like Hartree-Fock or B3LYP procedures, is straightforward to implement, and is easily generalized to take into account orbital-dependent density functionals other than the exact exchange considered in this work. Thus, the presented OEP approach opens the way to the development and application of novel orbital-dependent exchange-correlation functionals. It is shown that adequately taking into account the continuum part of the Kohn-Sham orbital spectrum is crucial for numerically stable Gaussian basis set OEP methods. Moreover, it is mandatory to employ orbital basis sets that are converged with respect to the used auxiliary basis representing the exchange potential. OEP calculations in the past often did not meet the latter requirement and therefore may have led to erroneously low total energies.

I. INTRODUCTION

Methods based on density-functional theory (DFT) represent the presently most widely used theoretical approach to investigate the electronic ground states of molecules, clusters, or solids. Despite their success, present density-functional methods suffer from severe shortcomings. They, for example, cannot account for dispersion interactions and often incorrectly describe bond breaking and transition states due to their failure to correctly account for static correlation. Furthermore, density-functional methods do not, in general, achieve chemical accuracy, i.e., accuracies in bonding energies of about 1 kcal/mol. The accuracy and reliability of Kohn-Sham (KS) methods depend on the quality of the employed functionals for the exchange-correlation energy and potential. These functionals are not known exactly and therefore need to be approximated. Several generations of approximate exchange-correlation functionals can be identified: first, the local density approximation (LDA), second, generalized gradient approximations (GGAs), and, lately, orbital-dependent functionals. LDA functionals depend directly on the electron density; GGA functionals depend on the density and its gradients. GGA functionals are the functionals that, at present, are employed in most applications, sometimes in hybrid methods, in conjunction with scaled nonlocal Hartree-Fock exchange potential and energy. The corresponding GGA and hybrid DFT methods that represent the present state of the art are those that suffer from the above mentioned shortcomings.

Orbital-dependent functionals arguably represent the most promising recent development in DFT to overcome the shortcomings of GGA and hybrid methods. As suggested by their name, this new type of functionals depends not only on the electron density and its gradients but also on KS orbitals. Because the orbitals are functionals of the density, also orbital-dependent functionals are implicit functionals of the density and the realm of DFT is not left by the introduction of orbital-dependent functionals. Examples of orbital-dependent functionals are functionals that depend on the kinetic energy density or the exact expression for the exchange energy (see below). KS orbitals contain much more accessible information than the electron density. Therefore, orbital-dependent functionals are very promising and may represent the future of DFT. Indeed, the largest part of the unknown exchange-correlation energy, the exchange energy, is known exactly in terms of the orbitals. The KS exchange energy $E_x$ is given by the expression

$$E_x = -\sum_{i}^{\text{occ}} \sum_{j}^{\text{occ}} \int d\mathbf{r}d\mathbf{r}' \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_i(\mathbf{r}') \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

which is the same expression as the one for the Hartree-Fock (HF) exchange energy. In Eq. (1) $\phi_i$ and $\phi_j$ are occupied KS
orbitals. For notational simplicity, we consider throughout this work, non-spin-polarized systems with a nondegenerate ground state and with doubly occupied orbitals that are chosen to be real valued. The spin degree of freedom is taken into account implicitly by appropriate prefactors. Note that the KS and HF exchange energies are different because the orbitals entering expression (1) for the exchange energy differ in the HF and KS formalism.

An important difference between traditional LDA and GGA KS methods and KS approaches with orbital-dependent functionals arises in the construction of the exchange-correlation potentials that are required in a self-consistent KS calculation. The exchange-correlation potential is the functional derivative with respect to the electron density of the corresponding functional for the exchange-correlation energy. This functional derivative is easily accessible for LDA and GGA functionals because their dependence on the density is explicitly known. The dependence of orbital-dependent functionals on the electron density, however, is not explicitly known because the dependence of the KS orbitals on the density is unknown. Therefore, the functional derivative of orbital-dependent functionals on the electron density, however, is not explicitly known because the dependence of the KS orbitals on the density is unknown. Therefore, the functional derivative of orbital-dependent functionals with respect to the density cannot be taken directly. The functional derivative is instead determined indirectly via the chain rule.4,10,11

For the KS exchange potential this leads to the following equation:

$$E = T + V_{xc} + \int d\mathbf{r} v_{ex}(\mathbf{r}) \rho(\mathbf{r})$$

under the constraint that the orbitals are eigenstates of a Schrödinger equation of the form

$$[-\frac{1}{2}\nabla^2 + v_t(\mathbf{r})] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}),$$

with a local multiplicative potential $v_t(\mathbf{r})$. The contributions to the total energy in Eq. (5) are the kinetic energy

$$T = \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle,$$

the interaction energy $\int d\mathbf{r} v_{ex}(\mathbf{r}) \rho(\mathbf{r})$ with the external potential $v_{ex}$, usually the electrostatic potential of the nuclei, and the electron-electron interaction energy $V_{xc}$, which is the sum of the Coulomb energy

$$U = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$$

and the exchange energy $E_{\text{xc}}(\phi_i)$ given in Eq. (1).

Searching the optimal, i.e., minimizing orbitals, is tantamount to searching for the optimal potential $v_t$. If the optimized potential $v_t$ is written as

$$v_t(\mathbf{r}) = v_{ex}(\mathbf{r}) + u(\mathbf{r}) + v(\mathbf{r})$$

with the Coulomb potential

$$u(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|,$$

then the exchange potential required to determine the optimized potential $v_t$ is given by the OEP equation [Eq. (2)]. Thus, the OEP equation is the Euler equation in an energy minimization, and a self-consistent OEP calculation is equivalent to carrying out a minimization of the total energy [Eq. (5)]. In contrast to, for example, the HF energy minimization, the OEP energy minimization is a constrained minimization that has to obey the condition that the orbitals obey a Schrödinger equation [Eq. (6)] with a local multiplicative potential $v_t$. OEP equations corresponding to orbital-dependent exchange-correlation functionals $E_{\text{xc}}(\phi_i)$ other than the exchange functional $E_{\text{xc}}(\phi_i)$ of Eq. (1) can also be obtained as sketched above by energy minimization. The electron-electron interaction energy then is given by the sum of the Coulomb energy $U$ plus the exchange-correlation functional $E_{\text{xc}}(\phi_i)$ instead of the exchange functional $E_{\text{xc}}(\phi_i)$ of Eq. (1). A third derivation of the OEP equation invokes a perturbation theory along the adiabatic connection between the KS model system and the real electron system and uses the requirement that the first order correction to the KS density, like all higher order corrections, has to vanish.10,11 This derivation shall not be considered any further here.

From now on we will concentrate on exact-exchange-only OEP methods, i.e., OEP methods that neglect the correlation part of the exchange-correlation functionals $E_{\text{xc}}$ and $v_{ex}$ and treat the exchange parts $E_x$ and $v_x$ exactly according to Eqs. (1) and (2). The results of this work, however, for the most parts, are valid in general. Exact-exchange-only OEP methods minimize the same energy functional as HF met-
11. Exact-exchange density functional theory

ods. However, due to the constraint in the OEP energy minimization, the resulting OEP total energies always have to be higher than or equal to the HF total energies, and the corresponding OEP and HF orbitals are different. That OEP and HF orbitals, in general, need to be different also follows from the fact that the corresponding Schrödinger equations determining the orbitals, the Fock equation and the OEP equation, differ in the exchange potential. The HF exchange potential is a nonlocal potential, whereas the OEP exchange potential, by definition, is a local multiplicative potential.

The first exact exchange OEP method was introduced before modern DFT was developed as an approximation to the HF method. This first OEP method was a numerical grid method that could only be applied to spherical systems, i.e., to atoms. Because this first OEP method does not lead to computational savings compared to HF, there was little reason to use it instead of HF. The exact exchange OEP method regained attention after it was discovered that it is formally identical to an exact-exchange-only KS method and that the OEP equation generally yields the functional derivative of orbital-dependent functionals.

In order to carry out OEP calculations for molecules and solids, basis set OEP methods were developed in the last decade. These methods use an orbital basis set to represent the KS orbitals and an auxiliary basis set to represent the exchange potential, the response function, and the right hand side of the OEP equation. Basis set OEP methods for solids employing orbital and auxiliary basis sets both consisting of plane waves turned out to be numerically stable and can be applied routinely without problems. Basis set OEP methods for molecules using Gaussian orbital basis sets turned out to suffer from numerical instabilities that could not be solved despite considerable efforts.

An important consequence of the numerical problems of previous Gaussian basis set OEP methods is that the highly promising route to further develop DFT via orbital-dependent functionals is blocked up to now, at least, if methods based on Gaussian basis sets and thus the methods mostly employed in chemistry shall be used. (Numerical grid OEP methods could be applied only to a few very small molecules.) Indeed, in Ref. 27 it is shown that OEP methods with unbalanced auxiliary and orbital basis sets do not represent KS methods and that the resulting OEP exchange potentials are physically meaningless and do not represent the KS exchange potential. In Ref. 28 it was even demonstrated that for highly unbalanced basis sets the OEP method may yield the HF total energy at the price of a highly oscillating completely unphysical exchange potential. Note that even in the case of unbalanced basis sets, the OEP method still works properly in so far as it still yields among all exchange potentials that can be represented by the auxiliary basis set the one that leads to the lowest total energy. Of course, the resulting exchange potential and total energy in such cases of unbalanced basis sets is of no use because only OEP methods that properly represent KS methods are physically meaningful. The fact that the total energy remains well behaved even for unbalanced basis sets, however, means that the total energy alone cannot be used as a criterion to balance auxiliary and orbital basis sets and to decide whether or not an OEP procedure represents a proper KS method.

In this work we solve the long-standing problem of developing numerically stable OEP methods based on Gaussian basis sets by presenting an approach consisting of an exact exchange OEP method (Sec. III) and an accompanying construction and balancing scheme for the involved auxiliary and orbital Gaussian basis sets (Sec. V C) that is numerically stable, that properly represents an exact exchange KS method, that allows one to approach the basis set limit, and that can be applied to quite large molecules. Following common practice in quantum chemistry or physics, in this work, we do not consider in full detail all mathematical questions and subtleties related to our approach.

The remainder of this work is organized as follows: In Sec. II the numerical stability of basis set OEP methods is discussed. In Sec. III we introduce our Gaussian basis set OEP method and the reasoning behind it. Section IV summarizes technical information and computational details about the calculations carried out in this work. Then, in Sec. V we present the balancing scheme for orbital and auxiliary basis sets. In Sec. VI the approach is applied to several test molecules. Finally, Sec. VII presents our summary and conclusions.

II. BASIS SET OEP METHODS AND THEIR NUMERICAL STABILITIES

In order to apply the OEP approach to nonspherical systems, the exchange potential \( v_x \) is expanded in an auxiliary basis set \( \{ f_p \} \).

\[
v_x(r) = \sum_p c_p f_p(r).
\]

(11)

The OEP equation generally turns into the matrix equation

\[
X_{\mathbf{c} \mathbf{t}} = \mathbf{t}
\]

(12)

for the vector \( \mathbf{c} \) consisting of the expansion coefficients \( c_p \) of the exchange potential \( v_x \), i.e., for the vector \( \mathbf{c} \) representing the exchange potential in the auxiliary basis set. The elements of the matrix \( X_{ia} \) representing the response function \( X_{ia} \) are given by

\[
X_{ia} = \frac{\sum_{ia} \langle \phi_i | f_p | \phi_a \rangle \langle \phi_a | f_p | \phi_i \rangle}{e_i - e_a}.
\]

(13)

and the vector \( \mathbf{t} \) representing the right hand side of the OEP equation contains the elements

\[
t_p = \frac{\sum_{ia} \langle \phi_i | f_p | \phi_a \rangle \langle \phi_a | v_{NL} \phi_i \rangle}{e_i - e_a}.
\]

(14)

Basis set OEP methods were first implemented for periodic systems using plane waves both as orbital basis sets to represent the KS orbitals and as auxiliary basis sets \( \{ f_p \} \) to represent the exchange potential. Such plane wave OEP methods are numerically stable and can be routinely applied to various solids, provided the auxiliary and the orbital basis set are balanced by choosing the energy cutoff for the auxiliary basis not larger than about two thirds of the energy.
cutoff for the orbital basis set. This, at first, seems to be counterintuitive because, naively, one would think that the larger the auxiliary basis set, the better the representation of the OEP exchange potential. Indeed, in plane wave methods the Coulomb potential is usually expanded in a plane wave auxiliary basis set with an energy cutoff four times as large as that of the orbital basis set in order to obtain an exact representation. The reason why the cutoff for the auxiliary basis set for the exchange potential has to be smaller than that for the orbital basis set follows from an analysis of the matrix elements of the response function. As an example, a diagonal element $X_{pp}$ shall be considered. If the auxiliary basis function $f_p$ was a plane wave with a wave vector of a length equivalent to, for example, four times the energy cutoff of the orbital basis set, then this plane wave would be a rapidly oscillating function compared to the occupied and unoccupied orbitals entering the summation [Eq. (13)] that yields the matrix element $X_{pp}$ because the orbital basis set does not contain rapidly oscillating functions due to its smaller cutoff and thus cannot lead to highly oscillating orbitals. In this case, however, the integrals $\langle \phi_i | f_p | \phi_i \rangle$ in the summation [Eq. (13)] would all be zero or, in practice, close to zero because integrals over products of a rapidly oscillating function, here $f_p$, and a smooth function, here the product $\phi_i \phi_i$, vanish. This would lead to eigenvalues of the response matrix $X$, with an erroneously small magnitude and, subsequently, to much too large contributions of the corresponding eigenfunctions in the exchange potential. As a result, the exchange potential would exhibit a completely unphysical, highly oscillatory behavior. If, now, the cutoff of the orbital basis was increased sufficiently, i.e., increased to a value of three-halves of the auxiliary basis cutoff, then additional highly oscillating unoccupied orbitals would emerge. Integrals $\langle \phi_i | f_p | \phi_i \rangle$ containing these additional unoccupied orbitals and, subsequently, the corresponding contributions in the summation [Eq. (13)] would no longer be zero. Because all contributions in the summation [Eq. (13)] have the same sign, this would increase the magnitude of the matrix elements and eventually of the eigenvalues of the response function to their correct values. Subsequently, a smooth and physically meaningful exchange potential would result. This means that in order to reach the basis set limit in a basis set OEP calculation, the limits of the auxiliary and the orbital basis have to be taken in the right order. First, for each auxiliary basis the orbital basis has to be converged, and then for combinations consisting of an auxiliary basis with a corresponding converged orbital basis, the basis set limit can be taken. By always choosing the energy cutoff for the auxiliary basis not larger than about two-thirds of that of the orbital basis set or, conversely, by always choosing an energy cutoff for the orbital basis not smaller than three-halves of that of the auxiliary basis set, it is guaranteed that the basis set limit is taken in the correct order. In Sec. V we show that this order of limits and the requirement of converged orbital basis sets are crucial not only for plane wave but also for Gaussian basis sets (see also Ref. 27).

OEP methods for molecules based on Gaussian basis sets were developed shortly after the described plane wave OEP methods. However, they turned out to be numerically unstable and to suffer from unphysical features except for very small systems. The main reason for these problems was that for Gaussian orbital basis sets no balanced auxiliary basis sets for the exchange potential could be constructed for the various versions of Gaussian OEP methods developed over the years despite the fact that quite a number of different types of auxiliary basis sets were tested, for example, auxiliary basis sets consisting of Gaussian functions, of products of Gaussian functions, of electrostatic potentials of Gaussian functions, or of products of KS orbitals. This even led to the question whether the OEP approach is mathematically a well-posed procedure.

One reason why the numerical problem of Gaussian basis set OEP methods could not be solved so far despite many efforts is that there are a number of intricately entangled potential causes for these numerical problems that will be listed below:

(i) The auxiliary basis set is linear dependent or nearly linear dependent.
(ii) The orbital basis set is not sufficiently converged for a given auxiliary basis set. In this case the matrix elements of the response function and the right hand side of the matrix OEP equation are corrupted, and, as described above, the response functions will have eigenvalues with erroneously small eigenvalues.
(iii) In particular, for large auxiliary basis sets, the response matrix exhibits eigenvalues with a very small magnitude even if all matrix elements are well converged by employing a sufficiently large orbital basis set. These eigenvalues with a very small magnitude are physically correct because the true exact KS response function has an infinite number of eigenvalues with a value infinitely close to zero.
(iv) The method of solving the OEP matrix equation [Eq. (12)], i.e., the solution of the corresponding system of linear equations, introduces numerical inaccuracies.

The potential problem (i) can easily be avoided by an appropriate choice for the auxiliary basis sets. The potential problem (ii) is a demanding one. In order to get it under control, a construction scheme for auxiliary and orbital basis sets that guarantees that the orbital basis is sufficiently converged for a given auxiliary basis set is required. Such a construction scheme is presented in Sec. V C. The potential problem (iii), again, is not easily solved. Some of the eigenvalues of the response function with a small magnitude originate from auxiliary basis functions that are either localized very tightly around the nuclei or quite diffuse. Fortunately, auxiliary basis functions localized very tightly around the nuclei or that are very diffuse do not contribute significantly to the exchange potential and thus can simply be omitted in the auxiliary basis set. Numerical problems due to moderately diffuse basis functions cannot be avoided that easily because these auxiliary functions contribute to the asymptotic region of the exchange potential. To some extent, numerical problems due to moderately diffuse functions could be handled by coping with the corresponding small magnitudes of eigenvalues of the response functions by monitoring the eigenvalues and carefully controlling the so-
lution of the OEP matrix equation [Eq. (12)]. A much more robust approach is to avoid the occurrence of this problem from the start by determining the asymptotic region of the exchange potential not exclusively via the OEP equation but also with the help of exact conditions obeyed by the KS exchange potential and by choosing the right type of auxiliary basis functions. This latter approach is employed in this work and presented in Sec. III. Whether problem (iv) shows up or not depends on the condition of the matrix OEP equation [Eq. (12)], particularly on the condition of the response matrix. In the approach presented in this work the solution of the matrix OEP equation never caused any numerical problems if appropriate auxiliary and orbital basis sets were chosen.

Because of the importance of numerically stable Gaussian basis set methods for the further development of DFT and because attempts to develop such methods have failed despite a lot of efforts, various approximate treatments of the exact exchange OEP equation [Eq. (2)] were developed over the years. The KLI method, named after their authors Krieger, Li, and Iafrate, replaces the summation over unoccupied orbitals in the response function and the right hand side of the OEP equation [see Eqs. (3) and (4)] by summations $\Sigma_{i,r} \Sigma_{d,a}$ over all orbitals but one and then sets the energy denominators in the summations all to a common value. The resulting method is numerically stable and yields exchange potentials and total energies that are good approximations to the corresponding full OEP quantities. A disadvantage of the KLI approximation is that it is not invariant with respect to unitary transformations of the occupied or unoccupied orbitals among themselves. The problem is cured by the localized Hartree-Fock (LHF) method, also called common energy denominator approximation (CEDA), which replaces only the magnitude of the eigenvalue differences by a common value but retains the sign (see also Ref. 33 and references therein). Again, good approximations to full OEP exchange potentials and total energies are obtained. The KLI and LHF/CEDA methods treat the asymptotic region of the exchange potential correctly, including the complicated asymptotic structures that can occur close to nodal planes of the highest occupied molecular orbital. The price, however, is that implementations of the LHF/CEDA method that are capable of treating these asymptotic structures require a numerically complicated asymptotic continuation scheme that is not easily applicable to certain types of molecules, such as chainlike molecules or large molecules with a ring structure. Another related approximate OEP approach that is termed effective local potential method has recently been developed by Staroverov et al.

Other approximate OEP methods consider the spectral representation of the response matrix in the auxiliary basis set [see Eqs. (3) and (13)], and then, in a first attempt, neglect the contributions corresponding to eigenvalues with magnitudes below a certain threshold, i.e., perform a singular value decomposition. This, however, does not remove the numerical instabilities. A certain smoothing of the oscillations in OEP exchange potentials can be accomplished by a Tikhonov regularization of the spectral representation of the response matrix, but, at the price of departing from the true OEP exchange potential and total energy. A third type of approximate OEP methods adds a term to the total energy expression minimized in the OEP procedure and in this way introduces a smoothing term in the OEP equation. Adding this term, of course, again means departing from the exact OEP energy and, subsequently, also from the exact OEP exchange potential.

In summary, the mentioned approximate OEP procedures are valuable temporary solutions as long as a numerically stable Gaussian basis set OEP method is not available. However, the great need for such a method, which shall be presented and discussed in the following sections, cannot be satisfied by the approximate approaches.

III. METHOD

The Gaussian basis set OEP method presented in this section is related to the approach of Ref. 19 and, like the latter, is a self-consistent field (SCF) KS procedure. In contrast to standard LDA or GGA KS procedures, however, the exchange potential is not obtained by evaluating an approximate density-dependent expression but by solving the OEP equation [see Eqs. (11)–(14)] in a way described in detail in this section. Like in the approach of Ref. 19, we employ for the representation of the exchange potential and the OEP auxiliary basis functions $f_p$ that are given by the electrostatic potentials of Gaussian functions $g_p$,

$$f_p(r) = \int d\mathbf{r}' \frac{g_p(r')}{|r - r'|}.$$  

The local exchange potential in Eq. (11) can then be expressed as

$$u_x(r) = \sum_p c_p \int d\mathbf{r}' \frac{g_p(r')}{|r - r'|}$$

$$= \int d\mathbf{r}' \sum_p c_p g_p(r') \frac{1}{|r - r'|}$$

$$= \int d\mathbf{r}' \rho_s(r') \frac{1}{|r - r'|},$$

with an exchange charge density

$$\rho_s(r) = \sum_p c_p g_p(r).$$

As a remark on the side, we note that in a similar way one can also define a correlation charge density $\rho_c$ whose electrostatic potential is the correlation potential. The sum $\rho_c = \rho_s + \rho_i + \rho_e$ represents an effective charge distribution that incorporates all effects of the electron-electron interaction in the sense that its electrostatic potential equals the effective KS potential $u_x$, that is experienced by an electron of the KS model system. This effective charge $\rho_c$ may be of interest for the interpretation of electronic structures.

Except on nodal surfaces of the highest occupied molecular orbital (HOMO), the exchange potential is known to decay far from a finite electronic system, i.e., an atom, molecule, or cluster, like $-1/r$, with $r$ denoting the distance from the charge center of the electronic system.
(-1/r) asymptotic of the exchange potential requires the exchange charge \( \rho_x \) to integrate to -1, i.e., leads to the condition
\[
\int dr \rho_x(r) = -1, \tag{18}
\]
which shall be called charge condition. Within the auxiliary basis set representation this condition reads as
\[
y^T c = -1, \tag{19}
\]
with the elements \( y_p \) of vector \( y \) given by
\[
y_p = \int dr g_p(r). \tag{20}
\]
Another exact condition, which shall be called HOMO condition, for the exchange potential is the relation
\[
\langle \phi_{\text{HOMO}} | y_p | \phi_{\text{HOMO}} \rangle = \langle \phi_{\text{HOMO}} | \delta_{\text{NL}}^x | \phi_{\text{HOMO}} \rangle, \tag{21}
\]
where \( \phi_{\text{HOMO}} \) is the HOMO of the Kohn-Sham system. Within the auxiliary basis set representation this condition assumes the form
\[
z^T c = \langle \phi_{\text{HOMO}} | \delta_{\text{NL}}^x | \phi_{\text{HOMO}} \rangle, \tag{22}
\]
with the elements \( z_p \) of the vector \( z \) given by
\[
z_p = \langle \phi_{\text{HOMO}} | f_p | \phi_{\text{HOMO}} \rangle. \tag{23}
\]
In the case of a set of \( n_{\text{degn}} \)-fold degenerate HOMOs \( \phi_{\text{HOMO},i} \), Eqs. (22) and (23) read as
\[
z^T c = \sum_{i=1}^{n_{\text{degn}}} \frac{1}{n_{\text{degn}}} \times \langle \phi_{\text{HOMO},i} | \delta_{\text{NL}}^x | \phi_{\text{HOMO},i} \rangle \text{ and } z_p = \sum_{i=1}^{n_{\text{degn}}} \frac{1}{n_{\text{degn}}} \times \langle \phi_{\text{HOMO},i} | f_p | \phi_{\text{HOMO},i} \rangle, \]
with \( k \) labeling the \( n_{\text{degn}} \) degenerate HOMOs.

The two conditions above are difficult to meet in Gaussian basis set OEP methods except for very large auxiliary and orbital basis sets if the exchange potential is determined directly according to the matrix OEP equation [Eq. (12)]. The reason is that, on the one hand, as shown above, the OEP method represents an energy minimization and, on the other hand, that the asymptotic region contributes very little to the energy. Therefore, in Ref. 19 the charge condition [Eq. (19)] was enforced via a Lagrange multiplier approach in the OEP method. In Ref. 43 this approach was modified in order to enforce the HOMO condition [Eq. (22)] instead of the charge condition [Eq. (19)]. Both conditions were simultaneously used in the OEP calculations reported in the work of Rohr et al. 25

Here, we present an alternative scheme that guarantees that both charge and HOMO conditions are obeyed. This scheme is based on the division of the local exchange potential into a reference potential \( \nu_x^{\text{ref}} \) and a remainder \( \nu_x^{\text{rest}} \),
\[
u_x(r) = \nu_x^{\text{ref}}(r) + \nu_x^{\text{rest}}(r). \tag{24}
\]
Both \( \nu_x^{\text{ref}} \) and \( \nu_x^{\text{rest}} \) shall be expanded in the same auxiliary basis \( f_p \) as the one described in Eq. (15). The expansion coefficients for \( \nu_x^{\text{ref}} \) and \( \nu_x^{\text{rest}} \) shall be contained in vectors \( c^{\text{ref}} \) and \( c^{\text{rest}} \), respectively. The charge and HOMO conditions are then imposed on the reference potential \( \nu_x^{\text{ref}} \), whereas the remaining potential \( \nu_x^{\text{rest}} \) does not contribute to the two conditions. This is achieved in the following way.

In a first step the reference potential, that is, \( c^{\text{ref}} \), is determined. To that end we define vector \( c_a \) according to
\[
c_{a,p} = \begin{cases} (1/N_{\text{aux}})(-1/y_p) & \text{if } y_p \neq 0 \\ 0 & \text{if } y_p = 0, \end{cases} \tag{25}
\]
where \( N_{\text{aux}} \) is the number of auxiliary functions with \( y_p \neq 0 \), i.e., the number of auxiliary basis functions that do not integrate to zero. Alternatively, vector \( c_e \) is defined according to
\[
c_{e,p} = \begin{cases} -1/\sum_p y_p & \text{if } y_p \neq 0 \\ 0 & \text{if } y_p = 0. \end{cases} \tag{26}
\]
Frequently, the asymptotic behavior of the exchange potential is modeled using the Fermi-Amaldi potential. If the electronic charge is expressed via density fitting in the auxiliary basis, then this leads to a representation of the Fermi-Amaldi potential in the auxiliary basis \( g_p \), which represents a further possibility to define vector \( c_c \),
\[
c_{c,p} = \sum_{q=1}^{N_{\text{aux}}} \left( S^{-1} g_q | \phi_{\text{HOMO}} \right) \frac{-1}{n_{\text{occ}}} \delta_{\text{NL}}^x g_q(r_p) | \phi_{\text{HOMO}} \rangle, \tag{27}
\]
where \( N \) denotes the number of electrons and \( N_{\text{aux}} \) the number of auxiliary basis functions. The matrix \( S \) constitutes the metric in the auxiliary basis set defined by the matrix elements \( S_{pq} = \langle g_p | g_q \rangle = \int dr dr' g_p(r) g_q(r')/|r-r'| \). The integrals \( \langle g_p | \phi_{\text{HOMO}} \rangle \) are given by \( \langle g_p | \phi_{\text{HOMO}} \rangle = \int dr dr' g_p(r) \psi_{\text{HOMO}}(r')/|r-r'| \). In this work we adopted the first choice for \( c_c \) [i.e., Eq. (25)].

Next, vector \( c_b \) is defined according to
\[
c_b = \langle \phi_{\text{HOMO}} | \delta_{\text{NL}}^x | \phi_{\text{HOMO}} \rangle z/z^T. \tag{28}
\]
In order to fulfill both conditions simultaneously, the coefficient vector \( c^{\text{ref}} \) representing \( \nu_x^{\text{ref}} \) is written as a linear combination,
\[
c^{\text{ref}} = ac_a + bc_b. \tag{29}
\]
The coefficients \( a \) and \( b \) are determined by solving the equation system
\[
\begin{pmatrix} y^T c_a & y^T c_b \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 1/\sum_p y_p & -1/\sum_{q=1}^{N_{\text{aux}}} \left( S^{-1} g_q | \phi_{\text{HOMO}} \right) \frac{-1}{n_{\text{occ}}} \delta_{\text{NL}}^x g_q(r_p) | \phi_{\text{HOMO}} \rangle \end{pmatrix}, \tag{30}
\]
The reference potential \( \nu_x^{\text{ref}} \) corresponding to \( c^{\text{ref}} \) then obeys the charge as well as the HOMO condition. The remaining potential \( \nu_x^{\text{rest}} \) obeys the modified OEP equation
\[
\int dr X_x(r,r')\nu_x^{\text{rest}}(r') = w(r), \tag{31}
\]
with the modified right hand side
\[
w(r) = 4 \sum_i \sum_{a=1}^{n_{\text{occ}}} \sum_{a=1}^{n_{\text{occ}}} \phi_i(r) \phi_a(r') | \phi_{\text{HOMO}} \rangle | \phi_{\text{HOMO}} \rangle - \nu_x^{\text{ref}} | \phi_{\text{HOMO}} \rangle, \tag{32}
\]
which turns into the matrix equation
\[
X_c c^{\text{rest}} = w, \tag{33}
\]
with the elements \( w_p \) of the right hand side given by
The coefficient vector $\mathbf{c}^{\text{ref}}$ has to be determined in such a way that it is orthogonal both to vector $\mathbf{y}$ originating from the charge condition and to vector $\mathbf{z}$ originating from the HOMO condition. Then, it is guaranteed that the corresponding potential $\tilde{v}_x$ does not make any contributions to the integral over the exchange charge density or the value of the expectation value $\langle \phi_{\text{HOMO}} \rangle\langle \mathbf{v}_i \rangle_{\text{HOMO}}$, and thus the charge and HOMO conditions remain obeyed if $\tilde{v}_x$ is added to $v_i^{\text{ref}}$ in order to obtain the full exchange potential $v_i$. This can be achieved by properly projecting out the space spanned by vectors $\mathbf{y}$ and $\mathbf{z}$ from the response matrix and right hand side before solving Eq. (33). The projection matrix can be obtained in two steps:

1. (Outproyjection of vector $\mathbf{y}$): The starting point is an $M_{\text{aux}} \times M_{\text{aux}}$ unit matrix $\mathbf{E}=(\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_{M_{\text{aux}}})$, with $M_{\text{aux}}$ denoting the dimension of the auxiliary basis set. First, column $\mathbf{e}_1$ which gives the scalar product $\mathbf{y}^T \mathbf{e}_1$ with the largest magnitude is removed to obtain a $M_{\text{aux}} \times (M_{\text{aux}}-1)$ matrix, which shall be denoted $\tilde{\mathbf{E}}=(\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_{M_{\text{aux}}-1})$. In principle, any $\mathbf{e}_i$ with $\mathbf{y} \cdot \mathbf{e}_i \neq 0$ could be removed. However, the above choice for the column to be removed contributes to a good condition of the response matrix that is eventually obtained by the projections. Next, an intermediate $M_{\text{aux}} \times (M_{\text{aux}}-1)$ projection matrix $\mathbf{Q}$ with columns

$$
\mathbf{q}_i = \mathbf{e}_i - \frac{\mathbf{e}_i^T \mathbf{y} \mathbf{y}^T}{\mathbf{y} \cdot \mathbf{y}}
$$

is constructed.

2. (Outproyjection of vector $\mathbf{z}$): First, vector $\mathbf{z}$ is orthogonalized to $\mathbf{y}$ in order to obtain a vector,

$$
\tilde{\mathbf{z}} = \mathbf{z} - \frac{\mathbf{z}^T \mathbf{y}}{\mathbf{y} \cdot \mathbf{y}} \mathbf{y}
$$

Next, column $\mathbf{q}_i$ of matrix $\mathbf{Q}$ that yields the scalar product $\tilde{\mathbf{z}}^T \mathbf{q}_i$ with the largest magnitude is removed from $\mathbf{Q}$ to obtain an $M_{\text{aux}} \times (M_{\text{aux}}-2)$ matrix that shall be denoted $\tilde{\mathbf{Q}}=(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_{M_{\text{aux}}-2})$. Then, the final $M_{\text{aux}} \times (M_{\text{aux}}-2)$ projection matrix $\mathbf{P}$ with columns

$$
\mathbf{p}_i = \mathbf{q}_i - \frac{\mathbf{q}_i^T \tilde{\mathbf{z}} \tilde{\mathbf{z}}^T}{\tilde{\mathbf{z}} \cdot \tilde{\mathbf{z}}}
$$

is constructed.

If only the charge constraint shall be taken into account, then vector $\mathbf{c}^{\text{ref}}$ has to be set equal to vector $\mathbf{c}_p$ given in Eq. (25), (26) or (27), and only the first step in the construction of the projection matrix is carried out. If only the HOMO constraints shall be considered, then vector $\mathbf{c}^{\text{ref}}$ has to be set equal to vector $\mathbf{c}_a$ given in Eq. (28), and again only the first step in the construction of the projection matrix is carried out, but with vector $\mathbf{y}$ replaced by $\mathbf{z}$.

Finally, the OEP equation [Eq. (33)] is transformed into

\begin{equation}
\tilde{\mathbf{X}}^T \mathbf{c}^{\text{ref}} = \tilde{\mathbf{w}},
\end{equation}

with

\begin{equation}
\tilde{\mathbf{X}} = \mathbf{P}^T \mathbf{X}_p
\end{equation}

and

\begin{equation}
\tilde{\mathbf{w}} = \mathbf{P}^T \mathbf{w}.
\end{equation}

In this work the linear equation system in Eq. (38) has been solved using a standard solver that performs an LU decomposition of the coefficient matrix. Vector $\mathbf{c}^{\text{ref}}$ solving the OEP equation [Eq. (38)] can be backtransformed via $\mathbf{c}^{\text{ref}} = \mathbf{P} \mathbf{c}^{\text{ref}}$ to obtain the final coefficients of the potential $\tilde{v}_x$. Note that the reference potential changes from SCF cycle to SCF cycle because the orbitals, including the HOMO, change. Subsequently also Eqs. (21), (22), (28), and (30) representing the HOMO condition and its handling change during the SCF process.

Furthermore, note that there are infinitely many choices for vectors $\mathbf{c}_p$ and $\mathbf{c}_a$ and thus for the reference potential $v_i^{\text{ref}}$ that obeys both charge and HOMO conditions. Equations (25)–(27) just represent three possible choices. However, the final exchange potential obtained by the presented method is independent of these choices. The reason is that the difference between two different potentials $v_i^{\text{ref}}$, more precisely between two different vectors $\mathbf{c}^{\text{ref}}$, is a vector that lies within the space considered in the determination of the remaining potential $v_i^{\text{rest}}$, i.e., a vector that does affect neither the charge nor the HOMO condition. This means that differences in choice of vector $\mathbf{c}^{\text{ref}}$ will be compensated by corresponding differences in the resulting vector $\mathbf{c}^{\text{ref}} + \mathbf{c}^{\text{est}}$, which represents the KS exchange potential, remains unchanged.

The OEP procedure presented here can be considered as an optimization of the energy with respect to the expansion coefficients $c_p$ of the full set of auxiliary basis functions under the constraint that the charge and HOMO conditions are obeyed. Indeed, it would be completely equivalent to take into account these conditions via a Lagrange multiplier approach. The projection approach chosen here, however, can easily be used in an iterative solution of the matrix OEP equation. Alternatively, the presented OEP procedure can be considered as an unconstrained minimization of the energy with respect to coefficient vectors representing exchange potentials $v_i$ in a space that is orthogonal to the space spanned by vectors $\mathbf{y}$ and $\mathbf{z}$ while the contributions of vectors $\mathbf{y}$ and $\mathbf{z}$ to the representation of $v_i$ are determined by the charge and HOMO conditions.

Exploiting the charge and HOMO conditions in the determination of the exchange potential and its asymptotic region, together with the specific choice of the type of the auxiliary basis functions made here [see Eq. (15)], increases the numerical stability of the presented Gaussian basis set OEP method, as explained in Sec. II in the discussion of the list of potential sources of numerical instabilities.

Regarding the computational efficiency of the basis set OEP method, it is noted here that in all calculations reported in this work the solution of the OEP equations using Eqs. (12)–(14) took much less computer time than the calculation...
and diagonalization of the Fock matrix. The presented OEP method, even in its present form, is applicable to systems with up to 100 and more electrons and/or 2500 orbital basis functions.

IV. COMPUTATIONAL DETAILS

The OEP method described in Sec. III has been used to calculate the exchange potentials and total energies for the atoms beryllium and neon and the six molecules CO, H₂O, NH₃, C₂H₆, cytosine, and pregnandiole.

For beryllium several combinations of orbital and auxiliary basis sets were used. In Sec. V A we investigate the general convergence behavior of orbital basis sets for a given auxiliary basis set. For the orbital basis set here even tempered basis sets of $s$ functions with exponents $\alpha$ ranging from 10 000 to 0.01 have been chosen. In order to control the quality of these basis sets, progression factors of 40 to $\sqrt{2}$ have been used. The exponents for the basis sets were generated by starting with the largest exponent of $\alpha=10000$ and dividing this value by the progression factor as long as $2\alpha > 0.01$ holds. Thus, the smallest orbital basis set with progression 40 contains 4 $s$ functions with a most diffuse exponent of 0.156, and the largest orbital basis set with progression $\sqrt{2}$ contains 42 $s$ functions with a most diffuse exponent of $\alpha=0.00674$.

As auxiliary basis sets for beryllium, three basis sets with increasing quality (again consisting only of $s$ functions) were used: an auxiliary basis obtained by adapting the quadruple zeta basis set of Dunning, (termed cc-pVQZ+1s), an auxiliary basis obtained by adapting the even tempered basis set introduced above with a progression factor of 1.5 [termed even(1.5) in the following]. The cc-pVQZ+1s auxiliary basis set contains 8 $s$ functions with exponents $\alpha$ between 16.5 and 0.04, the Partridge3 basis, (termed Partridge3+2s), and an auxiliary basis obtained by adapting the even tempered basis set introduced above with a progression factor of 1.5 [termed even(1.5) in the following]. The cc-pVQZ+1s auxiliary basis set contains 8 $s$ functions with exponents $\alpha$ between 16.5 and 0.04, the Partridge3+2s auxiliary basis set contains 11 $s$ functions with exponents $\alpha$ between 56.1 and 0.08, and the even(1.5) auxiliary basis set contains 21 $s$ functions with exponents $\alpha$ between 115.6 and 0.03. Further details about these basis sets and how they were constructed are given in Sec. V C.

For the neon atom the contracted and uncontracted d-aug-cc-pVXZ ($X=D,T,Q,5,6$) basis sets of Dunning were used. Only $s$ and $p$ functions were included in the orbital basis set, while for the auxiliary basis set only $s$ functions were needed due to the spherical symmetry of the OEP exchange potential. In order to come close to the basis set limit, a large even tempered orbital basis set with exponents between 100 000 and 0.01 for $s$ functions and between 100 and 0.01 for $p$ functions and a progression factor of 1.5 has been constructed, in the same way as is done for the beryllium atom described above. The corresponding auxiliary basis set (with only $s$ functions) has been constructed thereof by removing the 12 tightest and 4 most diffuse $s$ functions. This basis set is termed even(1.5).

In the case of the molecules CO, H₂O, NH₃, and C₂H₆ the doubly augmented cc-pVXZ ($X=D,T,Q,5$) basis sets of Kendall et al. were used. The corresponding auxiliary basis sets were constructed thereof along the lines described in Sec. V C. No functions with higher angular momenta than $g$ functions in the orbital basis sets and no functions with higher angular momenta than $d$ functions in the auxiliary basis sets were used. The doubly augmented cc-pVTZ (for cytosine) and the doubly augmented cc-pVDZ (for pregnandiole) balanced orbital and auxiliary basis sets have been employed. Data describing all basis sets used in the calculations are compiled in Table I.

The geometries for all molecules considered in this work have been taken from Ref. 47 with the exception of cytosine, where the geometry has been obtained from Ref. 48, and of pregnandiole, where the geometry has been taken from the benchmark suite of the MOLPRO program package. Some calculations were performed using the developer version of the MOLPRO quantum chemistry package. Some results of this work are also based on investigations made with the TURBOMOLE program. For beryllium and neon we have also performed highly accurate OEP calculations using the relativistic atomic structure Kohn-Sham (RELKS) program by Engel et al. 51–53 by considering the nonrelativistic limit, i.e., a very large speed of light that for practical purposes equals infinity. The RELKS program is a numerical grid OEP code. While numerical grid codes are not exempt from numerical problems, the technical details and settings in the RELKS program were chosen such that the calculated exchange potentials for beryllium as well as the one for neon can be considered as de facto exact. In order to obtain the KS orbitals and energies represented in a given Gaussian basis set from the numerical OEP potential, the potential is read in the DFT module of the MOLPRO program, which performs a numerical quadrature to obtain the exchange matrix elements. The numerical grid in this quadrature has been chosen to be sufficiently dense such that numerical errors produced by this method are smaller than all values reported in this work. The self-consistent OEP procedure then only optimizes the Coulomb potential because the exchange potential is fixed to the reference exchange potential. The OEP values obtained in this way will be denoted as “OEP(num)” in the following sections and are referred to as reference OEP results, which we will use to assess the accuracy of our basis set OEP method.

V. BALANCING OF GAUSSIAN ORBITAL AND AUXILIARY BASIS SETS IN OEP METHODS

A. General convergence behavior of orbital basis sets for a given auxiliary basis set

The following example demonstrates that the strategy to balance auxiliary and orbital plane wave basis sets that is described in Sec. II also is principally applicable to Gaussian basis sets, i.e., that for a given fixed auxiliary basis set one can obtain a stable OEP procedure by enlarging the orbital basis set until the exchange potential and/or the energy difference from Hartree-Fock does not change anymore: as a test system, the beryllium atom is chosen because only $s$-type functions are needed to describe the orbitals and the exchange potential.

For the OEP calculations we used the method described in Sec. III that guarantees that both charge and HOMO con-
TABLE I. Orbital and auxiliary basis sets for neon, carbon, oxygen, nitrogen, and hydrogen. The orbital basis sets taken are the doubly augmented cc-pVXZ (X=D,T,Q,5) basis sets of Kendall et al. (Ref. 46) with exception of neon/V6Z, for which the singly augmented cc-pV6Z basis set of Wilson et al. (Ref. 61) has been used. The fourth column gives the exponents of the additional orbital basis functions, and the sixth column the exponents of the additional auxiliary basis functions as compared to the standard orbital basis. The last two columns give the number of tight and diffuse auxiliary functions that were removed compared to the corresponding orbital basis set.

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11. Exact-exchange density functional theory
The differences of the OEP total energies to HF total energies for combinations of three auxiliary basis sets with various even tempered orbital basis sets are compiled in Table II. In Table II it can be seen that the basis sets with progressions between 40.0 and 9.0 contain four to seven functions and yield OEP energies that are nearly identical to HF, both for the cc-pVQZ+1s and the Partridge3+2s auxiliary basis sets and thus reconfirm the findings of Ref. 28 that one can obtain Hartree-Fock energies from the OEP method if the orbital and auxiliary basis sets are unbalanced with respect to each other. With a progression rate of 7.0 the orbital basis contains eight s functions, and one can see that from here on the energies of HF and OEP start to differ more clearly in the case of the cc-pVQZ+1s auxiliary basis. Then, from progressions 5.0 to 2.5 the energy difference changes dramatically by an amount of 0.41 mhartree for the cc-pVQZ+1s auxiliary basis and 0.51 mhartree for the Partridge 3+2s auxiliary basis set.

This can also be seen from the respective smallest eigenvalues of the response matrix $X_s$, which are displayed in the last column of Table II. For the smallest orbital basis set the smallest eigenvalue of $X_s$ is far below machine precision and thus is de facto zero. It shall be noted, however, that the OEP calculation still converged within a few SCF cycles. For the larger orbital basis sets the smallest eigenvalue of $X_s$ increases as expected and converges to a value of about $0.14 \times 10^{-6}$ a.u. for the cc-pVQZ+1s and $0.84 \times 10^{-10}$ a.u. for the Partridge 3+2s auxiliary basis set.

The fifth column of Table II shows the OEP-HF energy differences that were obtained by using always the de facto exact reference OEP exchange potential, obtained from the numerical grid RELKS code by Engel et al. 51–53 instead of the basis set OEP potentials emerging in the calculations. As described in Sec. IV, the OEP-HF energy difference of 0.591 mhartree for the orbital basis with a progression factor of $\sqrt{2}$ may be regarded as the exact energy difference between HF and OEP. A value of 0.59 mhartree for the difference between exact OEP and Hartree-Fock is also reported in the work by Krieger et al.,30 where a numerical grid OEP method is also used. A comparison of the OEP total energies for the basis set OEP method with the even(1.5) auxiliary basis and an extended even(1.5) tempered orbital basis set (further augmented by seven tight functions) given in the last row in Table II with the total energy yield by the RELKS program shows an agreement up to microhartree accuracy.
the basis set OEP gives an energy of $-14.572\,432$ hartree and the numerical grid OEP yields an energy of $-14.572\,433$ hartree. Taking the value of $0.591\,m$hartree for the basis set OEP gives an energy of $-14.572\,432$ hartree. The last column displays the smallest eigenvalue of the response matrix [Eq. (13)] in a.u.

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<th>$E_{\text{OEP}<em>{\text{num}}} - E</em>{\text{HF}}$</th>
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<td>0.389</td>
<td>0.450</td>
<td>$6.48 \times 10^{-7}$</td>
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<td></td>
<td>3</td>
<td>14</td>
<td>0.529</td>
<td>0.504</td>
<td>$9.97 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>16</td>
<td>0.575</td>
<td>0.548</td>
<td>$1.33 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21</td>
<td>0.614</td>
<td>0.582</td>
<td>$1.44 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>36</td>
<td>0.614</td>
<td>0.591</td>
<td>$1.44 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$\sqrt{2}$</td>
<td>42</td>
<td>0.614</td>
<td>0.591</td>
<td>$1.44 \times 10^{-6}$</td>
</tr>
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<td>Partridge3+2s</td>
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<td>0.000</td>
<td>0.007</td>
<td>$-1.13 \times 10^{-19}$</td>
</tr>
<tr>
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<td>0.002</td>
<td>7.953</td>
<td>$-1.55 \times 10^{-16}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7</td>
<td>0.005</td>
<td>0.864</td>
<td>$-3.07 \times 10^{-16}$</td>
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<tr>
<td></td>
<td>9</td>
<td>7</td>
<td>0.002</td>
<td>0.885</td>
<td>$-3.48 \times 10^{-17}$</td>
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<tr>
<td></td>
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<td>7</td>
<td>0.109</td>
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<tr>
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<tr>
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<td>10</td>
<td>0.000</td>
<td>0.304</td>
<td>$-$</td>
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<tr>
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<td>4</td>
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<td>0.406</td>
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<td>0.333</td>
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<td>0.584</td>
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<td></td>
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<td>0.592</td>
<td>0.591</td>
<td>$0.844 \times 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>$\sqrt{2}$</td>
<td>42</td>
<td>0.592</td>
<td>0.591</td>
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<td>Even(1.5)</td>
<td>1.5</td>
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<td>0.591</td>
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<td>0.591</td>
<td>$0.521 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>1.5+7tight</td>
<td>43</td>
<td>0.591</td>
<td>0.591</td>
<td>$0.392 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

The corresponding OEP exchange potentials for some of the orbital basis sets and the cc-pVQZ+1s auxiliary basis set as well as the reference OEP exchange potential are displayed in Fig. 1. It shows that the potential corresponding to a progression factor of 20.0 possesses dramatic oscillations and is clearly different from the reference OEP exchange potential, which has the well-known intershell peak at about 0.9 bohr and then smoothly approaches the correct asymptotic ($-1/r$) behavior for increasing distances from the nucleus. Upon increase of the orbital basis set by using smaller progression factors, Fig. 1 shows that the oscillations in the exchange potential get more and more damped and the exchange potential corresponding to a progression factor of 1.5 becomes indistinguishable from the reference OEP exchange potential near the nucleus and in the range beyond 2 bohrs. Note that the potential corresponding to a progression factor of 2.0 is de facto identical to the potential for a progression factor of 1.5 shown in Fig. 1. This demonstrates
that if the cc-pVQZ+1s auxiliary basis is chosen, a stable and meaningful OEP procedure is obtained by the orbital basis sets with progression factors from 1.5 to 20.0 and the cc-pVQZ+1s auxiliary basis set (see text).

In Fig. 2 OEP exchange potentials for different auxiliary basis sets and corresponding orbital basis sets are displayed. The recipe, which has been used to construct these basis sets and which we will describe in Sec. V C, guarantees that all displayed potentials are converged with respect to the orbital basis. For the Partridge3+2s auxiliary basis Fig. 2 shows that the corresponding OEP exchange potential is nearly indistinguishable from the exact one; slight deviations only exist in the intershell region. Finally, for the even(1.5) auxiliary basis set, no visible difference from the reference OEP exchange potential exists anymore.

B. The role of the continuum states in OEP methods

As shown in Sec. V A and as discussed in Sec. II, the following sections, and Ref. 27, stable Gaussian basis set OEP procedures require that the orbital basis set is converged with respect to a given auxiliary basis set. More precisely, the summations over unoccupied orbitals occurring in definitions (13) and (14) of the elements of the response matrix and the right hand side of the OEP equation [Eq. (12)] need to be converged. This, in turn, requires an orbital basis set that yields those unoccupied orbitals that are necessary for converging these summations. In order to test which type of orbitals are needed, we consider the response matrix emerging in the OEP treatment of beryllium with the even tempered auxiliary and orbital basis sets termed as even(1.5) (Sec. V A). Here, the orbital basis set was further augmented by seven tighter and nine-more diffuse basis functions. This calculation was fully converged with respect to both basis sets, yielded the same energy as a numerical OEP calculation on a grid, and therefore serves as a reference here. We now analyze the convergence of the summation \( \sum_a \langle \phi_i | f_p | \phi_a \rangle \langle \phi_a | f_p | \phi_i \rangle / (e_i - e_a) \) over unoccupied orbitals occurring in Eq. (13) for three typical diagonal elements \( X_{i,pp} \) of the response function, those corresponding to auxiliary basis functions \( f_p \) with exponents 15.22, 2.00, and 0.035. To that end we increase step by step the upper limit of the summation over the unoccupied orbitals, i.e., the summation over \( a \), from 0 to 49, the full number of unoccupied orbitals. Because the terms in the summation all have the same sign, they all add up. The results of this analysis are displayed in Fig. 3.

Figure 3 shows that, at first, there is a rapid convergence of the elements of the response function with unoccupied orbitals with negative eigenvalues, i.e., with bound unoccupied orbitals. The higher Rydberg orbitals 8–11 do not contribute at all to the elements of the response matrix. With the onset of positive KS eigenvalues, i.e., with the onset of orbitals representing the continuum, there is, however, a sharp increase of the magnitude of the elements of the response matrix. Indeed, the final matrix element of the auxiliary basis function with exponent 15.22 originates from 74% of the contributions corresponding to continuum orbitals. For the matrix elements of the auxiliary basis functions with exponents 2.00 and 0.035, this percentage still lies at 54% and 19%. This leads to a crucial conclusion: A proper description of the continuum is indispensable in OEP methods using Gaussian basis sets. This, of course, raises the question of how continuum one-particle states, i.e., orbitals with positive KS eigenvalues, can be described by Gaussian basis sets. To that end, we note that we are not interested in the asymptotic behavior of the continuum states. We only need to represent
the continuum in the region of the molecules because only this region contributes to the summations in Eqs. (13) and (14) due to the fact that the matrix elements in these summations contain products of occupied times unoccupied orbitals. Moreover, we do not need to describe individual continuum states but only their sum. (For a complete infinite basis set the sum turns into an integral. This can be achieved by Gaussian orbital basis sets, provided the basis set contains enough functions with high exponents, following Fig. 4, which displays the energetically lowest orbitals of beryllium as well as the first orbitals with positive eigenvalues. Figure 4 shows that the orbitals with positive eigenvalues representing the continuum are localized close to the nucleus and exhibit an oscillatory behavior close to the nucleus. Such a behavior clearly cannot be represented by standard contracted basis sets that are quite unflexible in the region close to the nuclei.

In Table III the differences between HF and OEP total energies are displayed for the auxiliary basis set cc-pVQZ +1s and different cc-pVQZ orbital basis sets. The latter start with the standard contracted cc-pVQZ basis set containing 12 primitive s functions, 9 of which are contracted together to two contractions resulting in a total of 5 orbital basis functions. Then, step by step primitive functions are taken out of the contractions. Eventually, a completely uncontracted basis set is obtained, which is then augmented by two additional primitive functions to obtain an orbital basis set that is converged with respect to the cc-pVQZ+1s auxiliary basis set (see Sec. V C). The corresponding exchange potentials are displayed in Fig. 5. Table III and Fig. 5 clearly show that contracting the orbital basis set leads to unphysical OEP results. For the fully contracted basis set the OEP energy equals the HF energy, which is a clear indication that the corresponding exchange potential is unphysical and does not represent a proper KS potential (see Fig. 5).

The conclusion of this subsection is that stable OEP methods using Gaussian functions require orbital basis sets with a lot of flexibility close to the nucleus. This is provided by, for example uncontracted basis sets. One reason why Gaussian basis set OEP schemes were numerically unstable up to now is that this flexibility in the orbital basis set was not provided to a sufficient extent in most cases.

C. Balancing scheme for orbital and auxiliary basis sets

In this section a simple recipe to construct and balance auxiliary and orbital basis sets consisting of Gaussian functions for OEP calculations is presented. This allows one to obtain numerically stable OEP potentials that represent proper KS exchange potentials and that are of good quality.
TABLE III. Beryllium atom: energy difference $E_{\text{OEP}} - E_{\text{HF}}$ in millihartree for various contracted cc-pVQZ orbital basis sets and the cc-pVQZ+1s auxiliary basis set (see text).

<table>
<thead>
<tr>
<th>Contraction</th>
<th>$E_{\text{OEP}} - E_{\text{HF}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12r/[5s]</td>
<td>0.000</td>
</tr>
<tr>
<td>12r/[6s]</td>
<td>0.343</td>
</tr>
<tr>
<td>12r/[7s]</td>
<td>0.462</td>
</tr>
<tr>
<td>12r/[8s]</td>
<td>0.511</td>
</tr>
<tr>
<td>12r/[9s]</td>
<td>0.527</td>
</tr>
<tr>
<td>12r/[10s]</td>
<td>0.541</td>
</tr>
<tr>
<td>12r/[11s]</td>
<td>0.541</td>
</tr>
<tr>
<td>12r</td>
<td>0.541</td>
</tr>
<tr>
<td>12r+2s</td>
<td>0.613</td>
</tr>
</tbody>
</table>

in the energetically important intershell regions. The recipe is applicable for any standard orbital basis set. Thus, it enables stable and meaningful Gaussian basis set OEP calculations without the need to use large even tempered orbital basis sets, as in the example of beryllium in Sec. V A. One can therefore perform physically meaningful OEP calculations for fairly large molecules.

In order to carry out the OEP basis set construction and balancing scheme described below, one chooses a small test molecule that contains the elements for which the basis sets shall be constructed for, for example, the carbon monoxide molecule to construct basis sets for carbon and oxygen. The following steps then have to be carried out for all atoms of the test molecules in parallel. If for some elements of the test molecule basis sets of the type to be constructed already exist, then those are used and the steps given below have to be carried out only for the remaining elements. If, for example, OEP orbital and auxiliary cc-pVTZ basis sets for oxygen shall be constructed using carbon monoxide as the test molecule and corresponding OEP basis sets for carbon are already available, then the steps of the basis set construction and balancing scheme are only carried out for oxygen. Typically, basis sets for only one or two elements are constructed at a time. Ideally, the basis sets obtained from the construction and balancing scheme, of course, should not depend on which test molecules were chosen for their construction. Indeed, the basis sets constructed in this work were applied to a number of different molecules, and the corresponding OEP calculation always turned out to be well behaved and yielded numerically stable results.

The basis set construction and balancing scheme comprises the following steps:

1. Choose a (standard) orbital basis set (of s, p, d, f, etc. functions) for a given test molecule and decontract it.
2. Use the same set of basis functions also for the auxiliary basis set, more precisely for the basis functions $g_\rho$ of Eqs. (15) and (17).
3. Augment the orbital basis set by adding functions whose exponents are the geometric means of the exponents of the initial basis (whenever possible, if the initial basis already progresses by factors lower than 2.5, this might introduce near linear dependencies). In addition, add one tight and one diffuse function for each angular momentum. The exponents for these functions can be determined by using the ratio between the two tightest/most diffuse functions. This step usually doubles the size of the orbital basis set, and so, in combination with the next step, leads to a converged orbital basis set with respect to the auxiliary basis set.
4. Remove the most diffuse functions for each angular momentum in the auxiliary basis set. Furthermore, remove some of the tightest s-type functions in the auxiliary basis set since they usually lead to small eigenvalues in the response matrix and produce unpleasant oscillations in the core region. Some more precise guidelines about how to carry out this step will be given later in this section. After this step one can already safely perform reasonable OEP calculations.
5. In order to increase the quality of the OEP exchange potential, one may add one (or even more) function(s) to each angular momentum in the auxiliary basis set. This function should stem from one of the additional orbital basis functions from step 3 and is chosen as the function that leads to the largest decrease in the energy difference between HF and OEP. This is usually achieved by those functions which contribute to the intershell regions of the atoms.
6. Stepwise, remove all orbital basis functions that were added in step 3 except two for $l=0,1$ and one for $l > 1$. The functions to be removed are chosen as the functions that lead to the smallest change in the OEP-HF energy difference as compared to a calculation with the full augmented orbital basis set. Typically, the energy changes should amount to about a few microhartree for atoms and a few tens of microhartree for small molecules. For example, in the case of the neon atom the energy change amounts to $-0.002 \text{ mhartree}$ with the triple zeta basis set, and in the case of the water molecule the energy change amounts to...

![FIG. 5. Beryllium atom: OEP potentials for differently contracted orbital basis sets. The auxiliary basis set chosen is the cc-pVQZ+1s basis set described in Sec. V C. The thick solid line is the exact OEP potential from a numerical grid method.](image-url)
−0.008 mhartree with the quadruple zeta basis set after the removal of the orbital basis functions. Moreover, the removal of the orbital basis functions should leave the OEP exchange potential de facto unchanged. Often, but not always, the functions that remain in addition to the orbital basis set initially chosen in step 1 are those that have been added in step 5 to the auxiliary basis set.

We now discuss the reasoning behind the above construction and balancing scheme for basis sets by considering how it circumvents the potential numerical problems of Gaussian basis set OEP methods that are listed in Sec. II. Linear dependencies of the auxiliary basis set, point (i) of the list of potential numerical problems, are avoided by employing auxiliary basis functions derived from orbital basis functions that are known to be chosen as linear independent functions, step 2 of the construction scheme. Steps 3, 4, and 6 of the construction scheme guarantee that the orbital basis set is converged with respect to the auxiliary basis set. See point (ii) of the list of potential numerical problems. Steps 3 and 4 achieve the convergence of the orbital basis set. The resulting orbital basis set, however, is very large and would thus lead to a computationally expensive OEP procedure. Therefore, by step 6 a balancing of orbital and auxiliary basis set is achieved. A balanced orbital basis set shall be the smallest orbital basis set that is still converged with respect to the auxiliary basis set. Steps 3 and 4 of the construction scheme, moreover, avoids the occurrence of small eigenvalues of the response function that are physically correct but nevertheless numerically problematic, point (iii) of the list of potential problems. Numerical problems in solving the matrix OEP equation, point (iv) of the list of potential numerical problems, as already mentioned in Sec. II, are avoided because the condition of the response matrix emerging for basis sets constructed according to the above scheme is good enough such that any standard solver for linear equations can be employed without problems. Step 5 of the construction scheme, finally, is included not to avoid numerical problems but to improve the representation of the exchange potential, i.e., to improve the quality of the auxiliary basis set.

Note that this recipe has to be regarded as a broad guideline. In special cases it might be useful to modify it slightly to obtain balanced basis sets. For example, in the case of hydrogen a further augmentation of the auxiliary basis according to step 5 was not necessary since hydrogen has no intershell region. Furthermore, if small orbital basis sets are used, it can happen that the addition of functions to the auxiliary basis sets leads to instabilities. Then, step 5 has to be omitted. The way to expose such instabilities is to inspect the shapes of the exchange potential. The other extreme situation, which can appear in step 5, is that none of the added auxiliary functions affects the energy to a notable extent. This indicates that these auxiliary functions are apparently not needed to describe the exchange potential, and they should not be added to the auxiliary basis set in order to avoid the introduction of numerical instabilities. If in step 6 a removal of all orbital basis functions added in step 3 except two for \( l = 0, 1 \) and one for \( l > 1 \) leads to significant changes of the OEP-HF energy difference or to significant changes of the OEP exchange potential, then less orbital functions should be removed. In the examples of this work, however, this situation never occurred. One possibility to assess the significance of a change of the OEP-HF energy difference upon removal of orbital basis functions is to compare it with the accompanying change of the HF energy.

In order to demonstrate the ability to obtain balanced orbital and auxiliary basis sets by using the above given recipe, the beryllium atom is again chosen as a test case. As a starting orbital basis set Dunnings quadruple zeta basis set (cc-pVQZ) is chosen.\(^{44}\) Performing steps 1–4 in the recipe yields an OEP-HF energy difference of 0.84 mhartree and the exchange potential shown in Fig. 2 as a curve labeled cc-pVQZ. It can be seen that the cc-pVQZ OEP exchange potential is smooth and shows the desired Coulombic long and short range behaviors as the exact reference OEP potential. However, the potential is too flat in the intershell region compared to the exact potential, which is also shown in Fig. 2. Performing the fifth step of the recipe reveals that the additional \( s \) function with exponent 10.2 leads to the largest decrease in the energy difference, which is then 0.614 mhartree. The exchange potential for this auxiliary basis set is given by the thin dashed line in Fig. 2 labeled cc-pVQZ+1s. The new cc-pVQZ+1s exchange potential with the one additional auxiliary \( s \) function clearly improves the initial potential and is both in the short and long range part indistinguishable from the exact OEP potential. If, finally, the sixth step of the recipe is carried out, then it shows that one can safely remove from the orbital basis set all functions added in step 3 except the ones with exponents 10.2 and 1.62 without seeing any significant changes in the OEP-HF energy difference or in the exchange potential.

In order to further improve the potential and to come even closer to the reference OEP potential, one has to use larger basis sets. In the present case the Partridge3 and an even tempered basis with a progression of 1.5 are chosen as initial orbital basis sets (again, only \( s \) functions were taken). For the Partridge3 basis in step 4 of the recipe the most diffuse and the five tightest auxiliary basis functions have been removed compared to the orbital basis. In step 5 two \( s \) functions were added with exponents 6.73 and 3.05. Finally, for the even tempered orbital basis with exponents between 10 000 and 0.01 and a progression factor of 1.5, a corresponding auxiliary basis was created by removing ten tight and four diffuse functions from the orbital basis. Given the already very dense orbital basis, no further augmentation of the orbital basis was possible and no further augmentation of the auxiliary basis set was needed. That is, steps 3, 5, and 6 of the recipe were obsolete in this case. Figure 2 displays the exchange potentials for these two basis sets and shows that convergence towards the exact OEP is achieved. Indeed, the Partridge3 exchange potential is almost indistinguishable and the even(1.5) exchange potential is completely indistinguishable from the reference exchange potential on the scale of Fig. 2.

For the decision on which tight and which diffuse functions should be removed in the auxiliary basis set (step 4 of the recipe), it is recommended that the effect the removal has
on the potential must be studied. Additionally, the effect on the OEP-HF energy difference can be considered. Note that the removal of tight and diffuse functions is not only required in order to balance auxiliary and orbital basis sets [see point (ii) in the list of potential numerical problems in Sec. II]. It is also necessary due to the limited absolute numerical accuracy of computations [see points (iii) and (iv) in the list of potential numerical problems in Sec. II]. This point was discussed above, focusing on the eigenvalues of the response functions, and we now reconsider it from the perspective of OEP methods as minimizations of the total energy. Very tight auxiliary functions affect the total energy very little. However, if the effect on the total energy of these auxiliary functions is lower than the necessarily limited energy convergence of the SCF procedure, then, clearly, the contribution of the corresponding tight auxiliary basis functions to the exchange energy cannot correctly be determined by the OEP method that represents an energy minimization procedure, as discussed in Sec. III. Such tight auxiliary basis functions also lead to very small eigenvalues of the response function that might have a magnitude smaller than the absolute computational accuracy even if they are accompanied by a converged orbital basis set containing enough tight orbital functions. The reason is that these small eigenvalues are physically correct because a change of the effective KS potential by very tight functions leads only to a very weak response of the electron density. The true response function, indeed, has an infinite number of eigenvalues infinitely close to zero. These eigenvalues and their eigenvectors, clearly, cannot be treated correctly in a practical computation due to the limited computational accuracy of the latter. Fortunately, the eigenvectors corresponding to these small eigenvalues do not contribute to the exchange potential and therefore do not need to be taken into account in an OEP method; i.e., they can be removed from the OEP treatment, which is done by removing tight functions from the auxiliary basis set. The same arguments hold for very diffuse functions.

In the Appendix we introduce some auxiliary quantities that can be used to gain more insight in the role of tight and diffuse functions.

### VI. EXAMPLES

The recipe described in Sec. V C has been applied to obtain balanced orbital and auxiliary basis sets for neon, hydrogen, carbon, oxygen, and nitrogen using the test molecules CO, H2O, NH3, and C2H2.

For the neon atom Table IV shows the differences between the OEP and HF total energies for all basis set combinations, together with the differences from the total energies of OEP calculations employing the de facto exact OEP exchange potential for neon from a numerical grid OEP method51–53 and the HF total energies for each orbital basis set. The third and fourth columns in Table IV, labeled as cVDZ and cVTZ, show the OEP-HF energy differences for the contracted double zeta and triple zeta orbital basis sets while in all other calculations uncontracted basis sets were used. The need for using uncontracted basis sets follows clearly from the values in Table IV: for all, even the smallest VDZ, auxiliary basis sets the energy difference from Hartree-Fock is effectively zero; i.e., the corresponding OEP calculations are clearly unphysical. This drastically changes if the uncontracted double zeta orbital basis set is used since then for all auxiliary basis sets the OEP-HF energy difference does not fall below 1.4 mhartree. By comparing the values for the several auxiliary basis sets in column 5 of Table IV referring to the VDZ orbital basis set, it is apparent, however, that there is a relatively large decrease in the OEP-HF energy difference from the VQZ to the V5Z auxiliary basis set by about 0.06 mhartree, which clearly indicates that then the basis sets start to get severely unbalanced. This can also be deduced from the fact that the OEP-HF energy difference then becomes smaller than the OEP-HF energy difference for the OEP calculation, with the exact exchange potential of neon obtained from the numerical grid OEP method. This latter value effectively represents a lower bound for the OEP-HF differences for this orbital basis set. If the OEP calculation yields an OEP-HF energy difference lower than this bound, then the calculation is unphysical, and the auxiliary and orbital basis sets have been unbalanced. Note, however, that the opposite does not hold. Even if the OEP-HF energy difference is above its lower limit, this does not guarantee a physically meaningful OEP calculation. As described in Sec. V C, the removal of the tight auxiliary basis functions has a small effect on the OEP-HF energy difference.
in Sec. V, in order to be certain that an OEP calculation is physically meaningful, it has to be guaranteed that the orbital basis is converged for a given auxiliary basis set, i.e., that the OEP exchange potential does not exhibit significant changes upon enlargement of the orbital basis set. In fact, all OEP calculations in which the corresponding cardinal number of the auxiliary basis set is smaller than or equal to the cardinal number of the orbital basis set can be regarded as stable, while in those cases where the cardinal number of the auxiliary basis is larger, the two basis sets might not be balanced anymore.

The OEP calculations are clearly becoming more stable when turning to larger orbital basis sets: in the case of the VTZ orbital basis the OEP-HF energy difference even for the V6Z auxiliary basis with 1.646 mhartree lies only moderately below its lower limit of 1.667 mhartree. If the largest auxiliary basis, even(1.5), is employed, then it is found that the OEP calculations do not converge for any of the orbital basis sets with the exception of the even(1.5) basis itself. This shows that all these calculations are numerically unstable. In order to converge the OEP calculations, a singular value decomposition of the response matrix was carried out, and many of the eigenvectors with the lowest eigenvalues were removed in the solution of the matrix OEP [Eq. (38)] that the OEP calculations converged again. The number of eigenvectors that needed to be removed is indicated by the numbers in parentheses in Table IV. It can be seen that this number decreases when going from the smallest to the larger orbital basis sets, but even in the V6Z orbital basis five eigenvectors still had to be removed. However, even though the OEP calculations can be converged with the help of the singular value decomposition, this does not lead to physical meaningful results. For all orbital basis sets except the even(1.5) one the OEP-HF energy difference remains below its lower limit if the even(1.5) auxiliary basis is used. For the combination of the even(1.5) orbital with the even(1.5) auxiliary basis the OEP-HF difference equals the reference value of 1.683 mhartree, resulting from a numerical grid OEP calculation.

The bold entries in Table IV correspond to balanced combinations of auxiliary and orbital basis sets constructed according to the scheme of Sec. V C. These entries nicely converge toward the basis set limit that equals the exact value. In this series of values the limit of the basis sets is taken in the correct order: first for each auxiliary basis set the orbital basis set is converged, and then the limit for combinations of the auxiliary with the appropriate orbital basis set is taken.

The convergence behavior of the OEP-HF energy difference for different auxiliary basis sets is also displayed in Fig. 6. Here, the curve with the filled circles represents the OEP-HF energy differences for OEP calculations with the exact exchange potential of neon. One can easily see that the curves for the larger auxiliary basis sets lie under this reference curve if small orbital basis sets are used. On the other hand, for all but the V6Z and the even(1.5) auxiliary basis sets, one can observe that the OEP-HF energy difference is already nearly converged for the VTZ orbital basis set and that all curves with the exception of the aforementioned ones lie well above the reference curve. However, it can also be seen that only with the largest V6Z and even(1.5) auxiliary basis sets is it possible to converge to the exact value from the numerical grid OEP method.

The convergence of the OEP exchange potentials for combinations of auxiliary and orbital basis sets balanced with the scheme of Sec. V C towards the exact OEP can also be seen in Fig. 7. In the lower part of Fig. 7 the potential is plotted up to a distance of 8 bohrs, and on this scale one cannot see any notable differences from the exact OEP potential of neon given by the thick solid line. An exception is the LHF exchange potential calculated for the even(1.5) orbital basis set, which is also shown in the lower panel of Fig. 7 by the thick dotted line. It deviates from the numerical OEP already on the scale of the bottom diagram in the inter-shell region, which is represented by the local maximum at about 0.3 bohr. The corresponding LHF-HF energy difference of 2.287 mhartree is much larger than that for all OEP calculations reported here. The upper diagram in Fig. 7 gives a close-up view on the inter-shell region. In this diagram it can be seen that the OEP potential for the smallest VDZ auxiliary basis set has an intershell maximum that is slightly lower than the one of the exact OEP exchange potential and that is also somewhat displaced to a larger distance from the nucleus. The deviation to the exact OEP exchange potential gets systematically smaller for the larger basis sets. For the largest even(1.5) basis one can hardly see any difference from the exact OEP exchange potential even on the scale of the upper diagram of Fig. 7.

The importance of exploiting the charge and HOMO conditions in the OEP method presented here is demonstrated in Table V. It shows KS eigenvalues for the balanced combination of the hextuple zeta auxiliary and orbital basis sets for neon that are obtained either by using both the charge and the HOMO condition or by using only the charge or only the HOMO condition. As a reference, also the KS eigenvalues resulting for the same orbital basis set and the de
11. Exact-exchange density functional theory

facto exact exchange potential from the numerical grid OEP method\textsuperscript{51–53} are listed. Table V shows that the deviations of up to 0.5 eV can occur and the corresponding eigenvalues will be unsuitable as input data for time-dependent density-functional methods. The latter calculations typically yield excitation energies with an accuracy of a few tenths of an eV. The deviations thus lie well below the accuracy of time-dependent density-functional methods. If only one condition is used, then deviations of up to 0.5 eV can occur and the corresponding eigenvalues will be unsuitable as input data for time-dependent density-functional methods. Table V also shows a similar comparison for the water molecule, here using a balanced combination of the triple zeta auxiliary and orbital basis sets. In the case of water no reference data with an exact OEP exchange potential are available. However, Table V shows that the unoccupied KS eigenvalues can change by more than 0.5 eV if one of the two conditions is not employed in the OEP procedure.

The basis set convergence of the OEP-HF energy difference for balanced auxiliary and orbital basis sets has also been analysed for the three molecules CO, H$_2$O, and C$_2$H$_2$. The results for the OEP-HF energy differences as well as the orbital energies for the HOMO and the lowest unoccupied molecular orbital (LUMO) are given in Table VI. It can be seen that, as with the neon atom, the OEP-HF energy differences change remarkably from the VDZ to the VTZ basis set by 0.2, −0.1, and −0.3 mhartree for CO, H$_2$O, and C$_2$H$_2$, respectively. Then, after further extension of the basis sets the OEP-HF energy differences become stable, and in the case of H$_2$O and C$_2$H$_2$ the change in the energy difference from Hartree-Fock is only 0.005 and −0.003 mhartree from the VQZ to the V5Z basis set. An exception is the CO molecule, where the change is somewhat larger with +0.02 mhartree. This behavior is also displayed by the exchange potentials plotted in Figs. 8–10. The dotted lines are the OEP potentials for the VDZ basis set, and one can see that these deviate slightly from the potentials in the larger basis sets. In contrast to this the exchange potentials for the VTZ to VSZ basis sets are very close to each other, which indicates that the exchange potential is nearly converged. Again, a close-up view of the intershell regions is shown in the upper panels in Figs. 8–10.

The fifth, sixth, and seventh columns in Table VI shows the HOMO energies for Hartree-Fock and OEP as well as the LUMO energies for OEP. The latter are well below zero, indicating a well represented LUMO in the respective basis set. (The HOMO energies of OEP are all very close to the Hartree-Fock ones.)

The italicized values in Table VI show the respective quantities obtained by the localized Hartree-Fock method calculated with the largest VSZ orbital basis set. While the HOMO and LUMO energies are close to the corresponding OEP values, which indicates that the asymptotic parts of the exchange potentials are close to each other at least in most regions of space, the LHF-HF energy differences are significantly higher by about 1 mhartree than the OEP-HF energy differences. As in the case of the neon atom, these differences originate from the too weakly pronounced intershell maximum of the LHF exchange potential compared to the OEP exchange potential. This can be seen in Figs. 8–10, which also include the LHF exchange potentials calculated with the V5Z basis set for the three molecules. However, at the site of the nuclei and in the long range part, it can be observed that the LHF and OEP potentials are relatively close to each other.

In order to demonstrate the applicability of the OEP approach presented in this work to larger molecules, we have also performed an OEP calculation for the cytosine molecule with a balanced combination of triple zeta orbital and auxiliary basis sets with 886 and 407 basis functions, respectively. Here, the calculation of the Coulomb matrix and the nonlocal exchange matrix has been sped up with the aid of density
fitting. For this the cc-pVQZ JKFit fitting basis set of Weigend has been chosen. A comparison of the CPU times for the construction of the Fock matrix and the solution of the OEP equations revealed that for this basis set the calculation of the OEP potential required only about 50% of the time needed to generate the Fock matrix itself. This shows that the OEP method, though certainly computationally somewhat more expensive than the Hartree-Fock method, is

<table>
<thead>
<tr>
<th>System</th>
<th>Orbital</th>
<th>OEP(num)</th>
<th>OEP(c+h)</th>
<th>OEP(c)</th>
<th>OEP(h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1s</td>
<td>−30.8200</td>
<td>−0.0001</td>
<td>0.0175</td>
<td>0.0000</td>
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<td></td>
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<td>0.0176</td>
<td>0.0000</td>
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<tr>
<td></td>
<td>2p</td>
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<td>0.0000</td>
</tr>
<tr>
<td></td>
<td>3s</td>
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<td>0.0018</td>
<td>0.0122</td>
<td>−0.0049</td>
</tr>
<tr>
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<td>3p</td>
<td>−0.1142</td>
<td>0.0019</td>
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<td></td>
<td>4s</td>
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<td>0.0058</td>
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<td>0.0012</td>
<td>0.0076</td>
<td>−0.0074</td>
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<td>0.2610</td>
<td>0.0011</td>
<td>0.0117</td>
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<tr>
<td></td>
<td>5p</td>
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<tr>
<td></td>
<td>6s</td>
<td>1.1676</td>
<td>0.0007</td>
<td>0.0153</td>
<td>−0.0021</td>
</tr>
</tbody>
</table>

H$_2$O

| LUMO   | −0.1998  | 0.0495   | 0.0036  |
|        | −0.1306  | 0.0407   | −0.0115 |
|        | −0.1114  | 0.0255   | −0.0239 |
|        | −0.0936  | 0.0251   | −0.0245 |
|        | −0.0795  | 0.0230   | −0.0238 |

TABLE VI. Importance of the charge and HOMO conditions [see Eqs. (18) and (21)]. KS eigenvalues for neon and the water molecule obtained with the presented OEP method using both the charge and HOMO conditions [OEP(c+h)] or only one of the two [OEP(c) or OEP(h)]. For neon the balanced hextuple zeta orbital and auxiliary basis set was used, and for water the balanced triple zeta orbital and auxiliary basis set (see Table I). For neon also reference values obtained with the hextuple zeta orbital basis set and the de facto exact exchange potential from the numerical grid method (Refs. 51–53) are displayed [OEP(num)]. In the case of neon columns 4–6 contain the absolute differences to the OEP(num) values, while in the case of water columns 5 and 6 contain the absolute differences to the OEP(c+h) values. The dotted horizontal lines mark the HOMO-LUMO crossover. All values are in hartrees.

<table>
<thead>
<tr>
<th>System</th>
<th>Orbital</th>
<th>Energy difference $\Delta E$ (millihartree)</th>
<th>$E_{\text{OEP}}$</th>
<th>$E_{\text{HF}}$</th>
<th>$E_{\text{OEP}} - E_{\text{HF}}$</th>
<th>$E_{\text{HF}} \pm 0.05$</th>
<th>$E_{\text{OEP}} \pm 0.05$</th>
</tr>
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<tbody>
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<td>CO</td>
<td>VDZ</td>
<td>−112.766489</td>
<td>5.980</td>
<td>−0.556</td>
<td>−0.555</td>
<td>−0.556</td>
<td>−0.555</td>
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<tr>
<td></td>
<td>VTZ</td>
<td>−112.782814</td>
<td>5.786</td>
<td>−0.555</td>
<td>−0.553</td>
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<td>−0.553</td>
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</tr>
<tr>
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<td>VSZ</td>
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<td>−0.553</td>
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<td></td>
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<td>−0.550</td>
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<td>H$_2$O</td>
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<tr>
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<td>−0.509</td>
<td>−0.509</td>
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<td>−76.066130</td>
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</tr>
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<td>−76.067313</td>
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<td>−0.509</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>3.311</td>
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<td>−0.507</td>
<td>−0.507</td>
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<tr>
<td>C$_3$H$_6$</td>
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<td>−76.840660</td>
<td>4.360</td>
<td>−0.411</td>
<td>−0.411</td>
<td>−0.411</td>
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<td></td>
<td>5.793</td>
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<td>−0.410</td>
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<td>−0.410</td>
</tr>
</tbody>
</table>
applicable to fairly large molecules. The exchange potential for cytosine plotted along the ring is presented in Fig. 11, again for both the OEP and the LHF method. The LHF calculations were done using the density fitting approximation of the Slater potential described in Ref. 47. It can be noticed that the OEP exchange potential is smooth and shows the known structure in the intershell regions for carbon and nitrogen, as in the case of the smaller molecules discussed above. Also, once more, one can observe that the localized Hartree-Fock method gives an exchange potential that is flatter in the intershell region while it is close to the OEP exchange potential in the core regions. Again, this affects also the difference from the Hartree-Fock energy of $-392.769$ hartree: the OEP-HF energy difference is equal to about 33 mhartree and the LHF-HF energy difference is equal to about 43 mhartree.

For a further demonstration of the applicability of the presented OEP approach, we performed an OEP calculation for pregnandiole ($C_{21}O_2H_{36}$) with a balanced combination of double zeta orbital and auxiliary basis sets, now with 1995 and 1171 basis functions, respectively. Again, the OEP calculation was perfectly stable and could be carried out without any problems.

VII. CONCLUSIONS

We have presented an OEP method employing Gaussian basis sets and an accompanying construction and balancing scheme for auxiliary and orbital basis sets that enables numerically stable OEP calculations. The presented OEP approach can be used routinely for the treatment of medium size and moderately large molecules. We have presented a first set of balanced auxiliary and orbital basis sets for a limited number of atoms. The construction of basis sets for other atoms is straightforward along the lines described in Sec. V C. The basis sets presented in this work and the balancing scheme itself can certainly be refined further in detail. Crucial points to be obeyed in any construction of basis sets for OEP calculations is that it is guaranteed that the orbital basis set is converged with respect to the auxiliary basis set and that the orbital basis set describes sufficiently well the

[Images of CO and H2O molecules showing OEP exchange potentials]
solution of the OEP matrix equation scales more favorably with the third power of the system size. Work along these lines is under way.\textsuperscript{55} Note, however, that the construction of the response function is not the step consuming most computational time. This is, like in HF calculations, the evaluation of the exact exchange energy and the construction of the matrix representation of the nonlocal exchange operator. An advantage of the OEP method presented here is that the asymptotic region of the exchange potential that contributes little to the total energy is determined to a large extent by considering two exact conditions for the exchange potential. This adds to the stability of the method.

In future work\textsuperscript{55} it shall be investigated how the specific asymptotic behavior of the exchange potential on nodal surfaces of the HOMO (Refs. 34 and 35) can be described within the framework of the presented approach.

We concentrated in this work for the most part on exchange-only OEP methods with respect to exchange-only KS methods. However, the OEP method and basis set balancing scheme presented here can also be applied to other orbital-dependent exchange-correlation functionals and to approaches using such functionals, for example, those of Refs. 9 and 56–60. Indeed, with the presented OEP method and the accompanying basis set balancing scheme, it is possible for the first time to carry out self-consistent KS calculations for orbital-dependent functionals in a numerically stable manner using Gaussian basis sets. This should enable a widespread use of such functionals, motivate the development of new orbital-dependent correlation functionals, and thus contribute to the further development of density-functional methods.

**ACKNOWLEDGMENTS**

Parts of the computer program used in this work have been written by Fred Manby during a stay of one of the authors (A.H.) in Bristol. The authors are grateful for the support of this work through the priority program 1145 of the Deutsche Forschungsgemeinschaft.
APPENDIX: THE ROLE OF TIGHT AND DIFFUSE AUXILIARY FUNCTIONS IN BASIS SET OEP METHODS

For a further, more quantitative analysis of the role of tight and diffuse auxiliary basis functions and the stability of the OEP method in general, the following auxiliary quantities are introduced:

\[ u_t = \int \rho_{x,\text{rest}}^r(r) \nabla^2 \rho_{x,\text{rest}}^s(r) \, dr = (c_{\text{rest}}^x)^T T_{\text{rest}}, \]  

(A1)

\[ u_s = \int \rho_{x,\text{rest}}^r(r) \rho_{x,\text{rest}}^s(r) \, dr = (c_{\text{rest}}^s)^T S_{\text{rest}}, \]  

(A2)

\[ u_r = \int \rho_{x,\text{rest}}^r(r_1) r_2 \rho_{x,\text{rest}}^s(r_2) \, dr_1 dr_2 = (c_{\text{rest}}^x)^T R_{\text{rest}}. \]  

(A3)

Here, \( \rho_{x,\text{rest}}^r \) is the exchange charge density [see Eq. (16)] of the potential \( v_{\text{rest}} \) of Eq. (24) that is determined by solving the OEP equations [Eqs. 38–40]. The matrix elements of the matrices \( T, S, \) and \( R \) in Eqs. (A1)–(A3) are the kinetic energy, the overlap, and the \( r_2 \) integrals for the auxiliary basis functions. The quantity \( u_t \) containing the Laplace operator measures how strongly \( \rho_{x,\text{rest}}^r \) tends to oscillate.\(^{38} \) It can be expected that it is sensitive to the addition of tight functions in the auxiliary basis since they often induce undesirable oscillations in the potential. On the other hand, \( u_r \) will hardly give indications about the influence of diffuse functions since they do not lead to oscillations with a short wavelength. The term \( u_s \) estimates how strongly the exchange charge is localized. Again, this term will be sensitive to the addition of tight functions as they tend to shift the charge towards the core regions while more diffuse functions will move charge into the outer regions. The latter effect can be well described by the quantity \( u_r \), which measures the charge delocalization of \( \rho_{x,\text{rest}}^r \) and therefore will be very sensitive with respect to the addition of diffuse functions. This stems from the fact that, usually, \( \rho_{x,\text{rest}}^r \) is mainly localized near the nuclei where the exchange potential has a minimum. If by the addition of diffuse functions in the auxiliary basis set the asymptotic region of the potential gets a dent or even becomes unbound, this shifts the charge into the asymptotic region and the integral in Eq. (A3) will obtain a significant contribution through this delocalized charge. Note that these effects remain localized in the sense that they occur in the region not too far from the system. The total exchange density of the potential \( v_{\text{rest}} \) integrates to zero by construction.

For a more sensitive analysis we consider contributions \( \rho_{x,\text{rest}}^r \) to \( \rho_{x,\text{rest}}^s \) associated with the eigenvalues of the response matrix \( X_s \), defined in Eq. (39). These contributions are given by

\[ c_i^x = P_i \tilde{X}_i^{-1} u_i^x \tilde{w}, \]  

(A4)

where \( P \) and \( \tilde{w} \) are defined in Eqs. (37) and (40) and \( u_i \) and \( \tilde{X}_i \) are the \( i \)th eigenvector and eigenvalue of the response matrix \( X_s \). The vector \( c_i^x \) represents the contribution \( \rho_{x,\text{rest}}^r \) to \( \rho_{x,\text{rest}}^s \).

The effect of adding tight and diffuse basis functions to the auxiliary basis set is investigated for beryllium for the OEP orbital basis set derived from the cc-pVQZ basis. The results are displayed in Figs. 12 and 13. First, gradually, all tight \( s \) functions contained in the cc-pVQZ orbital basis set were also included in the auxiliary basis set. The upper panel of Fig. 12 shows that if all five tight \( s \) functions are added, this leads to large oscillations of the potential in the core region while it has only a marginal effect in the intershell region. The corresponding OEP-HF energy difference changes only slightly from 0.613 to 0.601 mhartree compared to the case without tight \( s \) functions. However, the addition of tight \( s \) functions to the auxiliary basis strongly affects the magnitude of the lowest eigenvalue of the response matrix from \(-0.1 \times 10^{-6}\) to \(-0.8 \times 10^{-10}\), which is shown in Table VII. In Table VII also the maximal magni-
11. Exact-exchange density functional theory

FIG. 13. Exchange potentials of the beryllium atom. The thick solid line is the exact OEP potential from a numerical grid method, and the thin solid and dashed lines are the OEP potentials obtained using the cc-pVQZ+1s and cc-pVQZ+1s+diffuse auxiliary basis sets, respectively, and the corresponding cc-pVQZ orbital basis set. The numbers x in eig: x denote the respective eigenvector index, i.e., the eigenvector the respective curve belongs to (the eigenvectors are ordered in increasing order). The last numbers in the legend box give the number of diffuse functions which were added.

TABLE VII. Beryllium atom: effect of adding tight auxiliary basis functions. The reference is the auxiliary basis set adapted to the cc-pVQZ orbital basis (see text). The quantities \( v_{t}\), \( v_{s}\), and \( v_{r}\) are defined in Eqs. (A1)–(A3), respectively. The third column shows the value of \( v_{t}\) for the total exchange charge \( \rho_{t}^{\text{tot}} \) of the potential \( \varphi_{\text{tot}}^{\text{ref}} \), and the fourth to the sixth columns display from the contributions \( \rho_{t}^{\text{ref}} \), \( \rho_{s}^{\text{ref}} \) [see Eq. (A4)] those that are largest in magnitude. All values are in a.u., with the exception of the energy difference \( E_{\text{OEP}} - E_{\text{HF}} \), which is in millihartree.

<table>
<thead>
<tr>
<th>No. of tight functions</th>
<th>Smallest eigenvalue of ( \mathbf{X} )</th>
<th>( [v_{t}]_{\text{max}} )</th>
<th>( [v_{s}]_{\text{max}} )</th>
<th>( [v_{r}]_{\text{max}} )</th>
<th>( E_{\text{OEP}} - E_{\text{HF}} )</th>
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<tbody>
<tr>
<td>0</td>
<td>(-0.12 \times 10^{-5})</td>
<td>(7.9 \times 10^{1})</td>
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<td>(3.2 \times 10^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>(-0.25 \times 10^{-7})</td>
<td>(5.6 \times 10^{1})</td>
<td>(1.7 \times 10^{1})</td>
<td>(1.0 \times 10^{0})</td>
<td>(2.5 \times 10^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>(-0.93 \times 10^{-8})</td>
<td>(1.1 \times 10^{2})</td>
<td>(2.1 \times 10^{1})</td>
<td>(5.1 \times 10^{0})</td>
<td>(1.8 \times 10^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>(-0.48 \times 10^{-8})</td>
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<td>(2.2 \times 10^{1})</td>
<td>(1.3 \times 10^{-1})</td>
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<tr>
<td>4</td>
<td>(-0.18 \times 10^{-8})</td>
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<td>(2.1 \times 10^{1})</td>
<td>(9.5 \times 10^{-2})</td>
</tr>
<tr>
<td>5</td>
<td>(-0.78 \times 10^{-10})</td>
<td>(7.0 \times 10^{0})</td>
<td>(7.6 \times 10^{0})</td>
<td>(2.6 \times 10^{1})</td>
<td>(8.9 \times 10^{-2})</td>
</tr>
</tbody>
</table>

\( E_{\text{OEP}} - E_{\text{HF}} \)
tions are added. The numbers in the legend box report the numbers of the eigenvectors of the response matrix the plotted contributions $\rho_{E}^{\text{out}}$ belong to (the eigenvectors are sorted in increasing order). It can be observed that the contributions $\rho_{E}^{\text{out}}$ corresponding to $|\nu_{I}|_{\text{max}}$ belong to a relatively large eigenvalue if zero to two diffuse functions are added. This changes when three and more diffuse functions are included in the auxiliary and orbital basis set. As a consequence, these additional functions start to make the OEP calculation unstable. The values for $|\nu_{I}|_{\text{max}}$ in Table VIII underline this: for zero to two diffuse functions $|\nu_{I}|_{\text{max}}$ increases moderately from 0.32 to 15 a.u., but then it increases to a value of about 11 a.u. For four/five additional auxiliary/orbital basis functions. Note that for three diffuse functions the total exchange potential of beryllium is still strongly bound in the asymptotic region but contains a slight bump beyond 10 bohrs and clearly differs from the reference OEP exchange potential. This bump also appears for the exchange potentials with one and two additional diffuse functions, but to a much lower extent. In fact, the curve which is closest to the reference OEP exchange potential in the asymptotic region is the one without any additional diffuse functions in the auxiliary basis set.

This analysis shows that the addition of too tight or diffuse functions to the auxiliary basis set is, in general, dangerous, despite the fact that it has only a small effect on the energy because it can considerably affect the condition of the response matrix and thus can lead to instabilities of the OEP method. These instabilities cannot easily be removed by simply extending the orbital basis through the addition of more tight or diffuse functions. For example, in the above case for beryllium with four further diffuse auxiliary functions the addition of 20 more diffuse functions to the orbital basis set almost had no effect on the energy difference; the lowest response matrix eigenvalue still amounts to $-0.3 \times 10^{-11}$ a.u. and the potential still shows an unpleasant curvature at about 11 bohrs. While in this work it has been found to be very valuable to carefully monitor the OEP exchange potential in order to decide which tight and diffuse functions should be kept in the auxiliary basis set, as a rule of thumb, it can be assessed that for standard basis sets, at least for first row elements, the maximal absolute numbers of $|\nu_{I}|_{\text{max}}$ and $|\nu_{I}|_{\text{max}}$ should not be higher than a few hundred a.u.

### Table VIII

| No. of diffuse functions of $X_{i}$ | $|\nu_{I}|_{\text{max}}$ | $|\nu_{I}|_{\text{max}}$ | $|\nu_{I}|_{\text{max}}$ | $|\nu_{I}|_{\text{max}}$ | $E_{\text{OEP}} - E_{\text{HIF}}$ |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0                                | $-0.12 \times 10^{-6}$ | $1.2 \times 10^{-1}$ | $6.8 \times 10^{-1}$ | $8.7 \times 10^{-1}$ | $3.2 \times 10^{-1}$ | 0.6126 |
| 1                                | $-0.33 \times 10^{-7}$ | $1.3 \times 10^{-1}$ | $7.5 \times 10^{-1}$ | $9.7 \times 10^{-1}$ | $2.2 \times 10^{0}$ | 0.6115 |
| 2                                | $-0.52 \times 10^{-8}$ | $1.6 \times 10^{-1}$ | $4.8 \times 10^{-1}$ | $3.7 \times 10^{-1}$ | $1.5 \times 10^{0}$ | 0.6113 |
| 3                                | $-0.47 \times 10^{-8}$ | $3.5 \times 10^{-1}$ | $0.42 \times 10^{-1}$ | $0.37 \times 10^{-1}$ | $1.1 \times 10^{0}$ | 0.6113 |
| 4                                | $-0.32 \times 10^{-11}$ | $1.6 \times 10^{0}$ | $0.64 \times 10^{0}$ | $0.70 \times 10^{0}$ | $1.7 \times 10^{0}$ | 0.6055 |

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11. Exact-exchange density functional theory

11.4. Comparison between optimized effective potential and Kohn-Sham methods

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Comparison between optimized effective potential and Kohn–Sham methods

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Abstract

It is shown that, in general, Gaussian basis set xOEP methods cannot yield the HF total energy because, in general, products of occupied and unoccupied orbitals are effectively linearly dependent. xOEP methods can yield the HF total energy only if the quality of the employed orbital basis set is insufficient with respect to the computational accuracy. Furthermore it is shown that the basic equation underlying the xOEP method can be obtained via a weighted minimization of the difference between the occupied–virtual block of the xOEP and the HF exchange matrix, with weight factors given by inverse orbital eigenvalue differences.

1. Introduction

Recently, Staroverov et al. showed [1] that, within a Gaussian basis set framework, exchange-only optimized effective potential (xOEP) methods [2,3] can yield the corresponding Hartree–Fock (HF) total energy for certain combinations of Gaussian orbital basis sets and auxiliary basis sets \( \{ f_p \} \) that are employed to represent the exchange potential \( v_x \) according to

\[ v_x(r) = \sum_p c_p f_p(r). \]  (1)

This was a disturbing finding because it is known that in a real space representation, which corresponds to complete basis sets, the xOEP method represents an exchange-only Kohn–Sham (KS) method [4–7] that yields total energies that are always higher [8] than the corresponding HF total energy except for special cases like the homogeneous electron gas or two-electron systems. Indeed, Staroverov et al. showed [1] that, depending on the chosen basis sets, xOEP methods may yield not just one but infinitely many exchange potentials leading to an xOEP total energy that is equal to the corresponding HF total energy, i.e., the HF total energy resulting for the chosen orbital basis set. This means that different exchange potentials \( v_x \) resulting in different effective xOEP potentials, in violation of the Hohenberg–Kohn theorem, lead to the same xOEP determinant that equals the HF determinant. The exchange potentials in all these cases exhibit strong unphysical oscillations and are of no physical meaning. These findings raised doubts about the usefulness of basis set optimized effective potential (OEP) methods in general, in particular if Gaussian orbital basis sets are employed [1].

The practical applicability of Gaussian basis set OEP methods is a crucial prerequisite for the further development of density-functional methods, in particular for the development of new exchange-correlation functionals. Most of the functionals for the KS exchange-correlation energy that were presented in recent years [9–12] are orbital-dependent functionals. Orbital-dependent functionals are functionals that not only depend on the electron density and its gradients like functionals within the local density approximation (LDA) or within generalized gradient approximations (GGAs) but also on the KS orbitals. A difficulty arising for such orbital-dependent functionals is that for a given functional of the exchange-correlation energy
the corresponding exchange-correlation potential is not directly accessible. The KS exchange-correlation potential is the functional derivative of the exchange-correlation energy with respect to the electron density. For LDA or GGA functionals this functional derivative can be taken in a straightforward manner. For orbital-dependent functionals, on the other hand, this is not possible because the dependence of the KS orbitals on the electron density is unknown. Therefore the exchange-correlation potentials corresponding to orbital-dependent energy functionals have to be constructed in the KS self-consistency process by the OEP method. If the latter was not applicable in practice for Gaussian basis sets then self-consistent KS calculations with orbital-dependent basis sets would not be possible and the arguably most promising route for the future development of density-functional methods would be blocked, at least within a Gaussian basis set framework.

Very recently, in Ref. [13], it was shown that the xOEP method of Staroverov et al. yields the HF total energy only if, for a given orbital basis set, the products of occupied times unoccupied KS orbitals are linearly independent. If the products of occupied times unoccupied KS orbitals are linearly dependent then, in general, xOEP methods cannot yield the HF total energy. Moreover, it was shown in Ref. [13] that xOEP methods yield the HF total energy only if the orbital and the auxiliary basis set are unbalanced to each other. In this case xOEP methods do not represent KS methods, which explains why they can yield too low total energies that may equal the HF total energy. This means that the term xOEP method is more general than the term KS method and that xOEP methods may or may not represent exchange-only KS methods, depending on how they are set up. In a second step, in Ref. [14], a Gaussian basis set xOEP method and an accompanying basis set construction and balancing scheme was presented very recently that allows one to carry out numerically stable xOEP calculations that represent proper exchange-only KS calculations and that yield well-behaved physically meaningful KS exchange potentials and total energies that are always higher than the corresponding HF total energy.

With the method of Ref. [14] it is possible to carry out routinely exact exchange-only KS calculations with Gaussian basis sets. A generalization to other orbital-dependent functionals than the exact exchange energy is straightforward. For plane wave basis sets numerically stable OEP methods that represent KS methods are known since quite some time [15–17]. Thus density-functional methods employing orbital-dependent exchange-correlation functionals now can be carried out self-consistently both for finite and for periodic systems.

However, there still remains open one fundamental question that is of importance both from a formal point of view as well as with respect to the development of OEP methods for practical purposes. This is the question whether Gaussian orbital basis sets in general lead to products of occupied and unoccupied orbitals that are linearly independent or not. This is tantamount to the question whether, for a given orbital basis set, it is possible, in general, to find an auxiliary basis set that is unbalanced enough such that an xOEP method yields the corresponding HF total energy or not. In this work we will answer this question by showing that products of occupied and unoccupied orbitals resulting from Gaussian orbital basis sets, in general, are linearly dependent, at least if basis sets are chosen that, on the one hand, describe the occupied KS orbitals well and, on the other hand, also describe the energetically low lying unoccupied KS orbitals and/or the KS orbitals describing the energetically lowest part of the continuum sufficiently well. This means that xOEP methods, in general, lead to products of occupied and unoccupied KS orbitals that are linearly dependent and therefore cannot yield the HF total energy. Indeed we will show that xOEP methods can yield the HF total energy only in the case that the quality of the orbital basis set is insufficient with respect to the computational accuracy. This case, however, often exists for standard orbitals basis sets if they are contracted. Note that, in this context, it is important to take into account the computational accuracy in the definition of linear dependency. That means to distinguish between formal linear dependency, i.e., linear dependency with respect to an infinite computational accuracy, and effective linear dependency, i.e., linear dependency with respect to the actual computational accuracy.

As a further result of the analysis of xOEP methods we show that the basic equation underlying the xOEP method can be obtained via a weighted minimization of the difference between the occupied–virtual block of the xOEP and the HF exchange matrix, with weight factors given by the inverse eigenvalue differences of occupied and unoccupied orbitals. Omission of the weight factors leads to the approximate exchange potential presented in Ref. [18].

2. Formalism

We start by comparing the matrix representations of the HF and the xOEP Hamiltonian operators

\[ H_{\text{HF}} = T + V_{\text{H}} + V_{\text{NL}} + V_{\text{ext}} \]

and

\[ H^{\text{xOEP}} = T + V_{\phi} + T_{\text{H}} + V_{\phi} + V_{\text{ext}}. \]

respectively. We consider matrix representations of both, the HF and the xOEP Hamiltonian operator, with respect to the HF orbitals \( \phi \). This means that the matrices \( T, V_{\text{H}}, V_{\text{ext}}, V_{\text{NL}}, V_{\phi} \) and \( V_{\text{ext}} \) are defined by the corresponding matrix elements \( T_{ij} = \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_j \rangle, V_{\text{H}ij} = \langle \phi_i | v_{\text{H}} | \phi_j \rangle, V_{\text{ext}ij} = \langle \phi_i | v_{\text{ext}} | \phi_j \rangle, V_{\text{NL}ij} = \langle \phi_i | v_{\text{NL}} | \phi_j \rangle, V_{\phi i} = \langle \phi_i | v_{\phi} | \phi_j \rangle \), and \( V_{\phi i} = \langle \phi_i | v_{\phi} | \phi_j \rangle \), respectively, and by \( V_i = V_{\phi i} + V_{\text{ext}i} \). Here \( v_{\text{H}}, v_{\text{NL}} \), and \( v_{\phi} \) denote the Hartree potential, i.e., the Coulomb potential of the electron density, the external potential, usually the electrostatic potential of the nuclei, and a local multiplicative exchange potential, respectively. By \( v_{\text{NL}}^{\text{NL}} \) the nonlocal HF exchange operator is denoted. Atomic units are used throughout. For simplicity we consider closed
shell systems with non-degenerate ground states. In this case orbital basis functions as well as orbitals can all be chosen to be real-valued and all matrices are symmetric. The HF Hamiltonian matrix $\mathbf{H}^{\text{HF}}$, of course, is diagonal in the basis of the HF orbitals.

Next we consider [1,19,20] what happens if the exchange potential of Eq. (1) can be chosen such that the occupied–virtual block of the xOEP exchange matrix $\mathbf{V}_x$ equals the occupied–virtual block of the HF exchange matrix $\mathbf{V}_x^{\text{NL}}$. We then construct an effective potential $u_e(r)$ by adding to this exchange potential the HF Hartree potential and the external potential. The occupied–virtual block of the corresponding matrix $\mathbf{V}_x$ then equals the sum of the matrices $\mathbf{V}_{\text{Hf}}, \mathbf{V}_x^{\text{NL}}$, and $\mathbf{V}_{\text{ext}}$. Moreover, because the matrix $\mathbf{T}$ is equal in the xOEP and HF case, the occupied–virtual block of the complete xOEP Hamiltonian matrix equals that of the HF Hamiltonian matrix, i.e., equals zero in the basis of the HF orbitals and therefore a xOEP determinant that equals the HF determinant results for the following reason: if the xOEP and HF Hamiltonian matrices differ only in the occupied–occupied and virtual–virtual blocks then diagonalization of the xOEP Hamiltonian matrix just leads to a unitary transformation of the occupied and the unoccupied HF orbitals among themselves. If those xOEP orbitals related to the occupied HF orbitals by this unitary transformation are chosen as occupied xOEP orbitals then the xOEP determinant indeed equals the HF determinant and the xOEP total energy equals the HF one. Because the HF total energy is a lower bound for the energy of any Slater determinant and thus also for the xOEP total energy this shows that the effective potential $v_e$ we have constructed above indeed is the optimized effective potential in the sense that it yields the lowest total energy that can be obtained for any local effective potential, i.e., this shows that the above construction results in an optimized effective potential method. Furthermore also the xOEP and the HF electron densities are equal if the xOEP and HF determinants are equal. Subsequently also the xOEP Hartree potential equals the HF one. This means the HF Hartree potential we added to the exchange potential in order to obtain the effective potential equally well could have been called xOEP Hartree potential. Therefore the exchange potential we started from indeed is the potential that remains if the external potential and the xOEP Hartree potential are subtracted from the effective potential, as it should be in an xOEP method.

Now arises the crucial question: is it possible, for given orbital and auxiliary basis sets, to construct an exchange potential according to Eq. (1) such that the occupied–virtual block of the xOEP exchange matrix $\mathbf{V}_x$ equals the occupied–virtual block of the HF exchange matrix $\mathbf{V}_x^{\text{NL}}$. This question leads to the matrix equation [1,13,19,20]

$$\mathbf{A} \mathbf{c} = \mathbf{y}$$

(4)

for the vector $\mathbf{c}$ containing the expansion coefficients $c_p$ of the exchange potential in Eq. (1). The elements of the matrix $\mathbf{A}$ and the vector $\mathbf{y}$ are given by

$$A_{ap} = \langle \phi_i | f_p | \phi_a \rangle$$

and

$$y_{a} = \langle \phi_i | V_x^{\text{NL}} | \phi_a \rangle,$$

(5)

(6)

i.e., the vector $\mathbf{y}$ with the elements $y_a = y_{a} = V_x^{\text{NL}}$ collects the occupied–virtual elements of the HF exchange matrix. In Eqs. (5) and (6) the indices $i$ and $a$ denote an occupied and a virtual orbital, respectively, and are combined to one superindex $ia$ numbering one dimension of the matrix $\mathbf{A}$ and the elements of the vector $\mathbf{y}$. If Eq. (5) has a solution then the occupied–virtual matrix elements $\langle \psi_i | v_e | \psi_a \rangle = \langle \psi_i | \sum_p f_p | \psi_a \rangle = \sum_p A_{ip} c_p$ of the xOEP exchange matrix equal the occupied–virtual matrix elements $\langle \phi_i | V_x^{\text{NL}} | \phi_a \rangle$ of the HF exchange matrix $V_x^{\text{NL}}$.

In order to analyse whether Eq. (4) has none, one, or infinitely many solutions we consider the overlap matrix $\mathbf{D}$ for the products of occupied times unoccupied orbitals with matrix elements $D_{ia,\beta} = \langle \phi_i | \phi_\beta \rangle$. Small or zero eigenvalues of this matrix indicate effective linear dependencies in the occupied–virtual orbital products and this point will be important in the following context. The orthonormalized eigenvectors of the overlap matrix $\mathbf{D}$ shall be collected in the unitary matrix $\mathbf{U} = (U^T U^p)$. The part $U^p$ of the matrix $\mathbf{U}$ shall contain the coefficients of the eigenvectors $\mathbf{u}_\beta^p$ of the overlap matrix with nonzero eigenvalues, i.e., the eigenvectors $\mathbf{u}_\beta^p$ representing the space spanned by the products of occupied times unoccupied orbitals. Accordingly, the functions

$$Q^p_i(r) = \sum_m u_{im}^p \phi_i(r) \phi_m(r)$$

(7)

corresponding to the eigenvectors $\mathbf{u}_\beta^p$ constitute a set of linearly independent orthogonal functions that form the space spanned by the products of occupied times unoccupied orbitals. The part $U^0$ of the matrix $\mathbf{U}$ shall contain the coefficients of the eigenvectors $\mathbf{u}_\beta^0$ of the overlap matrix with zero eigenvalues. The linear combinations $\sum_{m} u_{im}^0 \phi_i(r) \phi_m(r)$ corresponding to the eigenvectors $\mathbf{u}_\beta^0$ equal zero, i.e.,

$$\sum_{m} u_{im}^0 \phi_i(r) \phi_m(r) = 0.$$  

(8)

Next, we assume that the auxiliary basis set $\{f_p\}$ has been chosen such that it is linearly independent. (In case that the initial auxiliary basis functions have been chosen linearly dependent we can form one set of linear combinations of the initial auxiliary basis functions that consists of linearly independent functions and a second set of linear combinations that are functions that are identical zero everywhere in space. This second set can be removed and the first set can be considered as new, linearly independent auxiliary basis set.) We recombine the auxiliary basis functions $f_p$ into linear combinations with coefficients collected in the columns of an orthonormal matrix $\mathbf{V} = (V^T V^p)$. The linear combinations of auxiliary basis functions corresponding to the columns $V^p_i$ of $V^p$ shall span the space of the occupied times unoccupied orbitals or a subspace of it.
while the linear combinations of auxiliary basis functions corresponding to the columns \( v_m^c \) of \( V \) shall span a space orthogonal to the space spanned by the occupied times unoccupied orbitals.

We now transform Eq. (4) according to

\[
U^T AVV^T c = U^T y
\]

leading to the equation

\[
\begin{pmatrix}
A^{pp} & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
c^0 \\
y^0
\end{pmatrix} =
\begin{pmatrix}
y^p \\
y^0
\end{pmatrix}
\]

(10)

with \( A^{pp} = U^{pT} AVP, \quad c^0 = V^{pT} c, \quad c^+ = V^{+T} c, \quad y^p = U^{pT} y \), and \( y^0 = U^{0T} y \). All parts of the transformed matrix \( U^T AV \) except the part \( A^{pp} \) are zero because they contain matrix elements that are either integrals over functions being identical to zero everywhere in space or integrals over orthogonal functions. If the linear combinations of auxiliary basis functions corresponding to \( V^p \) span the complete space of products of occupied times unoccupied orbitals then the matrix \( A^{pp} \) is quadratic and invertible because it contains the overlap of two sets of linearly independent functions, the functions \( Q^p_\nu \) of Eq. (7) and the linear combinations of auxiliary basis functions corresponding to \( V^\nu \), that span the same space. If the linear combinations of auxiliary basis functions corresponding to \( V^\nu \) spans only a subset of the space of products of occupied times unoccupied orbitals then the matrix \( A^{pp} \) is a rectangular matrix that cannot be inverted. However, by suitably augmenting the auxiliary basis set it is always possible to turn \( A^{pp} \) into an invertible quadratic matrix.

The form of Eq. (10) implies that, for a given orbital basis set, it is possible to find an auxiliary basis such that Eq. (10) and thus also Eq. (4) has at least one solution if either the products of occupied times unoccupied orbitals are all linearly independent and the corresponding matrix \( U \) thus does not contain a part \( U^0 \) or if the vector \( y^0 \) equals zero. Indeed, in these cases, any auxiliary basis set that contains the space spanned by the occupied times unoccupied orbitals leads to at least one solution of Eqs. (10) and (4). However, note that, in case the matrix \( U \) contains a part \( U^0 \), then, in general, \( y^0 \) does not equal zero because the sum \( \sum_{\mu \nu} a_{\mu\nu}^0 \langle \phi_\mu | c^0 | \phi_\nu \rangle \) does not need to equal zero even if the linear combinations \( \sum_{\mu \nu} a_{\mu\nu}^0 \langle \phi_\mu | c^0 | \phi_\nu \rangle \) are identically zero because orbitals \( \phi_\mu \) and \( \phi_\nu \) occur in the evaluation of the matrix elements \( \langle \phi_\mu | c^0 | \phi_\nu \rangle \) of the HF nonlocal exchange operator.

Indeed there is no reason why the vector \( y^0 \) should equal zero unless specific symmetries require it. A closed shell atom, neon, shall serve as an example for such specific symmetries. We consider the nine products \( \phi_\mu | \phi_\nu \) resulting from the three occupied 2p-orbitals and the three unoccupied 3p-orbitals. These nine products of occupied and unoccupied orbitals can be combined by angular momenta coupling to nine linear combinations of well-defined angular momentum, i.e., one linear combination of s-type, three of p-type, and five of d-type. It turns out that the three linear combinations of p-type are identical to zero while the six other linear combinations are linearly independent. This means that, in this case, the Clebsch–Gordan coefficients of the angular momentum coupling can be used to form a matrix \( U \) and that, in particular, the part \( U^0 \) of \( U \) is given by the Clebsch–Gordan coefficients leading to the three products of p-type. However, in this case, all elements of \( y^\mu \), i.e., the elements that correspond to linear combinations of p-type of products \( \phi_\mu | \phi_\nu \) with different arguments \( \mu \) and \( \nu \) are zero due to symmetry because the nonlocal HF exchange potential of a closed shell system is totally symmetric. This means that the vector \( y^0 \) is zero and the linear dependency of the nine products of the occupied 2p- and the unoccupied 3p-orbitals does not prevent the existence of a solution of the corresponding Eq. (10) or (4). Note that even \( y^0 \) corresponding to the linearly independent combinations of products of 2p- and 3p-orbitals contains various elements that equal zero due to symmetry, the elements namely that correspond to linear combinations of d-type. As a consequence, any xOEP exchange potential for neon corresponding to a solution of Eq. (10) or (4) is exclusively composed of s-type auxiliary basis functions. In a similar way also for other systems, atoms as well as molecules or solids, it may happen that certain linear dependencies of products of occupied and unoccupied orbitals are related to symmetry and do not prevent a solution of Eq. (10) or (4).

In the next section we will focus on the question whether, in practice, products of occupied times unoccupied orbitals exhibit linear dependencies unrelated to symmetry, i.e., on the question whether the matrix \( U \) contains a part \( U^0 \) leading to a nonzero vector \( y^0 \) that prevents a solution of Eqs. (10) and (4) and thus prevents the possibility of finding for a given orbital basis set an auxiliary basis set leading to an xOEP total energy equal to the HF total energy. In this context it is important to distinguish between formal linear dependency and effective linear dependency. Formal linear dependency means that a diagonalization of the overlap matrix \( D \) carried out with infinite numerical accuracy leads to eigenvalues that are exactly zero. The term ‘effective linear dependency’ is here defined as follows: if the inverse of the condition number \( \tau_D \) of the overlap matrix \( D \) between occupied–virtual orbital product functions, i.e., if the inverse of the ratio of the eigenvalue of \( D \) with the largest magnitudes to the eigenvalue with the smallest magnitude, is equal or even smaller than the numerical accuracy \( \eta \), i.e., if \( 1/\tau_D \leq \eta \), then the orbital products \( \phi_\mu \phi_\nu \) are called ‘effectively linear dependent’. In practice this means that, taking double precision accuracy as the default, an effective linear dependency is reached when the condition number of \( D \) has values larger than about \( 10^{14} \). Because practical calculations are always carried out with finite numerical accuracy, the question of effective linear dependency of products of occupied times unoccupied orbitals is the crucial one.

If the products of occupied times unoccupied orbitals for a given orbital basis set are effectively linearly depen-
dent then the matrix $U_0$ is formed by those eigenvectors of the overlap matrix $D$ that belong to eigenvalues with magnitudes that are smaller than the largest magnitude of an eigenvalue multiplied by the numerical accuracy $\eta$. If this effective linear dependency is not related to symmetry, then there is no reason why the corresponding vector $y^0$ shall be effectively zero, i.e., shall contain only elements with a magnitude that is smaller than a typical element of $y^0$ multiplied by the numerical accuracy $\eta$. As a consequence it is not possible to solve Eq. (10) or (4), no matter what auxiliary basis set is chosen and it is not possible to obtain the HF total energy with the xOEP method for the given orbital basis set.

In practice one does not attempt to construct the xOEP potential by solving Eq. (10) or (4). Instead one carries out a standard basis set xOEP calculation [1,13-17,21,22]. In such a calculation the coefficients $c_p$ of Eq. (1) for the exchange potential are obtained by solving in each cycle of the xOEP self-consistency process the xOEP matrix equation [15,16,21,22]

$$X \cdot c = t$$

(11)

for the vector $c$ consisting of the expansion coefficients $c_p$ of Eq. (1) for the exchange potential $v_{\text{x}}$. The elements of the matrix $X$, representing the KS response function are given by

$$X_{s,p} = 4 \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \frac{\langle \phi_i | f_p^T | \phi_a \rangle \langle \phi_a^T | f_p | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}$$

(12)

with $\varepsilon_i$ and $\varepsilon_a$ denoting the eigenvalues of the occupied and unoccupied orbitals $\phi_i$ and $\phi_a$, respectively. The vector $t$, on the right hand side of Eq. (11) contains the elements

$$t_p = 4 \sum_{ia} \langle \phi_i | f_p | \phi_a \rangle \sqrt{\frac{\langle \phi_i | \hat{N}^L | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}}.$$  

(13)

The xOEP Eq. (11) can be written as

$$A^T \cdot \lambda \cdot c = A^T \cdot y$$

(14)

with the elements $\lambda_{ia,jb}$ of the diagonal matrix $\lambda$ given by $\lambda_{ia,jb} = 4\delta_{ia,jb}/(\varepsilon_i - \varepsilon_a)$. If the latter equation is transformed by multiplication with $V^T$ and insertion of $I = UU^T$ and $I = VV^T$ then it turns into

$$\begin{pmatrix} A^{pp^T} \cdot \lambda^{pp} \cdot A^{pp} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c^p \varepsilon_p^p \end{pmatrix} = \begin{pmatrix} A^{pp^T} \lambda^{pp} y^p + A^{pp^T} \lambda^{pp} y^0 \\ 0 \end{pmatrix}$$

(15)

with $A^{pp} = U^{pp^T} A^{pp} U^{pp}$ and $\lambda^{pp} = U^{pp^T} \lambda^{pp} U^{pp}$. Eq. (15) and thus also the original xOEP Eq. (11) always have a solution because $A^{pp^T} \lambda^{pp} A^{pp}$ is invertible due to the fact that it is a negative definite matrix like its constituents $A^{pp}$ and $\lambda$. If the products of occupied times unoccupied orbitals are linearly independent then the upper part of Eq. (15) turns into $A^{pp^T} \lambda^{pp} A^{pp} c^p = A^{pp^T} \lambda^{pp} y^p$ because $y^p = 0$. Multiplication of the latter equation by $[A^{pp^T} \lambda^{pp}]^{-1}$ turns Eq. (15) into Eq. (10). Note that in this case $\lambda^{pp}$ and $A^{pp^T}$ and thus $[A^{pp^T} \lambda^{pp}]^{-1}$ are invertible.

Thus, in this case, Eq. (15) and the original xOEP Eq. (11) are equivalent to Eq. (10) and thus also to Eq. (4) and the xOEP method yields the HF energy. If, however, the products of occupied times unoccupied orbitals are linearly dependent or in practice effectively linearly dependent then Eqs. (11) and (4) are not equivalent. While Eq. (11) and a corresponding xOEP method nevertheless have a solution, Eq. (4) has no solution and the xOEP total energy is therefore higher than the HF energy for any auxiliary basis set. If orbital and auxiliary basis sets are well-balanced such that the xOEP method properly represents an exchange-only KS method then the auxiliary basis functions span a space that is smaller than and contained in the space of the products of occupied times unoccupied orbitals. In this case Eq. (15) and thus the original xOEP Eq. (11) have a unique solution while Eq. (4) has none and the xOEP method then again yields a total energy higher than the HF total energy.

If Eq. (4) has no solution because the products of occupied times unoccupied orbitals are linearly dependent and/or because the auxiliary basis set does not span the complete space of occupied times unoccupied orbitals we can try to find an exchange potential, i.e., a vector $c$, that minimizes the norm of the difference $A c - y$, i.e., that minimizes $(A c - y)^T (A c - y)$. Differentiation with respect to the coefficients $c_p$ leads to the equation

$$A^T A c = A^T y,$$

(16)

which is the basis of the effective exact exchange methods of Ref. [18], an approximation to an exact exchange KS method. If, however, we determine the vector $c$ by minimizing the vector $A c - y$ with respect to the norm given by the matrix $\lambda$, i.e., if we minimize $(A c - y)^T \lambda (A c - y)$ then we obtain Eqs. (14) and (11), the basis set xOEP equation. This means the basis set xOEP Eq. (11) can be obtained by a weighted minimization of the difference between the occupied–virtual block of the xOEP and the HF exchange matrix, with weight factors given by the inverse eigenvalue differences of occupied and unoccupied orbitals.

3. Results

In order to highlight the dependence of the condition number $\tau_p$ of the overlap matrix $D$ on the number of products of occupied times unoccupied orbitals and thus indirectly on the quality of the orbital basis set we have performed xOEP and Hartree–Fock calculations for beryllium with various Gaussian orbital and auxiliary basis sets. The employed orbital basis sets are the (augmented) cc-pV(X)Z basis sets ($X = D,T,Q$) sets from Dunning [23]. In order to approach the basis set limit two even larger basis sets were considered, namely the Partridge3 basis set [24] and a self constructed even tempered basis set with a progression factor of 1.5 termed as even(1.5) that yields occupied and energetically low unoccupied exchange-only KS orbitals that can be regarded as exact in this context. The orbital even(1.5) basis set contains 52 s-type basis functions
with exponents $a$ between $a = 1.71 \times 10^5$ and $a = 1.21 \times 10^{-2}$ and the corresponding auxiliary basis set has been constructed thereof by removing the 18 tightest and 13 diffusest functions. The auxiliary basis sets for the other orbital basis sets have been constructed according to the basis set construction and balancing scheme described in Ref. [14]. Note that for contracted orbital basis sets the accompanying auxiliary basis sets are those belonging to the corresponding uncontracted orbital basis sets. In case of the contracted orbital basis set cc-pVTZ(cont.) and the aug-cc-pVTZ orbital basis set we have considered in addition extended basis sets with 3, respectively, 2 additional diffuse functions in order to obtain a larger number of Rydberg orbitals in the xOEP calculations. Only s-type basis functions were used for the beryllium calculations. All basis sets used in this work are available as supplementary material. All calculations were performed using the MOLPRO quantum chemistry program [25].

Table 1 displays the condition numbers $\tau_0$ of the overlap matrices $D$ for products of the two occupied orbitals of beryllium with a varying number of unoccupied orbitals. In case of the aug-cc-pVTZ+diffuse and even(1.5) basis sets the effective number $N_{\text{virt}}$ of virtual orbitals considered in the overlap matrix $D$ had to be limited because if more virtual orbitals are taken into account then the condition number is that large that numerical problems in the determination of the eigenvalues of the overlap matrix $D$ occur. Table 1 shows that for the contracted cc-pV(X)Z basis sets the condition number $\tau_0$ of $D$ is rather small and indicates that the products of occupied times unoccupied orbitals are linearly independent. This changes dramatically if one either adds diffuse functions to the basis set or if the basis set is uncontracted. In both cases, as can be observed in Table 1, the condition number rises by at least seven orders of magnitude. This finding holds for both xOEP and Hartree–Fock orbitals. Also for the uncontracted basis sets a distinctive increase of the condition number $\tau_0$ is observed if diffuse functions are added as can be seen by the numbers for the aug-cc-pVTZ+diffuse basis in Table 1. Here only six of 15 possible virtual orbitals were needed to create an effective (see above) linearly dependent set of occupied times unoccupied orbitals. The same also holds for the largest even(1.5) basis set where it took only five virtual orbitals to reach an effective linear dependence of the orbital products. In order to investigate the influence of the xOEP orbitals representing the continuum, i.e., the energetically lowest xOEP orbitals with positive eigenvalues, on the condition numbers of $D$ we have also considered overlap matrices $D$ for the even(1.5) basis set that were constructed without Rydberg orbitals. The results displayed in Table 1 show that in this case the condition numbers grow more slowly with the number of virtual orbitals compared to the case taking into account Rydberg orbitals. However, it can be seen that even then one rapidly reaches an effective linear dependence of the products of occupied times unoccupied orbitals. Thus in an almost complete basis set it would not suffice to just neglect the Rydberg orbitals in order to prevent linear dependence of the products of occupied times unoccupied orbitals.

Fig. 1 explains these findings. Here the products of the occupied beryllium 2s- with bound unoccupied ns-orbitals with $n = 3–13$ are displayed. It is immediately seen that for $n \geq 5$ the products are virtually identical. (Products of occupied and different unoccupied orbitals representing the continuum interestingly seem to remain different.)

Table 1 and Fig. 1 show that for any orbital basis set that can properly describe the lowest five or six s-orbitals of beryllium the products of occupied and unoccupied orbitals are effectively linearly dependent with respect to

<table>
<thead>
<tr>
<th>Basis set</th>
<th>$N_{\text{virt}}$</th>
<th>$n_{\text{Rydberg}}$ virtual</th>
<th>$N_{\text{virt}}$</th>
<th>$\tau_0$(OEP)</th>
<th>$\tau_0$(HF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-pVDZ(cont.)</td>
<td>1</td>
<td>0</td>
<td>All</td>
<td>$9.0 \times 10^5$</td>
<td>$8.5 \times 10^5$</td>
</tr>
<tr>
<td>cc-pVTZ(cont.)</td>
<td>2</td>
<td>1</td>
<td>All</td>
<td>$5.6 \times 10^5$</td>
<td>$5.7 \times 10^5$</td>
</tr>
<tr>
<td>cc-pVTZ+diffuse</td>
<td>5</td>
<td>3</td>
<td>All</td>
<td>$2.3 \times 10^4$</td>
<td>$1.9 \times 10^4$</td>
</tr>
<tr>
<td>cc-pVQZ(cont.)</td>
<td>3</td>
<td>1</td>
<td>All</td>
<td>$4.6 \times 10^3$</td>
<td>$4.5 \times 10^3$</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
<td>10</td>
<td>1</td>
<td>All</td>
<td>$1.1 \times 10^2$</td>
<td>$1.0 \times 10^2$</td>
</tr>
<tr>
<td>aug-cc-pVTZ</td>
<td>12</td>
<td>1</td>
<td>All</td>
<td>$3.8 \times 10^2$</td>
<td>$1.4 \times 10^2$</td>
</tr>
<tr>
<td>aug-cc-pVTZ+diffuse</td>
<td>15</td>
<td>4</td>
<td>6</td>
<td>$2.3 \times 10^4$</td>
<td>$1.7 \times 10^4$</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>13</td>
<td>1</td>
<td>All</td>
<td>$7.2 \times 10^3$</td>
<td>$4.4 \times 10^3$</td>
</tr>
<tr>
<td>Partridge3</td>
<td>18</td>
<td>1</td>
<td>2</td>
<td>$3.9 \times 10^1$</td>
<td>$2.1 \times 10^1$</td>
</tr>
<tr>
<td>Even(1.5)</td>
<td>50</td>
<td>11</td>
<td>2</td>
<td>$9.5 \times 10^5$</td>
<td>$8.6 \times 10^5$</td>
</tr>
<tr>
<td>Even(1.5)*</td>
<td>39</td>
<td>0</td>
<td>2</td>
<td>$8.4 \times 10^3$</td>
<td>$3.5 \times 10^3$</td>
</tr>
</tbody>
</table>

The xOEP orbitals are obtained with a de facto exact basis set xOEP potential calculated with the balanced even(1.5) orbital and auxiliary basis sets. $N_{\text{virt}}$ denotes the total number of virtual orbitals in the corresponding basis set, $n_{\text{Rydberg}}$ the number of Rydberg orbitals that are obtained with the xOEP method and $N_{\text{virt}} \leq N_{\text{virt}}$ denotes number of virtual orbitals that were considered in the construction of $D$.

* No Ryberg orbitals included.
the typical numerical accuracy of about \( \eta = 10^{14} \) of quantum chemical calculations. As a result the xOEP energy will be higher than the HF energy even if an unbalanced auxiliary basis set is chosen that yields unphysical exchange potentials. A similar behavior can also be found for other systems. Table 2 summarizes an investigation on whether it is possible or not to reach via an xOEP approach the HF total energy for different combinations of orbital and auxiliary basis sets in the case of beryllium. Table 2 clearly shows that this, in general, is not the case. Indeed only for the smallest considered basis sets, contracted valence-double/triple/quadruple-zeta basis sets, the HF total energy can be obtained by an OEP method. In all other cases, even auxiliary basis sets that are de facto complete, entirely unbalanced to the orbital basis set, and lead to completely unphysical exchange potentials, do not yield the HF total energy. This is demonstrated by using an even larger even tempered auxiliary basis set termed as even(1.5)+ which has been obtained from the original even(1.5) auxiliary basis set by adding 17 more tight functions such that the total range of exponents \( \alpha \) lies in between \( \alpha = 1.13 \times 10^5 \) and \( \alpha = 3.48 \times 10^{-2} \) and spans about the same range as a corresponding cc-pV5Z standard orbital basis set. It can be observed that none of the calculations for this auxiliary basis set were possible without a singular value decomposition of the xOEP response matrix of Eqs. (11) and (12) and a subsequent omission of eigenvectors with small eigenvalues. The appearance of eigenvalues in the response matrix that are effectively zero indicates that the space spanned by the auxiliary basis set is larger than the space of occupied times unoccupied orbitals and that subsequently the matrices \( A \) and \( X_s \), see Section 2, are effectively singular. The total number of eigenvalues which were neglected are given in parentheses appended to the energy differences in Table 1. It can be seen that even for the largest even(1.5)+ auxiliary basis set it is not possible to reach the Hartree–Fock energy using the smallest uncontracted cc-pVDZ orbital basis set. This is also demonstrated by Fig. 2 in which the energy difference \( E(\text{OEP}) - E(\text{HF}) \) of the xOEP and HF total energies \( E(\text{OEP}) \) and \( E(\text{HF}) \), respectively, is plotted for various uncontracted orbital basis sets against the number of basis functions in the different auxiliary basis sets used for the expansion of the xOEP exchange potential. It can be observed that for all orbital basis sets displayed in Fig. 2 the energy difference \( E(\text{OEP}) - E(\text{HF}) \) remains well above zero and for the larger basis sets even seems to converge with the number of auxiliary basis functions. We have also performed xOEP calculations for the neon atom with various orbital and auxiliary basis sets (see Ref. [14] for technical details). The results shown in Fig. 3 confirm the result found for beryllium that for larger orbital basis sets it is no longer possible to reach the Hartree–Fock total energy.

In order to further support these findings we have additionally performed OEP calculations for the molecules CO and H\(_2\)O both with a contracted and an uncontracted cc-pV5Z basis set and corresponding auxiliary basis sets which were constructed by enlarging the orbital basis set by adding exponents which are the geometric mean of the exponents of the original basis set. This leads to auxiliary basis sets of about twice the size of the orbital basis set. For both molecules the xOEP response matrix was highly singular and thus a singular value decomposition of it had to be performed in order to converge the xOEP self-consistency process. In case of CO 38 response eigenvectors and in case of H\(_2\)O 25 response eigenvectors had to be removed in order to reach this convergency. For the CO molecule the energy difference to Hartree–Fock amounts to only 0.21 milliHartree for the small contracted orbital basis set and grows to a value of 3.72 milliHartree for the uncontracted orbital basis set. For H\(_2\)O the xOEP total energy nearly reaches the Hartree–Fock total energy with the contracted orbital basis set while an energy difference

Fig. 1. Beryllium atom: products of the xOEP HOMO orbital with the first Rydberg xOEP orbitals (a) and the first xOEP orbitals representing the continuum (b). Products are first normalized to one at \( r = 0 \) and then multiplied with the squared radial distance \( r^2 \) from the nucleus. (orbital basis set: even(1.5), i.e., even tempered basis with progression 1.5, auxiliary basis set: even(1.5) basis set, details see text.)

\[
\begin{align*}
\text{Table 2:} & \quad \text{Comparison of xOEP and HF total energies for different auxiliary basis sets.} \\
 & \quad \text{The results shown in Fig. 3 confirm the result found for beryllium that for larger orbital basis sets it is no longer possible to reach the Hartree–Fock total energy.}
\end{align*}
\]
of 1.85 milliHartree is obtained using the uncontracted orbital basis set.

We thus conclude that, in general, products of occupied and unoccupied orbitals are effectively linearly dependent and that, in general, Gaussian basis set OEP methods cannot yield the HF total energy even if unphysical exchange potentials are introduced that do not correspond to the KS exchange potential.

The effective linear dependence of products of occupied and unoccupied orbitals also indicates that these products are not a suitable basis set to represent the exchange potential in OEP methods.

<table>
<thead>
<tr>
<th>Orbital basis</th>
<th>( N_{\text{occ}}N_{\text{virt}} )</th>
<th>( VDZ )</th>
<th>( VTZ )</th>
<th>( VQZ )</th>
<th>Partridge3</th>
<th>Even(1.5)</th>
<th>Even(1.5)+</th>
<th>OEP(num)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cVDZ</td>
<td>3</td>
<td>0.000(3)</td>
<td>0.000(4)</td>
<td>0.000(5)</td>
<td>0.000(7)</td>
<td>0.000(17)</td>
<td>0.000(34)</td>
<td>0.115</td>
</tr>
<tr>
<td>cVTZ</td>
<td>3</td>
<td>0.000(1)</td>
<td>0.000(2)</td>
<td>0.000(3)</td>
<td>0.000(5)</td>
<td>0.000(15)</td>
<td>0.000(32)</td>
<td>0.197</td>
</tr>
<tr>
<td>cVTZ+d</td>
<td>10</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000(3)</td>
<td>0.000(12)</td>
<td>0.000(28)</td>
<td>0.217</td>
</tr>
<tr>
<td>cVQZ</td>
<td>6</td>
<td>0.016</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000(3)</td>
<td>0.000(13)</td>
<td>0.000(30)</td>
<td>0.347</td>
</tr>
<tr>
<td>VTZ</td>
<td>20</td>
<td>0.624</td>
<td>0.608</td>
<td>0.603</td>
<td>0.538</td>
<td>0.526(8)</td>
<td>0.525(23)</td>
<td>0.572</td>
</tr>
<tr>
<td>VTZ+d</td>
<td>24</td>
<td>0.629</td>
<td>0.608</td>
<td>0.604</td>
<td>0.584</td>
<td>0.551(6)</td>
<td>0.552(22)</td>
<td>0.579</td>
</tr>
<tr>
<td>VQZ</td>
<td>26</td>
<td>0.629</td>
<td>0.608</td>
<td>0.604</td>
<td>0.584</td>
<td>0.552(5)</td>
<td>0.546(20)</td>
<td>0.579</td>
</tr>
<tr>
<td>Partridge3</td>
<td>36</td>
<td>0.629</td>
<td>0.609</td>
<td>0.607</td>
<td><strong>0.595</strong></td>
<td>0.583(5)</td>
<td>0.582(17)</td>
<td>0.589</td>
</tr>
<tr>
<td>Even(1.5)</td>
<td>100</td>
<td>0.630</td>
<td>0.610</td>
<td>0.607</td>
<td>0.595</td>
<td><strong>0.591(2)</strong></td>
<td>0.591(2)</td>
<td>0.591</td>
</tr>
</tbody>
</table>

The last column gives the energy differences to xOEP calculations with the de facto exact xOEP potential from a numerical grid method [26–28]. The parenthesized values show that the corresponding xOEP calculation had to be performed using a singular value decomposition for the inversion of the response matrix and the numbers in parentheses denote the number of eigenvectors which have been filtered out. The combinations of auxiliary and orbital basis sets resulting from the balancing scheme of Ref. [14] are indicated by bold numbers.

Finally, the following point shall be made: it is not possible to decide whether or not a Gaussian basis set xOEP calculation has yielded a physically meaningful KS exchange potential by simply inspecting the exchange potential. If OEP calculations yield the HF total energy then the exchange potential usually is highly oscillating and obviously unphysical. If, however, the xOEP total energy lies just somewhat below the exact exchange-only KS total energy then the corresponding exchange potentials may be very smooth and well-behaved looking. Nevertheless they are unphysical and do not represent a KS exchange potential. A test to decide whether an orbital basis is converged with respect to a given auxiliary basis...
set or not is to enlarge the orbital basis set and to test whether the exchange potential remains unchanged and whether the difference between xOEP and HF total energies is stable. Note that some of the Gaussian basis set OEP results published in recent years may be corrupted in the sense that the OEP exchange potentials might not represent physical KS exchange potentials and that the published OEP total energies might lie below the correct KS total energy.

4. Summary and conclusions

We have shown for atoms and molecules that products of occupied times unoccupied HF or xOEP orbitals, in general, are effectively linearly dependent and that therefore Gaussian basis xOEP methods, in general, do not yield the HF total energy even if completely unphysical xOEP exchange potentials are accepted that do not represent KS exchange potentials. Indeed, Gaussian basis set xOEP methods can yield the HF total energy only if inadequate orbital basis sets are used. An indication that an orbital basis set is inadequate for xOEP methods is given by the inverse of the condition number of the overlap matrix \( D \) of products of occupied times unoccupied orbitals, i.e., by the ratio of the eigenvalue with the smallest magnitude of this overlap matrix to the eigenvalue with the largest eigenvalue. For a computational accuracy of 14–16 digits an orbital basis set is inadequate if the inverse of the condition number is distinctively larger, i.e., five or six order of magnitudes larger, than \( 10^{-14} \) to \( 10^{-16} \).

Note that in the basis set limit the inverse of the condition number of the overlap matrix \( D \) approaches zero. Furthermore, note that, on the other hand, a small enough inverse of the condition number of the considered overlap matrix does not guarantee an adequate orbital basis set. Only orbital basis sets that describe both the occupied and energetically low lying unoccupied orbitals as well as the orbitals representing the energetically low region of the continuum sufficiently good are adequate in the sense that they lead to the small eigenvalues of the overlap matrix \( D \) that should be present for physical reasons. In order to carry out physically meaningful xOEP calculations that properly represent exchange-only KS calculations orbital basis sets furthermore have to be balanced with respect to the employed auxiliary basis sets.

If one assumes that it was possible to construct an arbitrarily large orbital basis set whose products of basis functions are always formally, i.e., with respect to infinite computational accuracy, linearly independent, then a subtle relation between computational accuracy and the possibility to obtain the HF energy with an xOEP procedure arises. Given any of such orbital basis sets it is possible, at least in a Gedanken experiment, to increase the computational accuracy such that the products of occupied and unoccupied orbitals are effectively linearly independent and it is then possible to find an auxiliary basis set such that the xOEP and HF energies are equal. On the other hand, for any given computational accuracy it is possible to increase the orbital basis set such that the products of occupied and unoccupied orbitals become effectively linearly dependent indicated by an inverse of the condition number of the overlap matrix \( D \) that is lower than the computational accuracy. As a consequence, it is then not possible to obtain the HF energy by an xOEP procedure. This means we cannot consider computational accuracy and basis set size independently from each other. A meaningful quantum chemical computation must be converged with respect to the basis set. This means for any given computational accuracy we first have to increase the basis set sufficiently enough to reach satisfying basis set convergence and in a second step we can increase the computational accuracy. If the limits of large basis sets and computational accuracy are taken in this order then, however, the products of occupied and unoccupied orbitals always are linearly dependent and the HF and xOEP energies are different.

Standard contracted orbital basis sets, e.g., Dunning’s aug-cc-pVXZ basis sets, were shown to be inadequate for xOEP methods. Physically meaningful OEP methods require uncontracted orbital basis sets.

Another consequence of the finding that products of occupied times unoccupied orbitals, in general, are linearly dependent is that these products do not seem to be a suitable auxiliary basis set for expanding the exchange potential in xOEP methods. Indeed, in atoms and also in other highly symmetric systems even the smallest Gaussian orbital basis sets lead to products of occupied times unoccupied orbitals that exhibit linear dependencies related to symmetry. These linear dependencies related to special symmetries are not relevant for the question whether or not xOEP methods yield the HF total energy but nevertheless may affect the usefulness of products of occupied times unoccupied orbitals as auxiliary basis sets in xOEP methods.

Furthermore we emphasize that the question whether or not a Gaussian basis set xOEP calculation can yield the HF total energy only arises for those Gaussian basis set xOEP calculations that do not properly represent KS calculations. Gaussian basis set xOEP calculations properly representing KS calculations, i.e., xOEP calculations carried out with an appropriate xOEP procedure and well-balanced orbital and auxiliary basis sets, see Ref. [14], as required by the basic formalism, lead to total energies that are always higher (in case of systems containing more than two electrons) than the corresponding HF total energy and yield well-behaved physically meaningful KS exchange potentials.

Finally we have shown that the basis set xOEP equation, Eq. (11) determining the expansion coefficients of the exchange potential can be obtained by a weighted minimization of the difference of the occupied–virtual block of the xOEP and the HF exchange matrix using inverse orbital eigenvalue differences as weight factors. Neglecting these weight factors leads to the approximate exchange potential given in Ref. [18].
References

11.5. Density-Functional Theory with Orbital-Dependent Functionals: Exact-exchange Kohn-Sham and Density-Functional Response Methods

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- optimised effective potential method
- orbital-dependent functionals
- determinantal overlap
- pyridine molecule
Density-Functional Theory with Orbital-Dependent Functionals: Exact-exchange Kohn-Sham and Density-Functional Response Methods

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Kohn-Sham methods with orbital-dependent exchange-correlation functionals, in particular exact-exchange methods, are discussed. The numerical stability of optimized-effective-potential methods to construct the exchange-correlation potential in the case of orbital-dependent energy functionals is considered. A numerically stable exact-exchange Kohn-Sham method is briefly presented. A new ansatz for time-dependent density-functional methods in the response regime is considered and an exact-exchange time-dependent density-functional method based on it is discussed and it is demonstrated that this methods is able to treat qualitatively correctly charge-transfer excitations.

1. Introduction

Conventional density-functional theory (DFT) methods like those based on the local density approximation (LDA) [1–3] or generalized gradient approximations (GGAs) [1–5] employ approximate functionals for the exchange-correlation (xc) energy that are integrals over functions of the electron density or, in the case of GGAs, of the electron density and its gradient. GGA methods nowadays are widely and successfully employed routine methods to investigate electronic ground states and their properties in chemistry and solid state physics [3,6,7]. Electronic excitations and the energies of excited states can be treated via time-dependent density-functional theory (TDDFT) [8,9] relying also on functionals

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within the LDA or GGA. However, despite their success, conventional DFT methods are not accurate enough for many questions of interest. For example energies of transition states of chemical reactions often are unreliable, Van-der-Waals interactions can not be described, or charge-transfer excitations are described qualitatively wrong [10–15]. These problems have their origin in shortcomings of the employed GGA functionals. In recent years, therefore, a new generation of DFT methods emerged that uses functionals that not only depend on the electron density and its gradients but also on Kohn-Sham (KS) orbitals. Such functionals shall be referred to as orbital-dependent functionals (ODFs) [82]. Examples are functionals that contain the kinetic energy density, meta-GGA functionals [16–23], or functionals that contain the exchange energy density, hyper-GGA functionals [17,24–32] and local hybrid functionals [28,33–35]. Because the orbitals are functionals of the electron-density, ODFs lie within the realm of DFT.

The evaluation of the xc energy for ODFs poses no principal difficulty. However, within DFT methods, more precisely within KS methods, not only the xc energy but also the xc potential, the functional derivative of the xc energy with respect to the electron density, is required during the self-consistency process to obtain the orbitals. The evaluation of this functional derivative is straightforward for GGA functionals because these functionals are known in terms of the electron density and their gradients. For ODFs, however, this step is problematic because the dependence of the orbitals on the density is not known and the functional derivative of an ODF with respect to the electron density cannot simply be taken via the chain rule. In practice, for meta- and hyper-GGA functionals, instead of taking the functional derivative of the xc energy with respect to the electron density the derivative with respect to the KS orbitals is taken [20,36] in order to obtain an xc potential. An xc potential obtained in this way, however, is not the correct KS xc potential and the resulting approach is, strictly speaking, no longer a KS method.

The KS exchange energy is exactly known in terms of the KS orbitals, i.e., as ODF. For a closed shell system the KS exchange energy in terms of the orbitals has exactly the same form as the Hartree-Fock (HF) exchange energy, i.e., is given by the well-known expression for the exchange energy of a Slater determinant. The value of the KS and HF exchange energy is different because the expression is evaluated for different orbitals, i.e., for KS or for HF orbitals. If the exchange potential is determined as functional derivative of the exchange energy with respect to orbitals the nonlocal HF exchange potential is obtained, while if the exchange potential is determined as functional derivative of the exchange energy with respect to the electron density the local multiplicative KS exchange potential is obtained. This means the difference between the HF method and an exact exchange-only KS method, which shall be denoted EXX (exact exchange) method, is the type of the functional derivative of the exchange energy taken to obtain the exchange potential. While HF and EXX total energies differ very little, the KS orbitals and eigenvalues, in particular, the unoccupied
orbitals and their eigenvalues are completely different. Since KS orbitals and eigenvalues are the input quantities for the calculation of response properties, in particular, excitation energies via TDDFT, it is crucial that the correct functional derivative with respect to the electron density is taken. Similar as for EXX and HF methods, the common practice of taking the ‘wrong’ functional derivative within meta- and hyper-GGA methods in most cases probably has relatively little effect for the calculation of total energies, whereas it is less clear whether this holds true also for the resulting KS orbitals and eigenvalues.

Unoccupied HF orbitals mostly have positive eigenvalues and therefore little physical meaning. The eigenvalue spectra of conventional LDA or GGA methods is qualitatively wrong due to the presence of unphysical Coulomb self-interactions in these methods and, e.g., does not exhibit Rydberg series. EXX methods, on the other hand, yield physical eigenvalue spectra that contain Rydberg series [37,38,83]. As a result TDDFT methods based on LDA or GGA functionals yield very poor excitation energies for transitions in states with Rydberg character [39], which, e.g., often are present as low-lying excited states in organic molecules. EXX orbitals and TDDFT methods based on them, on the other hand, describe Rydberg states very well [37,38]. This demonstrates that it is of importance to employ correct KS xc potentials, i.e., functional derivatives of the xc energy with respect to the electron density. Moreover it seems unsatisfying from a formal point of view to devise density-functional methods which use an xc potential which is wrong in the sense that it is not the xc potential required according to the underlying formalism.

The functional derivative of an ODF with respect to the electron density can, in principle, be obtained via the optimized effective potential (OEP) approach [40–43,82]. Numerically stable OEP methods for atoms based on numerical representations of orbitals and potentials on grids [40,41] as well as for periodic systems based on plane wave basis sets are known [44–46]. OEP methods for molecules employing Gaussian basis sets were proposed [47,48] shortly after plane wave OEP methods were introduced. However, such Gaussian basis set OEP methods suffered from numerical instabilities [47,49–53], the origin of which is closely related to the KS response function which has to be effectively inverted when solving the OEP equation.

Numerically stable OEP methods are a prerequisite for using orbital-dependent xc functionals in self-consistent KS methods, which arguably represent the future of DFT methods. Various attempts to develop numerically stable OEP methods for molecules were made in recent years [37,38,47–50,54–58,60–62,84–87]. Some of these employ regularizations of the basis set representation of the KS response functions [55] or add smoothing terms to the total energy [56]. Other approaches introduce approximations in the one-particle Green's functions occurring in the OEP equation [37,38,61,62]. Within the DFG priority project 1145 we analysed in detail the origin of the numerical instabilities of OEP methods [52,53] and developed a numerically stable Gaussian basis set OEP method [54].
TDDFT methods, using ODFs, in particular time-dependent exact-exchange (TDEXX) methods for molecules [63–65] employing Gaussian basis sets, are numerically even more demanding than EXX KS methods or OEP methods in general. The reason is that in TDEXX methods not only one but two KS response functions occur which have to be effectively inverted. Moreover the frequency-dependent instead of the static KS response function is required. First straightforward implementations of TDEXX methods employing Gaussian basis sets suffer from numerical instabilities [66,67]. Within the DFG priority project 1145 we therefore analysed density-functional response methods [68,75,76] and reformulated the basic TDDFT response equation in such a way that inverse KS response functions no longer occur in TDEXX methods, or generally in TDDFT methods employing ODFs [68]. In this way the source of the numerical instabilities could be removed. The resulting TDEXX approach is numerically stable and can correctly describe charge-transfer excitations [68].

The manuscript is organized as follows: In the next Section OEP methods, in particular EXX methods, their relation to the HF method, and the sources of their numerical instabilities are discussed. Moreover the numerically stable EXX method developed within the DFG priority project 1145 is presented. In Section 3 we present the reformulation of the basic TDDFT response equation and the TDEXX approach based on it. Furthermore the relation between TDEXX and time-dependent HF is discussed. In Section 4 a brief summary and outlook is given. A point that is crucial for OEP and TDDFT methods, but which often is not considered sufficiently, is that the nature of these methods is closely related to the fact that products of occupied and unoccupied KS orbitals form a linearly dependent set. We will therefore put special emphasis to this point in the following.

2. OEP and EXX methods

2.1 Basic formulas and relation between EXX and HF methods

The OEP equation for the KS xc potential $v_{xc}$ corresponding to an ODF for the xc energy is given by

$$\int dr' \chi_s(r, r') \nu_{xc}(r') = t(r)$$

or

$$\nu_{xc}(r) = \int dr' \chi_s^{-1}(r, r') t(r')$$

with the static KS response function

$$\chi_s(r, r') = 4 \sum_{i, a}^{\text{occ., unocc.}} \frac{\varphi_i^{KS}(r) \varphi_a^{KS}(r') \varphi_a^{KS}(r') \varphi_i^{KS}(r')} {\varepsilon_i^{KS} - \varepsilon_a^{KS}}$$

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containing the occupied and unoccupied KS orbitals \( \varphi_i^{KS} \) and \( \varphi_a^{KS} \), respectively, and their eigenvalues \( \epsilon_i^{KS} \) and \( \epsilon_a^{KS} \). Non-spin-polarized systems with real-valued orbitals shall be considered throughout. Spin is taken into account by appropriate prefactors. The right hand side \( i \) of the OEP equation (1) depends on the xc functional. From now on we will concentrate on the exact exchange energy as ODF. For simplicity correlation shall be neglected and we will deal exclusively with the EXX approach. Addition of a conventional GGA correlation functional, however, is straightforward. Parts of the following discussion, in particular questions of the numerical stability of EXX methods, are valid for OEP methods in general, i.e., are valid also for other orbital-dependent xc functionals. The EXX method, in this case, serves as a specific example.

In the exact exchange-only case the right hand side \( i \) of the OEP equation (1) has the form

\[
i(r) = 4 \sum_{\text{occ. unocc.}} \frac{\varphi_i^{EXX}(r) \varphi_a^{EXX}(r) \langle \varphi_a^{EXX} | \hat{v}_x^{NL} | \varphi_i^{EXX} \rangle}{\epsilon_i^{EXX} - \epsilon_a^{EXX}}
\]  

with \( \hat{v}_x^{NL} \) being a nonlocal exchange operator of the form of the HF exchange operator, however, constructed from KS orbitals. Because we consider the special case of an EXX approach the superscript KS at the orbitals and eigenvalues is replaced by the superscript EXX.

In the EXX case the OEP equation (1) can be rearranged in the form

\[
0 = Q^T(r) \Delta_x
\]

with the vectors \( Q(r) \) and \( \Delta_x \) defined by their elements

\[
Q_{ia}(r) = \varphi_i^{EXX}(r) \varphi_a^{EXX}(r)
\]

and

\[
\Delta_{x,ia} = \frac{\langle \varphi_a^{EXX} | \hat{v}_x^{NL} | \varphi_i^{EXX} \rangle - \langle \varphi_a^{EXX} | \hat{v}_x | \varphi_i^{EXX} \rangle}{\epsilon_i^{EXX} - \epsilon_a^{EXX}}.
\]

The dimension of the vectors \( Q(r) \) and \( \Delta_x \) equals the number of products of occupied times unoccupied EXX orbitals. The indices \( i \) and \( a \) of the occupied and unoccupied orbitals, respectively, form a superindex \( ia \) labelling the elements of the vectors \( Q(r) \) and \( \Delta_x \). Throughout, indices \( i \) or \( j \) will label occupied, indices \( a \) or \( b \) will label unoccupied orbitals.

If the products of occupied times unoccupied orbitals, i.e., the functions \( Q_{ia}(r) \), would form a linearly independent set then from Eq. (5) would immediately follow that the vector \( \Delta_x \) equals the zero vector, i.e., that the identity

\[
\langle \varphi_a^{EXX} | \hat{v}_x | \varphi_i^{EXX} \rangle = \langle \varphi_a^{EXX} | \hat{v}_x^{NL} | \varphi_i^{EXX} \rangle
\]

holds for the matrix elements of the KS exchange potential \( v_x \). The latter identity, however, would imply that the exchange-only KS and the HF determinants would be identical. To show this we add the operator

\[
\hat{\Delta}_x = \hat{v}_x^{NL} - \hat{v}_x
\]

to the exchange-only KS Hamiltonian operator.
to obtain the Hamiltonian operator

\[ \hat{H}^{\text{HF}} = \hat{T} + \hat{v}_{\text{ext}} + \hat{v}_H + \hat{v}_x^- \]  

which has the form of the HF Hamiltonian operator, the Fock operator, but is constructed from EXX orbitals. In the definitions (10) and (11) the operators \( \hat{T} \), \( \hat{v}_{\text{ext}} \), and \( \hat{v}_\text{H} \) are the operators of the kinetic energy, the operator corresponding to the external potential \( v_{\text{ext}} \), usually the electrostatic potential of the nuclei, and the operator corresponding to the Hartree potential \( v_H \), respectively.

In the basis of the EXX orbitals the Hamiltonian operator (11) is represented by the matrix

\[ H^{\text{HF}} = \begin{pmatrix} \epsilon^{\text{EXX,occ}} & 0 \\ 0 & \epsilon^{\text{EXX,unocc}} \end{pmatrix} + \begin{pmatrix} \Delta^{\text{occ}} & 0 \\ 0 & \Delta^{\text{unocc}} \end{pmatrix} \]  

with the diagonal matrices \( \epsilon^{\text{EXX,occ}} \) and \( \epsilon^{\text{EXX,unocc}} \) containing the EXX eigenvalues \( \epsilon_i^{\text{EXX}} \) and \( \epsilon_a^{\text{EXX}} \) of the occupied and unoccupied EXX orbitals, respectively. The matrix elements of the matrices \( \Delta^{\text{occ}} \) and \( \Delta^{\text{unocc}} \) are given by

\[ \Delta V_{x,ij}^{\text{occ}} = \langle \varphi_i^{\text{EXX}} | \hat{\nu}_x^{\text{NL}} - \hat{v}_x^- | \varphi_j^{\text{EXX}} \rangle \]  

\[ \Delta V_{x,ab}^{\text{occ}} = \langle \varphi_a^{\text{EXX}} | \hat{\nu}_x^{\text{NL}} - \hat{v}_x^- | \varphi_b^{\text{EXX}} \rangle \]  

There are no matrix elements coupling occupied and unoccupied KS orbitals, i.e., no matrices \( \Delta V_{x,\text{occ,unocc}} \) or \( \Delta V_{x,\text{unocc,occ}} \), because the elements of those matrices are the ones collected in \( \Delta_x \) which were zero if the products of occupied times unoccupied orbitals were linearly independent. This means if we diagonalize the above Hamiltonian operator (12) then the eigenstates will be obtained by unitary transformations within the occupied and within the unoccupied EXX orbitals, respectively, and the Slater determinant formed by those eigenstates resulting from the unitary transformation of occupied EXX orbitals is the same as the one resulting from the occupied EXX orbitals itself. The Hamiltonian operator obtained by adding \( \Delta_x \) to the exchange-only KS Hamiltonian operator has the form of the Fock operator, however, is constructed from EXX orbitals. Because all terms in this Hamiltonian operator are either independent of the orbitals, \( \hat{T} \) and \( \hat{v}_{\text{ext}} \), or invariant with respect to unitary transformations of the occupied orbitals among themselves, \( \hat{v}_H \), and \( \hat{v}_x^{-\text{NL}} \), the Hamiltonian operator remains unchanged if we replace the EXX orbitals by those orbitals that diagonalize the Hamiltonian operator (12). This means we have obtained orbitals that are eigenstates of a Hamiltonian operator of the form of the Fock operator and this Fock operator can be constructed from the orbitals. In other words, the orbitals are HF orbitals and the Hamiltonian operator (12) is the Fock operator represented in the basis of the EXX orbitals.

The products of occupied times unoccupied EXX orbitals and generally of KS orbitals are linearly dependent and therefore Eq. (8) does not hold true ex-
Table 1. Deviation from unity of the overlap between the HF determinant and the EXX and PBEx (Perdew, Burke, Ernzerhof exchange density functional) determinants in units of $10^{-3}$. The uncontracted triple zeta basis sets from Ref. [54] were used.

<table>
<thead>
<tr>
<th>System</th>
<th>EXX</th>
<th>PBEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.01</td>
<td>1.94</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.12</td>
<td>2.72</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.20</td>
<td>2.51</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.36</td>
<td>1.83</td>
</tr>
<tr>
<td>CO</td>
<td>0.45</td>
<td>4.11</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.69</td>
<td>3.19</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.69</td>
<td>4.73</td>
</tr>
</tbody>
</table>

Exactly and the EXX and HF determinants are different. However, in practice the differences are very small. In Table 1 the deviation from unity of the overlap of EXX and HF determinants is displayed for a number of molecules. The finding that the differences between the EXX and HF determinants are small does not mean that the canonical EXX and HF orbitals and their eigenvalues are almost identical. Even if the EXX and the HF determinant were exactly identical the EXX and HF orbitals and their eigenvalues could strongly differ from each other. In fact, the spectra of the unoccupied EXX and HF orbitals are completely different. The former is physically meaningful whereas the latter has little physical meaning. Indeed there are usually only very few if any bound unoccupied HF orbitals. On the other hand, the similarity of EXX and HF determinants means that neglecting their differences is a good approximation. This approximation leads to the localized Hartree-Fock approximation [37] for the KS exchange potential which proved to be quite accurate and which can alternatively be derived via a common energy denominator approximation [62].

2.2 Numerical stability of basis set OEP methods, Gaussian basis set

OEP methods for molecules [47–50,54–56,60,82] and solids [44–46] usually employ two basis sets, the orbital basis set to represent the KS orbitals and an auxiliary basis set to represent the KS exchange potential, the KS response functions, and the right hand side of the OEP equation (1). The latter then turns into a matrix equation [47,48] which is readily solved. However, methods that straightforwardly solve the OEP equation in this way and are based on Gaussian basis sets, in contrast to methods based on plane waves, turn out to be numerically instable [47,49–53]. The resulting xc potentials may exhibit unphysical features and oscillations [51–54]. The main source of the numerical problems is that the basic theorem of DFT, the Hohenberg-Kohn theorem, does not hold for finite orbital basis sets [52,53]. This can easily be seen: If the orbital basis set is localised in a certain region of space, usually the region around the molecule, then we can add an auxiliary function to the effective KS potential which is
localized elsewhere without changing the electron density because the auxiliary function added to the effective KS potential will not overlap with the orbital basis set and therefore not couple to the latter. Even if the auxiliary basis set is localized in the same region of space as the orbital basis set it may happen that certain linear combinations of auxiliary basis functions couple either too weakly or not at all to the orbital basis set. As a result the KS response matrix will have eigenvalues with an erroneously small magnitude. Ultimately this means that for a given auxiliary basis set the orbital basis set has to be chosen large enough such that the KS response matrix corresponding to the auxiliary basis set is converged with respect to the orbital basis set. If for a given orbital basis set the auxiliary basis set is enlarged this will inevitably lead to numerical instabilities [52–54].

One might think that the problem could be solved by a regularization of the response matrix through a singular value decomposition or, e.g., by a Tikhonov regularization [50,55]. This, however, does not solve the problem. If the KS response matrix contains corrupted matrix elements which are not converged with respect to the orbital basis set, then these matrix elements will also affect the regularization and the resulting regularized KS matrix. Another seemingly self-evident solution of the problem is to use products of occupied times unoccupied KS orbitals as auxiliary basis set to represent the KS exchange potential [59,60]. Because the KS response function is constructed from exactly these products one would think that the coupling between auxiliary basis set and response function is perfect and the KS response function is fully converged. However, this is not the case as shown in Ref. [52,53]. The problem is also not solved if the same basis set is used for the orbitals and for the exchange potential, the response function, and the right hand side of the OEP equation [45,46,52,54,88].

The strategy towards a numerically stable basis set OEP method is to choose an auxiliary basis set that is as small as possible but still sufficiently large to represent the exchange potential accurate enough. Then an orbital basis set has to be chosen large enough to obtain a converged response matrix. For periodic systems with plane wave orbital and auxiliary basis sets such a balancing of the basis sets is straightforward. The energy cutoff for the plane waves of the orbital basis set has to be larger by a certain factor (usually a factor of about 1.75) than the cutoff for the plane waves of the auxiliary basis set [45,46]. For Gaussian orbital basis sets such a balancing is not as simple. In Ref. [54,53] it was found that the EXX orbitals corresponding to the continuum part of the KS eigenvalue spectrum, i.e., KS orbitals with positive eigenvalues, give an important contribution to the KS response matrix. In order to represent this part of the KS spectrum it turned out [54,53] that the basis set needs flexibility within the regions close to the nucleus. This means standard Gaussian orbital basis sets have to be decontracted or augmented by tight basis functions, i.e., Gaussian functions with high exponents. At first it seems strange to represent KS orbitals in the continuum with Gaussian basis sets. Indeed due to their boundary conditions individual KS orbitals within the continuum, and in particular their asymptotic behavior, cannot
be represented by Gaussian basis functions. However, we only need to represent sums over KS orbitals in the continuum in the region where the occupied orbitals are localized, see Eqs. (3),(4) and (7). This is possible with suitable Gaussian basis sets, that is with Gaussian basis sets containing functions with high exponents [54].

Instead of Gaussian functions itself, electrostatic potentials of Gaussian functions turned out to be a suitable choice for the auxiliary basis functions [47,54]. This means the actual auxiliary basis functions $f_k(r)$ are given by

$$f_k(r) = \int dr' \frac{g_k(r')}{|r - r'|} \quad (15)$$

with $g_k(r')$ denoting a Gaussian basis function. The functions $f_k(r)$ are atom-centered like the functions $g_k(r)$ but unlike the latter have a long-range Coulombic tail. The exchange potential is then given by the linear combination

$$v_x(r) = \sum_k v_{x,k} f_k(r) = \sum_k v_{x,k} \int dr' \frac{g_k(r')}{|r - r'|} \quad (16)$$

with coefficients $v_{x,k}$. The above representation of the KS exchange potential can alternatively be interpreted as follows. We define an exchange charge density $\rho_x$ as a density whose electrostatic potential yields the KS exchange potential

$$v_x(r) = \int dr' \frac{\rho_x(r')}{|r - r'|} \quad (17)$$

and we then represent the exchange charge density $\rho_x$ by Gaussian basis functions $g_k(r)$

$$\rho_x(r) = \sum_k v_{x,k} g_k(r) \quad (18)$$

The exchange charge density $\rho_x$ is of interest in itself. We can similarly define a correlation charge density whose electrostatic potential yields the KS correlation potential. The sum of the electron density plus the exchange and correlation charge densities is an effective electron density that takes into account exchange and correlation effects, i.e., the many-body effects.

By calculating the exchange potential via the exchange charge density $\rho_x$ it is straightforward to enforce the correct asymptotic behavior of the KS exchange potential. The KS exchange potential has to approach $-1/r$ at large distances $r$ away from the molecule [70,71], except on nodal surfaces of the highest occupied molecular orbital [38,69]. The $(-1/r)$ asymptotic can easily be enforced via the condition [47,54]

$$\int dr \rho_x(r) = \int dr \sum_k v_{x,k} g_k(r) = -1 \quad (19)$$

Enforcement of a second condition,

$$\langle \phi_{\text{HOMO}}^{\text{EXX}} | v_x | \phi_{\text{HOMO}}^{\text{EXX}} \rangle = \langle \phi_{\text{HOMO}}^{\text{EXX}} | v_{\text{NL}} | \phi_{\text{HOMO}}^{\text{EXX}} \rangle \quad (20)$$

with $\phi_{\text{HOMO}}^{\text{EXX}}$ denoting the highest occupied molecular orbital leads to a further increase in the numerical stability [54].
In summary, the approach of Ref. [54] not only turned out to be numerically stable but also to be quite efficient (comparable to HF methods with the same orbital basis set) and easy to implement. Moreover it is a purely analytical approach, no integration grids are needed. As an example Figure 1 displays the KS exchange potential obtained with the OEP method of Ref. [54] for the pyridine molecule. For comparison also the localized Hartree-Fock exchange potential [37] is shown in Figure 1.

3. TDDFT and TDEXX methods

The calculation of excitation energies of molecules within TDDFT or more precisely with density-functional response methods in most cases is carried out on the basis of the eigenvalue equation [72–75]

$$\left[ \varepsilon^2 + 4 \varepsilon^{1/2} K(\omega) \varepsilon^{1/2} \right] z_n(\omega) = \omega^2_n z_n(\omega). \tag{21}$$

The dimension of Eq. (21) is given by the product of the number of occupied times the number of unoccupied KS orbitals. In Eq. (21) the eigenvalue $\omega^2_n$ equals the square of the excitation energy of the $n$-th excited state. The eigenvectors $z_n(\omega)$ determine the density-density (potential-density) response function and are commonly used to analyse excitations in terms of the involved occupied and unoccupied orbitals. The elements $K_{ia,jb}(\omega)$ of the matrix $K(\omega)$ are given by

$$K_{ia,jb}(\omega) = \int dr dr' \varphi_i(r) \varphi_a(r) f_{\text{xc}}(r, r', \omega) \varphi_j(r') \varphi_b(r'). \tag{22}$$
and the elements of the diagonal matrix $\varepsilon$ by $\varepsilon_{ia,jb} = \delta_{ia,jb} (\varepsilon_a - \varepsilon_i)$. The sum of the Coulomb kernel $1/|\mathbf{r} - \mathbf{r}'|$ and the xc kernel $f_{xc}$, the frequency-dependent functional derivative of the KS xc potential with respect to the electron density, is denoted by $f_{uxc}$. In standard TDDFT methods the adiabatic approximation is made, i.e., the frequency-dependence of the xc kernel is neglected. The kernel then turns into the second derivative of the xc energy functional with respect to the electron density which can easily be evaluated for LDA or GGA functionals.

A crucial drawback of TDDFT methods within the adiabatic LDA or GGA approximation is that charge transfer (CT) excitations cannot be described correctly [10,11,13–15]. CT excitations are characterized in a one-electron picture by an excitation from an occupied orbital $\varphi_i$ localized in one region of space into an unoccupied orbital $\varphi_a$ localized in another region of space. If the overlap of the involved orbitals $\varphi_i$ and $\varphi_a$ approaches zero then, for a finite xc kernel, the matrix elements $K_{kl,jb}(\omega)$ with $kl = ia$ and/or $jb = ia$ equal zero. This leads to an eigenvector $z_n(\omega)$ that is a unit vector with the entry of 1 at the component $ia$ and an accompanying eigenfrequency $\omega$ equal to $\varepsilon_a - \varepsilon_i$. If the two involved orbitals are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) then the CT excitation energy should approach $I - A - 1/R$ for increasing distance $R$ of the fragments and for $I$ and $A$ denoting the ionization energy and the electron affinity, respectively. While the negative of the KS eigenvalue $\varepsilon_{HOMO}$ in the KS formalism equals the ionization energy the negative of the eigenvalue $\varepsilon_{LUMO}$ does not equal the electron affinity. For conventional LDA or GGA functionals even $-\varepsilon_{HOMO}$ is not a very good approximation for the ionization energy $I$. Moreover the $(-1/R)$ distance behavior is not found in conventional TDDFT methods.

In order to obtain CT excitation energies with density-functional response methods that differ from the HOMO-LUMO eigenvalue difference the xc kernel has to approach infinity in such a way that the vanishing overlap of HOMO and LUMO is compensated and the matrix elements of the xc kernel remain finite. One might assume that this generally requires frequency-dependent kernels. However, we could show [76] that in the special case of CT excitations in the system He H+ the qualitatively correct CT excitation energy is obtained without any frequency-dependent kernel. In fact in this simple two electron case the exact-exchange kernel equals half the Coulomb kernel and is frequency-independent. In the He H+ case the correct behavior of the CT energy with the distance $R$ is obtained via the distance behavior of the difference $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ of the involved orbital eigenvalues. This demonstrates that not only the xc kernel but also the eigenvalues may be of importance in order to correctly describe CT excitation energies.

For systems with more than two electrons the xc kernel plays a crucial role for describing CT excitations. A first step to go beyond conventional adiabatic LDA and GGA kernels in density-functional response methods is to use orbital-dependent xc kernels, in particular, the exact-exchange kernel $f_x(r,r',\omega)$, which is frequency-dependent. The exchange kernel obeys the equation [63–65]
In Eq. (23) \( h_x \) is an orbital-dependent function given in the Appendix, see also Refs. [63–65] and \( \chi_s \) now is the frequency-dependent KS response function. Eq. (23) is numerically even more demanding than the OEP equation (2) because it contains not only one but two inverse KS response functions. Moreover the involved KS response function is not the static one but the frequency-dependent one. Indeed even first attempts to employ the simpler adiabatic exact-exchange kernel in density-functional response methods suffered from numerical instabilities [66,67].

In order to avoid the occurrence of inverse KS response functions in density-functional response methods we reformulated the underlying basic equations [68]. The basic equation for the first order response \( \rho^{(1)}(r', \omega) \) of the electron density on a frequency-dependent external perturbation \( \nu^{(1)}(r', \omega) \) is [8]

\[
\int dr' \left[ \delta(r-r') - \int {dr''} {\chi_s(r, \omega)} f_{\text{ex}}(r', r'', \omega) \right] \rho^{(1)}(r', \omega) = \int dr' \chi_s(r, r', \omega) \nu^{(1)}(r', \omega) \tag{24}
\]

Eq. (24) can be derived [73] directly from the Runge-Gross theorem [78] without referring to the formally problematic [77] action formalism as in the original derivation. The response of the electron density in TDDFT can be expressed by

\[
\rho^{(1)}(r, \omega) = \int dr' \chi_s(r, r', \omega) \nu^{(1)}_s(r', \omega) \tag{25}
\]

with \( \nu^{(1)}_s \) denoting the linear response of the effective KS potential that corresponds according to the Runge-Gross theorem [78] to the perturbation \( \nu^{(1)} \). If we neglect the correlation contribution to \( f_{\text{ex}} \), separate the Coulomb and exchange contributions, and insert Eqs. (23) and (25) into the basic equation (24) we obtain [68]

\[
\int dr' \chi_s(r, r', \omega) = \int {dr''} {dr'''} {\chi_s(r, \omega)} f_{\text{ex}}(r'', r''', \omega) \chi_s(r'', r', \omega) \frac{\nu^{(1)}_s(r', \omega)}{|r''' - r''|} - h_x(r, \omega) \nu^{(1)}_s(r', \omega) = \int dr' \chi_s(r, r', \omega) \nu^{(1)}(r', \omega), \tag{26}
\]

Eq. (26) no longer contains the kernel \( f_s \) but the function \( h_x \), which is known [63–65], see Appendix, and in contrast to \( f_s \) can be evaluated without solving an integral equation, like Eq. (23), that contains inverse response functions. Eq. (26) is an equation for the response \( \nu^{(1)}_s \) of the effective KS potential instead of the electron density. On the basis of Eq. (26) a TDEXX approach, i.e., a density-functional response method employing the exact frequency-dependent exchange kernel could be implemented [68].

Within the TDEXX approach qualitatively correct CT excitation energies were obtained. In this way it was demonstrated that CT excitation energies can
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Fig. 2. He(1s) → Be(2px,y) charge-transfer excitation energies calculated using time-dependent Hartree-Fock (TDHF), time-dependent exact exchange (TDEXX), time-dependent DFT with Perdew-Burke-Ernzerhof xc potential and kernel [79] (PBE), and equation-of-motion coupled cluster singles and doubles (EOM-CCSD). Calculations were done using the aug-cc-pVQZ basis sets from Dunning et al. [80,81].

be treated within TDDFT and that ODFs are of interest in TDDFT. As an example Figure 2 displays the distance behaviour of the excitation energy for the CT transition characterized in a one-electron picture as excitation from the He(1s) to the Be(2px,y) orbital in the He Be dimer.

When reconsidering the basic equations of TDDFT and their derivation in order to develop a TDEXX approach we made the unexpected observation [75] that there exist simple valence-valence single-electron excitations in atoms or diatomics that principally cannot be treated in density-functional response methods because these excitations are not accompanied by a first order response of the electron density. For these excitations the usually employed equation (21) does not represent a proper density-functional response equation and yields as excitation energy a difference of KS eigenvalues [75].

4. Summary and outlook

With the development of a numerically stable and efficient Gaussian basis set OEP method [54] it is now possible to perform self-consistent KS calculations with orbital-dependent xc functionals for molecules. So far the exact treatment of exchange was implemented. For the future the development of correlation functionals that are well suited for a combination with an exact treatment of exchange is desirable. Present xc functionals benefit from an error cancellation between their exchange and correlation energy, which no longer is present if the
exchange energy is treated exactly. However, note that this error cancellation
does not occur between present exchange and correlation potentials, both of
which in almost all cases are short-range. The correct asymptotic behavior of the
effective KS potential is only obtained with an exchange-correlation potential
that exhibits the asymptotic behavior of the exact-exchange potential.

With the response equation for the effective KS potential (26) ODFs can also
be employed in TDDFT methods. The finding that with a TDEXX approach
charge-transfer excitation energies can be treated qualitatively correctly in con-
trast to conventional LDA or GGA TDDFT methods shows that ODFs are of
interest in TDDFT. The TDEXX method, in contrast to the TDHF method, is a
nonlinear method due to the frequency-dependence of the exact-exchange kernel.
In how far this leads to additional excitations beyond the number of occupied
times unoccupied KS orbitals, in particular whether this enables a description of
two-electron excitations, is an interesting question to be investigated in the fu-
ture. Moreover, also in the case of TDDFT the development of orbital-dependent
correlation kernels accompanying the exact-exchange kernel is desirable.

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Appendix

In this appendix, in contrast to the main text, we consider the somewhat more
general case that the molecular orbitals may be complex. The function $h_x(r, r', \omega)$
defining the exchange kernel of equation (23) can be decomposed into four terms
$h^p_x(r, r', \omega)$ with $p = 1, 2, 3, 4$:

$$h_x(r, r', \omega) = \sum_{p=1,4} h^p_x(r, r', \omega).$$

The four terms are given by:

$$h^1_x(r, r', \omega) = -2 \sum_{i \neq j} \sum_{ab} \left[ \frac{\varphi^*_i(r)\varphi_a(r)(a j i b)\varphi^*_b(r')\varphi_j(r')}{(\epsilon_i - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_b + \omega + i\eta)} \right],$$

$$h^2_x(r, r', \omega) = -2 \sum_{i \neq j} \sum_{ab} \left[ \frac{\varphi^*_i(r)\varphi_a(r)(a b j i)\varphi^*_j(r')\varphi_b(r)}{(\epsilon_i - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_b - \omega - i\eta)} \right],$$

$$h^3_x(r, r', \omega) = -2 \sum_{i \neq j} \sum_{ab} \left[ \frac{\varphi^*_i(r)\varphi_a(r)(b j i a)\varphi^*_j(r')\varphi_b(r)}{(\epsilon_i - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_b - \omega - i\eta)} \right],$$

$$h^4_x(r, r', \omega) = -2 \sum_{i \neq j} \sum_{ab} \left[ \frac{\varphi^*_i(r)\varphi_a(r)(i j b a)\varphi^*_b(r')\varphi_j(r)}{(\epsilon_i - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_b + \omega + i\eta)} \right].$$

11. Exact-exchange density functional theory
\begin{equation}
\hat{h}_x^3(r, r', \omega) = -2 \sum_{ij} \sum_a \left[ \frac{\varphi_i^*(\mathbf{r})\varphi_a(\mathbf{r})\langle j|\hat{\nu}_x^NL|l\rangle \varphi^*_a(\mathbf{r}')\varphi_j(\mathbf{r})}{(\epsilon_i - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_a + \omega + i\eta)} + \frac{\varphi^*_a(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_j(\mathbf{r}')\varphi_a(\mathbf{r})}{(\epsilon_i - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_a - \omega - i\eta)} + \frac{\varphi^*_a(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_j(\mathbf{r}')\varphi_b(\mathbf{r})}{(\epsilon_i - \epsilon_a + \omega + i\eta)(\epsilon_i - \epsilon_b + \omega + i\eta)} + \frac{\varphi^*_a(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_j(\mathbf{r}')\varphi_b(\mathbf{r})}{(\epsilon_i - \epsilon_a - \omega - i\eta)(\epsilon_i - \epsilon_b - \omega - i\eta)} \right] \tag{30}
\end{equation}

and

\begin{equation}
\hat{h}_x^4(r, r', \omega) = -2 \sum_{ij} \sum_a \left[ \frac{\varphi_j^*(\mathbf{r})\varphi_a(\mathbf{r})\langle a|\hat{\nu}_x^NL|l\rangle \varphi_i(\mathbf{r}')\varphi_j(\mathbf{r})}{(\epsilon_j - \epsilon_a + \omega + i\eta)(\epsilon_i - \epsilon_a)} + \frac{\varphi_j^*(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_a(\mathbf{r}')\varphi_j(\mathbf{r})}{(\epsilon_i - \epsilon_a)(\epsilon_j - \epsilon_a + \omega + i\eta)} + \frac{\varphi^*_a(\mathbf{r})\varphi_j(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_i(\mathbf{r}')\varphi_j(\mathbf{r})}{(\epsilon_i - \epsilon_a)(\epsilon_j - \epsilon_a - \omega - i\eta)} + \frac{\varphi^*_a(\mathbf{r})\varphi_j(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_j(\mathbf{r}')\varphi_a(\mathbf{r})}{(\epsilon_i - \epsilon_a)(\epsilon_j - \epsilon_a - \omega - i\eta)} + \frac{\varphi^*_a(\mathbf{r})\varphi_b(\mathbf{r})\langle a|\hat{\nu}_x^NL|l\rangle \varphi^*_j(\mathbf{r}')\varphi_a(\mathbf{r})}{(\epsilon_i - \epsilon_a + \omega + i\eta)(\epsilon_i - \epsilon_a)} + \frac{\varphi^*_a(\mathbf{r})\varphi_b(\mathbf{r})\langle a|\hat{\nu}_x^NL|l\rangle \varphi^*_j(\mathbf{r}')\varphi_a(\mathbf{r})}{(\epsilon_i - \epsilon_a + \omega + i\eta)(\epsilon_i - \epsilon_a)} + \frac{\varphi^*_b(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi_a(\mathbf{r}')\varphi_b(\mathbf{r})}{(\epsilon_i - \epsilon_b)(\epsilon_i - \epsilon_a + \omega + i\eta)} + \frac{\varphi^*_b(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi_a(\mathbf{r}')\varphi_b(\mathbf{r})}{(\epsilon_i - \epsilon_b)(\epsilon_i - \epsilon_a + \omega + i\eta)} + \frac{\varphi^*_b(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_i(\mathbf{r}')\varphi_b(\mathbf{r})}{(\epsilon_i - \epsilon_b - \omega - i\eta)(\epsilon_i - \epsilon_a)} + \frac{\varphi^*_b(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_i(\mathbf{r}')\varphi_b(\mathbf{r})}{(\epsilon_i - \epsilon_b - \omega - i\eta)(\epsilon_i - \epsilon_a)} + \frac{\varphi^*_b(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_i(\mathbf{r}')\varphi_a(\mathbf{r})}{(\epsilon_i - \epsilon_b - \omega - i\eta)(\epsilon_i - \epsilon_a)} + \frac{\varphi^*_b(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{\nu}_x^NL|l\rangle \varphi^*_i(\mathbf{r}')\varphi_a(\mathbf{r})}{(\epsilon_i - \epsilon_b - \omega - i\eta)(\epsilon_i - \epsilon_a)} \right] \tag{31}
\end{equation}

Matrix elements of the type \( \langle aj|bi \rangle \) are defined by

\begin{equation}
\langle aj|bi \rangle = \int d^3r \int d^3r' \varphi^*_a(\mathbf{r}) \varphi_j(\mathbf{r}') \varphi^*_b(\mathbf{r}) \varphi_i(\mathbf{r}') |r - r'|. \tag{32}
\end{equation}

References

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12. Time-dependent density functional theory

12.1. Static and Frequency-Dependent Dipole-Dipole Polarizabilities of All Closed-Shell Atoms up to Radium: A Four-Component Relativistic DFT Study

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- relativistic density functional theory
- asymptotic correction
- Coulomb attenuated functionals
1. Introduction

It is the cost/performance ratio that makes density functional theory (DFT) today’s most popular method in computational chemistry. Although a hierarchy of physical sophistication exists for the present day’s approximate functionals, this hierarchy does not guarantee convergence towards exact solutions, in contrast to wavefunction-based methods with a limit that is known (full configuration interaction) but for most practical purposes is out of reach. The performance of DFT has to be tested and any shortcomings addressed by identification of the missing physics.

Time-dependent DFT (TDDFT) enables the calculation of the modification of observables by external (periodical) time-dependent perturbations as well as the evaluation of electronic excitation energies via the poles of linear response functions, for instance the electric dipole–dipole polarizability (from now on, polarizability for short). This is the property of interest herein.

The efficient handling of electron correlation makes (TD)DFT all the more attractive for the treatment of systems containing heavy elements, where electron correlation is certainly no less important when compared to light atoms and where its accurate description becomes even more expensive, as a result of the large number of electrons and the typically large active spaces required in multiconfiguration approaches. For these systems, the quality of the calculation is not only limited by the treatment of electron correlation, but also relativistic effects become significant and have to be accounted for—ideally by using the four-component relativistic Hamiltonian, which is typically approximated by the Dirac–Coulomb (DC) Hamiltonian (Eq. (1)):
where the $4 \times 4$ identity matrices $1_{4\times4}$ emphasize the four-component structure of this operator. The operator provides spin-same, but not spin-other orbit interaction.

As the generic form of the DC Hamiltonian is independent of the model for the one- and two-electron interaction, DFT can (at least formally) be readily extended to the four-component relativistic framework. The source of electromagnetic fields in Maxwell’s equations is the four-current density $j^\mu = (\rho, j_x, j_y, j_z)$, which should be the basic variable for relativistic DFT. However, until relativistic density functionals depending on the four-current density become available, the common practice of relativistic quantum chemistry packages is to use nonrelativistic (NR) functionals that depend on the (number) density, and possibly its gradient, and kinetic energy density for the calculation of the exchange-correlation (XC) energy. For spectroscopic constants, electronic excitation energies, and polarizabilities, this is a good approximation since these properties probe only the valence region, where the effect of relativistic corrections to XC functionals is insignificant.

Implementations of (TD)DFT based on two- or four-component relativistic Hamiltonians using the noncollinear magnetization, in addition to the density in combination with NR functionals, have been reported by several groups.

In addition to the finite basis set problem (and possibly the treatment of relativativity), practical (TD)DFT imposes limitations owing to the use of approximate XC functionals, potentials, and kernels, since their exact forms are not known. A uniform quality is not provided for lowest, higher-lying, and especially electronic excitation energies associated with long-range charge transfer.

Approximate functionals are often used beyond their “trust region”. This is especially true for heavy elements, as the widely used G2 and G3 test sets consist of molecules with chlorine being the heaviest element. However, systematic TDDFT benchmark studies including heavy elements are scarce.

In the NR regime conventional functionals have known deficiencies within TDDFT (see refs. [14, 18, 21–30], and references therein). In their seminal paper, Perdew et al. extended DFT to noninteger particle numbers and demonstrated that the exact XC potentials differ by a system-dependent constant $\Delta_{\text{xc}}$ over all space, including the asymptotic region (contrary to what is stated in ref. [27]), at the electron-deficient and electron-abundant sides of integer electron number $N$. The extension also fixes the potential such that the exact XC potential of an $N$-electron system, taken as the electron-deficient limit, goes strictly to zero, that is [Eq. (4)]:

$$\lim_{\rho \to 0, \Delta \to -\infty} v_{\text{xc}}(N - \Delta) = 0; \quad \lim_{\rho \to 0, \Delta \to \infty} v_{\text{xc}}(N + \Delta) = \Delta_{\text{xc}}$$

(Note that the order of the limits is important for the electron-abundant side.) Continuum functionals such as LDA and GGA do not feature derivative discontinuities and their XC potentials therefore approximately average the exact XC potentials at the electron-deficient and electron-abundant sides of integer electron number in energetically important regions (bulk).

Hybrid functionals, with a fraction $\gamma$ of orbital exchange, only partially recover the derivative discontinuity. The long-range behavior of continuum and hybrid functionals is ideally represented by Equation (5):

$$\lim_{r \to \infty} v_{\text{xc}}(r) = \frac{1}{r} + v_{\text{xc}}(\infty).$$

in contrast to the $-1/r$ behavior of the exact XC potential.

The potential asymptote $v_{\text{xc}}(r)$ is the sum of the ionization potential (IP) and the HOMO orbital energy $\varepsilon_{\text{HOMO}}$, that is, $\varepsilon_{\text{HOMO}} - v_{\text{xc}}(\infty) = \mu = -\text{IP}$, where the latter equality follows from the use of the electron-deficient limit of the chemical potential $\mu$. The XC potential of most continuum functionals goes asymptotically to zero and falls off faster than the Coulombic decay indicated above. Their HOMO orbital energy $\varepsilon_{\text{HOMO}}$ is generally found to be higher than $-\text{IP}$, in contrast to exact Kohn–Sham values, which reflects the averaging behavior in the bulk region discussed above. There is indeed numerical evidence that GGA functionals can at best display the average behavior over electron-deficient and electron-abundant sides, and should therefore be constructed to go asymptotically to a nonzero positive constant approximating half the derivative discontinuity. These features of approximate functionals lead to errors in, for instance, polarizabilities, hyperpolarizabilities, and Rydberg excitation energies. Various asymptotic corrections to standard XC potentials have therefore been proposed in the literature. In this work, we tested the performance of two interpolation schemes for asymptotic corrections: the gradient-regulated asymptotic connection (GRAC) procedure and the statistical averaging of (model) orbital potentials (SAOP). Note, however, that accurate Rydberg excitation energies can alternatively be obtained by extracting the quantum defect from orbitals at intermediate distances, or by using explicitly orbital-dependent XC functionals that treat exchange interactions exactly.

The correct long-range behavior can also be introduced by a partitioning of the two-electron operator, which introduces 100% exchange and thus correct behavior at long range. The CAMB3LYP functional uses a more general partitioning [Eq. (6)]:

$$\frac{1}{r_{12}} = \frac{[\alpha + \beta \varepsilon(\mu_{12})]}{r_{12}} + \frac{1 - [\alpha + \beta \varepsilon(\mu_{12})]}{r_{12}}$$

than the original proposal by Hirao and coworkers, the latter corresponding to $\alpha = 0.0$, $\beta = 1.0$, and $\mu = 0.33$. The $\alpha$ and $\beta$ parameters of CAMB3LYP were fitted to atomization energies, giving $\alpha = 0.19$ and $\beta = 0.46$. Although a nonzero $\alpha$ is crucial for improved atomization energies, the condition $\alpha + \beta = 1$ must be satisfied for correct asymptotics.

Herein, we tested the performance of 12 XC functionals, including GRAC, SAOP, and CAMB3LYP, within the four-component relativistic Kohn–Sham framework by calculating static and frequency-dependent polarizabilities of all (ground-state) closed-shell atoms up to Ra. The results are compared to experimental data or to accurate ab initio results. The reference static electric dipole polarizability of Pd was obtained by finite-
field calculations using the coupled-cluster singles, doubles, and perturbative triples method [CCSD(T)].

2. Calculation of Frequency-Dependent Polarizabilities

The applied formalism of closed-shell linear response at the four-component relativistic density functional level is outlined in ref. [50]. Here, we recapitulate only the expressions important for later discussion of our results. The implicit summation of repeated indices is employed. In the following we use indices $i, j, \ldots$ for occupied orbitals, indices $a, b, \ldots$ for virtual orbitals, and indices $p, q, \ldots$ for general orbitals.

The linear response of the electric dipole operator to a periodic external electric field at frequency $\omega$ is formally given by [Eq. (7)]:

$$
\langle \langle A, \beta \rangle \rangle_\omega = -E_0^{-1} \left( E_0 - \omega S^2 \right) E_0^{-1}
$$

(7)

where $E_0[\tau]$ is the property gradient of the operator $A$, $E_0[\tau]$ the electronic Hessian, and $S[\tau]$ the so-called generalized metric (see ref. [50] and references therein for details). Here, $A = B$ is the electric dipole operator. For closed-shell atoms it is sufficient to consider only one component. Instead of calculating the electronic Hessian $E_0[\tau]$ explicitly, the linear response equations are solved iteratively, where the key step is the contrac-
tion $\sigma = E_0[\tau] \cdot b$ of $E_0[\tau]$ with a trial vector $b$ to form the so-called $\sigma$ vector.

The elements of the XC contribution to the $\sigma$ vector can be expressed by Equation (8):

$$
\sigma_{\sigma, \omega} = -\left( F_{\sigma, \sigma}^{(1)} + G_{\omega, \sigma} \right)
$$

(8)

Here, $F_{\sigma, \sigma}^{(1)}$ are the elements of the one-index transformed XC part of the Kohn–Sham matrix with [Eq. (9)]:

$$
F_{\sigma, \sigma}^{(1)} = B_{\sigma} F_{\sigma, \sigma}^{\text{shift}} - B_{\sigma} F_{\sigma, \sigma}^{\text{pert}} - B_{\sigma} = 0; \quad B_{\sigma} = -b_{\sigma}
$$

(9)

where $F_{\sigma, \sigma}^{\text{shift}}$ denotes a matrix element of the XC potential in the MO basis.

The second term on the right-hand side of Equation (8) can be written as [Eq. (10)]:

$$
G_{\omega, \sigma} = W_{\sigma, \omega} \cdot b_{\omega}
$$

(10)

and contains the matrix elements $W_{\sigma, \omega}$ of the XC kernel. In addition, hybrid functionals contribute with minus the exchange term $\gamma^{\text{shift}} \cdot b_{\omega}$ to $G_{\omega, \sigma}$, where $\gamma$ represents the weight of Hartree–Fock (HF) exchange. A particularity of the present implementation is a quaternion symmetry scheme that automatically provides maximum point-group and time-reversal symmetry reduction of the computational effort.[31] As discussed in refs. [50] and [52], trial vectors are classified according to time-reversal symmetry and hermiticity. To accommodate time-antisymmetric operators in the quaternion symmetry scheme, a purely imaginary phase is extracted such that the operator becomes time symmetric and antihermitian. In contrast to the calculations published in ref. [50], the contribution of time-reversal symmetric antihermitian trial vectors as a result of HF exchange is now included within the calculations of frequency-dependent polarizabilities. On the other hand, spin polarization owing to the antihermitian part of trial vectors $b$ is currently neglected in the calculation of frequency-dependent polarizabilities.

3. Connecting Potentials: Gradient Regulation versus Orbital Density Control

Baerends and co-workers have introduced two smooth interpolation schemes to correct the asymptotic part of the XC potential: the GRAC procedure[29] and SAOP.[28] They connect a bulk XC potential $\nu^{\text{bulk}}$, with an asymptotically correctly behaving outer potential $\nu^{\text{outer}}$ according to the interpolation formula [Eq. (11)]:

$$
\nu_\omega(r) = (1 - f(r)) [\nu^{\text{bulk}}(r) - \nu^{\text{outer}}] + f(r) [\nu^{\text{outer}}(r) (1 - \gamma^{\text{bulk})}]
$$

(11)

where a suitably chosen interpolation factor $f(r)$ ($0 \leq f(r) \leq 1$) switches between these two potentials. The HF exchange operator naturally corrects the unphysical coulombic self-interaction for the occupied states, and so the weight of HF exchange $\gamma^{\text{bulk}}$ has to be subtracted from the outer potential in the case where the bulk functional is of the hybrid type.[30] The error of subtracting an exchange factor from an exchange plus correlation (XC) potential is small, since the correlation contribution is generally much smaller than exchange and furthermore falls off rapidly in the (corrected) outer part of the potential.

Both schemes employ a zero-potential asymptote $\nu_\omega(\infty) = 0$. This corresponds to the electron-deficient limit of the exact functional rather than the averaging potential discussed in Section 1. For response, both approaches are completely equivalent since only orbitals and orbital energy differences are used. The choice of asymptote leads in the GRAC scheme to the introduction of a downward shift $\nu^{\text{shift}} = \text{IP} + \zeta^{\text{IP/GRAC}}$ of the bulk potential, which corresponds roughly to half the derivative discontinuity. The IPs may either be obtained from experimental data or additional quantum chemical calculations (e.g. ASCF). No bulk shift is introduced in the SAOP scheme ($\nu^{\text{bulk}} = 0$), since the GLBB bulk potential[30] is deeper than conventional XC potentials. This makes the SAOP approach more attractive, especially for molecular calculations, as it does not require the input of the IP.

The GRAC interpolation factor $f^{\text{GRAC}}(r)$ is determined by the dimensionless reduced density gradient $x(r)$ and two suitably chosen parameters $\alpha$ and $\beta$, not to be confused with the parameters of the CAMB3LYP potential [Eq. (12)]:

$$
f^{\text{GRAC}}(r) = \frac{1}{1 + \exp[-\alpha(x(r) - \beta)]}; \quad x(r) = \frac{|\nabla \rho(r)|}{\rho(r)^{3/4}}
$$

(12)
The parameters $a$ and $b$ determine the slope and location of the point of inflection of $f_{\text{GRAC}}(r)$, respectively, and have been chosen from atomic calculations. As in the original paper, we used the values $a = 0.5$ and $b = 40$ bearing in mind that they have been fitted to light-atom data. In the course of the reported work we found that the use of effective core potentials (ECPs) combined with the GRAC interpolation is problematic, because the outer potential may already be switched on in the bulk region, as is discussed further later. This problem does not arise in the all-electron calculations presented herein.

The SAOP interpolation factor [Eq. (13)]:

$$f_{\text{SAOP}}(r) = \frac{\tilde{\rho}(r)}{\rho(r)}$$

(13)

can be expressed in a compact way using the auxiliary density [Eq. (14)]:

$$\tilde{\rho}(r) = \sum_{\lambda \delta} \sum_{pq} c_{\lambda \delta pq} \phi_{\lambda \delta} \phi_{pq}(r) = \sum_{\lambda \delta} \sum_{pq} c_{\lambda \delta pq} \phi_{\lambda \delta} \phi_{pq}(r)$$

(14)

where $\phi_{\lambda \delta}(r)$ is the orbital overlap distribution of $\phi_{\lambda}(r) \phi_{\delta}(r)$ and where $\lambda \delta$ and $pq$ are indices over atomic and molecular orbitals (AO and MO), respectively. This requires the calculation and storage of only one additional auxiliary density matrix. The elements of the auxiliary density matrix in its MO representation are [Eq. (15)]:

$$\tilde{D}_{\lambda \delta} = \delta_{pq} n_p \exp \left[-2(r_{\text{HOMO}} - \varepsilon_p)\right]$$

(15)

where $n_p$ is the occupation number and $\varepsilon_p$ the energy of orbital $p$. This ensures occupation $n_p$ of the HOMO orbital (which may be degenerate) and a switch function $f_{\text{SAOP}}(r)$ close to one in the regions where the HOMO density is close to the total density.

While the connection procedures GRAC and SAOP can, in principle, be applied to the connection of any bulk potential with any asymptotically correct outer potential, we chose the combinations PBE0gracLB94 (PBE0[64] as bulk GRAC-connected to LB94[65] and GLLBsaopB3LYP as used in the original SAOP publication[28]. The former functional, also known as PBE0AC, was chosen because it has successfully been applied to the calculation of intermolecular interaction energies[52] as well as first- and second-order electric molecular properties of small molecules[50]. In addition, we combined B3LYP[37, 58] with LB94 (B3LYPgracLB94).

For the calculation of the XC contribution to the energy gradient using GGA functionals, the XC potential is not calculated explicitly as this may require the calculation of the Laplacian or the full Hessian of the density at each integration point [Eq. (16)]:

$$\int \, d\mathbf{r} \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \nabla \Omega_{\rho \rho} = \int \, d\mathbf{r} \left[ \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} - \nabla \cdot \frac{\partial \varepsilon_{xc}(\rho)}{\partial \nabla \rho} \right] \Omega_{\rho \rho}$$

(16)

where $\varepsilon_{xc}$ is the XC energy density. In practice the derivation is rather moved to the basis functions using integration by parts and giving [Eq. (17)]:

$$\int \, d\mathbf{r} \left[ \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} - \nabla \cdot \frac{\partial \varepsilon_{xc}(\rho)}{\partial \nabla \rho} \right] \Omega_{\rho \rho} = \int \, d\mathbf{r} \left[ \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \frac{\partial \Omega_{\rho \rho}}{\partial \rho} + \frac{\partial \varepsilon_{xc}(\rho)}{\partial \nabla \rho} \nabla \Omega_{\rho \rho} \right]$$

(17)

The computationally useful form is automatically obtained with the second-quantization formalism used in refs. [50], [59], and [60].

The GRAC scheme employed in our work connects GGA bulk potentials PBE0 and B3LYP to the LB94 functional. For this we re-express the explicitly scaled GGA bulk functional $\nu_{\text{bulk}}$ as [Eq. (18)]:

$$\int \, d\mathbf{r} \left[ 1 - f_{\text{GRAC}} \right] \nu_{\text{bulk}} \Omega_{\rho \rho} \approx$$

$$\int \, d\mathbf{r} \left[ 1 - f_{\text{GRAC}} \right] \frac{\partial \nu_{\text{bulk}}}{\partial \rho} \Omega_{\rho \rho} + \left[ 1 - f_{\text{GRAC}} \right] \frac{\partial \nu_{\text{bulk}}}{\partial \nabla \rho} \nabla \Omega_{\rho \rho}$$

(18)

This means that we neglect the additional integrand [Eq. (19)]:

$$\Omega_{\rho \rho} \frac{\partial \nu_{\text{bulk}}}{\partial \nabla \rho} \nabla \left[ 1 - f_{\text{GRAC}} \right]$$

(19)

because the term $\nabla \left[ 1 - f_{\text{GRAC}} \right]$ again requires the Laplacian of the density. We tested this approximation for GRAC-corrected BLYP by comparing to an explicitly scaled $\nu_{\text{bulk}}$ and found no significant difference.

4. Basis Sets

The systematic study of polarizabilities of all closed-shell atoms up to Ra requires an appropriate choice of all-electron basis sets with reasonable and comparable quality. For the property under study, these basis sets have to exhibit enough flexibility, in particular in the outer valence region. After extensive preliminary studies we chose the triple-zeta basis sets d-aug-cc-pVTZ[62] for He, Ne, aug-cc-pVTZ[63] for Ar, aug-cc-pVTZ-DF[64] for Zn, Sadlej’s pVTZ[57] for Be, Mg, Ca, and the relativistic all-electron basis sets of Dyall[58] for Sr, Ba, Ra, Pd, Cd, Hg, Kr, Xe, Rn. All basis sets were used in the decontracted form, except the Pd basis for the finite-field CCSD(T) calculations. The basis sets for Be, Mg, and Ca were augmented by 1s1p1d exponents (using the outermost quotient of each angular momentum). The basis sets for Zn and Ar were further augmented by 2s2p2d2f exponents. This produces basis sets of doubly increased triple-zeta quality for all the studied atoms.

To obtain the reference static polarizability of Pd by finite-field CCSD(T) calculations, we used the Stuttgart/Dresden ECP-28-MWB[65] combined with Ahlrichs’ QZVPV valence set[66]. To this set 2s2p2d2f3g even-tempered exponents (using the outermost quotient of each angular momentum) were added as well as two optimized h exponents (16.0 and 8.0). This gave a final valence set of 11s10p9d6f5g2h (contracted to 9s7p6d6f5g2h).
5. Results and Discussion

All calculated static and frequency-dependent polarizabilities are presented in Table 1 together with experimental or ab initio reference values. We found it useful to present the results for different families of functionals and for different sets of atoms separately by means of a statistical analysis (discussed later) to illustrate their performance on the studied property.

5.1. Statistical Analysis

Following the practice in the systematic model investigations of Helgaker et al.,[29] we present our data by a statistical analysis based on relative errors [Eq. (20)]:

$$\Delta = \frac{C - R}{R}$$  \hspace{1cm} (20)

where C and R are the calculated and reference values, respectively, for a given combination of method and atom. From the relative errors we calculated, for each method and for different sets of atoms, the mean error $\Delta$ and the standard deviation $\Delta_{std}$ [Eq. (21)]:

$$\Delta = \frac{1}{n} \sum_{i=1}^{n} \Delta_i$$

$$\Delta_{std} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\Delta_i - \Delta)^2}$$  \hspace{1cm} (21)

For the visual presentation of the mean errors (indicating the accuracy) and the standard deviations (indicating the precision) of a model, we approximate the calculated distributions by normal distributions.

5.2. Accuracy and Precision of Reference Values

It is beyond the scope of this article to discuss experimental techniques in detail or to review all computational efforts in this field, and we refer to two very useful reviews[94, 95] and references therein. The experimental reference values for He,[80] Ne,[81] Ar,[82, 83] Kr,[82] Xe,[84] Zn,[91] Cd,[92] and Hg[93] have been determined by measurements of the refractive index or the dielectric constant in the gas phase. Only frequency-dependent polarizabilities are directly accessible by this technique. We only use the frequency-dependent polarizabilities and not the extrapolated static values, since errors may be introduced in the Cauchy moment fitting procedure to obtain the latter quantities.[94] For atoms, a precision of 0.05% may be reached.[96] The experimental polarizabilities for Ca,[88] Sr,[89] and Ba[89] have been obtained by atomic-beam experiments which have a considerably higher uncertainty (rarely smaller than 5%)[94] and are static values. For Ca, Sr, and Ba these values have an uncertainty of 8–10%. Given these large experimental uncertainties, we chose to rather compare our data for Ca, Sr, and Ba to ab initio results.[90] The recommended static polarizabilities in Table XIII of ref. [90] are 157.9, 199.0, and 273.5 a.u. for Ca, Sr, and Ba, respectively.

Table 1. Calculated static and frequency-dependent polarizabilities for HF and various density functionals (all values are in a.u.). B3LYPgrav is B3LYPgravLB94, PBEgrav is PBEgravLB94, and SAOP is GLLBsaopLBx. The reference values are experimental data. For atoms without an experimental polarizability the most accurate calculated value is given together with the method. The frequency $\omega = 0.072$ a.u. corresponds to the He–Ne laser line.

<table>
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<tr>
<th>$\omega$</th>
<th>HF</th>
<th>LDA</th>
<th>BLYP</th>
<th>B3LYP</th>
<th>B3LYPgrav</th>
<th>LB94</th>
<th>CAMB3LYP</th>
<th>mCAMB3LYP</th>
<th>PBE</th>
<th>PBE0</th>
<th>PBEgrav</th>
<th>SAOP</th>
<th>LBx</th>
<th>Ref. value</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>He</td>
<td>0.072</td>
<td>1.33</td>
<td>1.67</td>
<td>1.58</td>
<td>1.51</td>
<td>1.41</td>
<td>1.40</td>
<td>1.53</td>
<td>1.53</td>
<td>1.59</td>
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<td>1.42</td>
<td>1.44</td>
<td>1.44</td>
<td>1.380(2)</td>
</tr>
<tr>
<td>Ne</td>
<td>0.072</td>
<td>2.39</td>
<td>3.07</td>
<td>3.13</td>
<td>2.90</td>
<td>2.73</td>
<td>2.62</td>
<td>2.89</td>
<td>2.83</td>
<td>3.09</td>
<td>2.83</td>
<td>2.70</td>
<td>2.61</td>
<td>2.62</td>
<td>2.67(03)</td>
</tr>
<tr>
<td>Ar</td>
<td>0.072</td>
<td>10.85</td>
<td>12.16</td>
<td>12.29</td>
<td>11.79</td>
<td>11.38</td>
<td>11.56</td>
<td>11.63</td>
<td>11.33</td>
<td>12.07</td>
<td>11.51</td>
<td>11.28</td>
<td>11.72</td>
<td>11.32</td>
<td>11.07(07)</td>
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<tr>
<td>Kr</td>
<td>0.072</td>
<td>16.75</td>
<td>18.49</td>
<td>18.88</td>
<td>18.09</td>
<td>17.44</td>
<td>17.27</td>
<td>17.73</td>
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<td>18.55</td>
<td>17.67</td>
<td>17.30</td>
<td>17.77</td>
<td>17.21</td>
<td>17.07(13)</td>
</tr>
<tr>
<td>Xe</td>
<td>0.072</td>
<td>27.63</td>
<td>29.82</td>
<td>30.60</td>
<td>29.37</td>
<td>28.39</td>
<td>27.90</td>
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<td>30.06</td>
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<td>29.38</td>
<td>27.98</td>
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<tr>
<td>Rn</td>
<td>0.072</td>
<td>34.99</td>
<td>37.79</td>
<td>38.90</td>
<td>37.43</td>
<td>36.18</td>
<td>34.23</td>
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<td>35.97</td>
<td>36.79</td>
<td>34.77</td>
<td>33.18(0)</td>
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<tr>
<td>Be</td>
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<td>52.99</td>
<td>50.61</td>
<td>50.31</td>
<td>47.99</td>
<td>44.87</td>
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<tr>
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<td>81.22</td>
<td>70.89</td>
<td>71.35</td>
<td>67.97</td>
<td>68.57</td>
<td>60.32</td>
<td>71.46</td>
<td>71.55</td>
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<td>73.33</td>
<td>78.00</td>
<td>63.21</td>
<td>71.80(0)</td>
</tr>
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<td>0.000</td>
<td>182.45</td>
<td>145.91</td>
<td>148.56</td>
<td>151.61</td>
<td>144.70</td>
<td>121.34</td>
<td>152.97</td>
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<td>160.14</td>
<td>165.64</td>
<td>128.93</td>
<td>168.7(169)</td>
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<tr>
<td>Sr</td>
<td>0.000</td>
<td>322.54</td>
<td>181.40</td>
<td>182.99</td>
<td>187.55</td>
<td>179.69</td>
<td>142.39</td>
<td>189.92</td>
<td>195.65</td>
<td>195.63</td>
<td>202.71</td>
<td>199.00</td>
<td>190.00</td>
<td>184.3(148)</td>
<td>[89]</td>
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<tr>
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<td>0.000</td>
<td>323.80</td>
<td>238.92</td>
<td>246.34</td>
<td>253.71</td>
<td>243.60</td>
<td>189.34</td>
<td>259.50</td>
<td>270.42</td>
<td>265.68</td>
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<td>274.25</td>
<td>258.69</td>
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<td>Ra</td>
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<td>224.14</td>
<td>171.89</td>
<td>235.71</td>
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<td>252.23</td>
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<td>186.80</td>
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</tr>
<tr>
<td>Pd</td>
<td>0.000</td>
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<td>26.11</td>
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<td>26.612(0)</td>
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<tr>
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<td>0.072</td>
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<td>40.96</td>
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<td>33.80</td>
<td>33.10</td>
<td>42.03(32)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.072</td>
<td>75.29</td>
<td>50.10</td>
<td>52.09</td>
<td>53.20</td>
<td>50.36</td>
<td>37.05</td>
<td>52.78</td>
<td>54.02</td>
<td>53.93</td>
<td>55.93</td>
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<td>42.51</td>
<td>40.46</td>
<td>54.20(95)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.072</td>
<td>50.06</td>
<td>36.06</td>
<td>37.36</td>
<td>38.03</td>
<td>36.42</td>
<td>29.22</td>
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<td>31.75</td>
<td>30.92</td>
<td>35.746(310)</td>
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</tbody>
</table>

[a] Ref. value Ref. value

The reference values are experimental data. For atoms without an experimental polarizability the most accurate calculated value is given together with the method. The frequency $\omega = 0.072$ a.u. corresponds to the He–Ne laser line.
5.3. Conventional Functionals

Normal distributions for the conventional, that is, noninterpolating, density functionals and HF indicating the accuracy for the calculation of frequency-dependent polarizabilities of the Group 18 atoms (He–Rn) are plotted in Figure 1. The normal distributions for pure functionals are plotted above, and for hybrid functionals below the abscissa.

Figure 1. Group 18 atoms (He–Rn): Normal distributions indicating the accuracy and precision of HF and different functionals for the calculation of static and frequency-dependent polarizabilities. Relative error (in %) along abscissa. The normal distributions for pure functionals are plotted above, and for hybrid functionals below the abscissa.

The admixture of exact exchange moves the accuracy of hybrid functionals, plotted below the abscissa in Figure 1, towards the mean error of HF, close to the line indicating the ideal accuracy. Both PBE0 and CAMB3LYP with 25 and 65% (long-range) HF exchange, respectively, perform slightly better than B3LYP with 20% HF exchange. The mCAMB3LYP functional, with correct asymptotic as a result of $\alpha + \beta = 1$, is slightly more precise but less accurate than CAMB3LYP. Altogether we can state that for conventional (noninterpolating) functionals, the performance for the Group 18 atoms (He–Rn) is independent of a gradient correction and dictated by the amount of exact exchange admixture.

This picture changes somewhat when the results for all studied atoms are included (see Figure 2). HF globally overestimates polarizabilities ($\Delta = +0.12$) but shows a very broad distribution ($\Delta_\text{std} = 0.18$). The pure functionals LDA, BLYP, and PBE perform significantly better, especially the PBE functional. In contrast to the rare gases, the LDA functional tends to underestimate polarizabilities for the Group 2 and Group 12 atoms. In passing we note that uncoupled LDA calculations, that is, replacing the fully interacting response with the response of the noninteracting Kohn–Sham system, leads to a systematic and severe overestimation of polarizabilities ($\Delta = +0.67$, $\Delta_\text{std} = 0.20$). The effect of exact exchange admixture can be studied by comparing the plots below the abscissa in Figure 2: HF exchange does not alter the accuracy but improves their precision, in contrast to what is observed for the Group 18 atoms alone. PBE0 stands out as the most precise functional, but misses the mark slightly as a result of some apparent systematic error.

5.4. Interpolating Functionals

Normal distributions indicating the accuracy and precision of the asymptotically corrected functionals SAOP (GLLBsaopLB), PBE0gracLB94, and B3LYPgracLB94 for the calculation of frequency-dependent polarizabilities of the Group 18 atoms (He–Rn) are plotted in Figure 3. Here, the very good performance of the LB94 and LBa functionals is also shown for the rare-gas atoms, in line with previous results.[21]

The distributions further indicate that the GRAC correction does indeed further improve the already good performance of the hybrid functionals PBE0 and B3LYP. Both PBE0gracLB94 and B3LYPgracLB94 yield values that accurately reproduce the reference polarizabilities. For the GRAC scheme, both the asymptotic correction and the bulk shift $v_{\text{sh}}$ [see Equation (11)] are crucial for improving performance. If the bulk potential is
not shifted, as shown in Figure 3 ("no bulk shift"), it is too shallow relative to the chosen zero asymptote and the polarizabilities are overestimated. In contrast, the SAOP potential, which does not shift the bulk potential and therefore is used without the input of IP, performs very well. In fact SAOP yields the best performance among pure functionals for Group 18 atoms.

On analyzing the results for all studied atoms (see Figure 4), a similar picture can be observed. The positions of the distributions (accuracies) have the same ordering as for the Group 18 atoms. In this case, however, the distributions are generally broader, and we note in particular that the performance of the pure LB94 and LBx functionals is not very satisfying. In addition, the precision of PBE0 is significantly better than that of B3LYP. This also holds for the shape-corrected (GRAC) forms. The precision of SAOP degrades when taking the complete set of atoms into account. Again, GRAC and the shift of the bulk potential go in opposite directions.

To demonstrate the different approaches for the interpolation, we plotted the GRAC and SAOP switching functions $f$ [Eq. (11)] for Ne and Rn in Figure 5 and 6. They are plotted together with the normalized radial HOMO probability function. By construction SAOP activates the outer potential in regions where the total density is dominated by the HOMO density—this can be nicely seen for both examples. GRAC, on the other hand, activates the outer potential at much larger radii: 3 a.u. compared to about 0.5 a.u. for Ne and 6 a.u. compared to about 2 a.u. for Rn. This means that while the connection procedures GRAC and SAOP can in principle be applied to the connection of any bulk potential with any asymptotically correct outer potential, they have different physical motivations.
and one should not expect the same results from the two connection procedures.

5.5. GRAC and Effective Core Potentials

The asymptotic correction of the GRAC form should not be used in combination with ECPs. To make this point clear we plotted the GRAC switching function $f_{GRAC}(r)$ [Eq. (11)] for the (NR) BLYP density using the Stuttgart/Dresden RLC ECP\cite{97, 98} in Figure 7.

![Figure 7. GRAC switching function $f$ [Eq. (11)] for Mg and Rn using the Stuttgart/Dresden RLC ECP.](image)

The GRAC switching functions were plotted for only two elements, Mg and Rn, but the observation holds for all ECPs. One can see that $f_{GRAC}(r)$ is already close to 1 in the bulk region, then falls off at around 1 a.u. and increases again in the outer region, as expected and desired. This behavior simply occurs because the valence density (and therewith also the dimensionless gradient $x(r)$) vanishes also for $r \to 0$ [see Eq. (12)]. One remedy for the failure of GRAC in the ECP case would be to use the Handy–Tozer variant for the asymptotic correction,\cite{24} since it uses scaled Bragg radii to detect the bulk and the asymptotic regions.

6. Conclusions

We have presented four-component relativistic HF and DFT calculations of static and frequency-dependent electric dipole–dipole polarizabilities of all (ground-state) closed-shell atoms up to Ra. For this study 12 NR functionals, including three asymptotically shape-corrected functionals, were considered. The best overall performance was obtained by using hybrid functionals and their GRAC shape-corrected versions. The performance of SAOP was found to be among the best for nonhybrid functionals and their GRAC shape-corrected versions. The best overall performance was obtained by using hybrid functionals and their GRAC shape-corrected versions. The best overall performance was obtained by using hybrid functionals and their GRAC shape-corrected versions.

Owing to the vanishing valence density in the core region, we find that the rare gases are not a fully representative testing ground for the calibration of new functionals for the calculation of polarizabilities.

Computational Details

The static and frequency-dependent polarizabilities were calculated within a linear-response approach at the HF and DFT level using the functionals LDA (SVWN5),\cite{69, 70} BLYP,\cite{71, 72} B3LYP,\cite{57, 58} CAM-B3LYP,\cite{95} PBE,\cite{73} PBE0,\cite{74} PBE0gracLB94, and GLLBsaopLXn (SAOP),\cite{75} as well as B3LYPgracLB94. For PBE0gracLB94, the GRAC parameters $\alpha = 0.5$ and $\beta = 40$ were used as in ref. [29]. For LBx the parameters of ref. [28] were chosen. In addition to CAMB3LYP, we also investigated a modified CAMB3LYP functional, herein denoted mCAMB3LYP, with parameters $\alpha = 0.2$, $\beta = 0.8$, and $\mu = 0.4$, chosen such that $\alpha + \beta = 1$ and correct asymptotics are obtained. The necessary IPs were taken from ref. [74]. All HF and DFT calculations were carried out using a development version of the DIRAC code.\cite{76}

The two-electron Coulomb integrals (SS|SS), which involve only the small components, were eliminated in both the SCF and the linear response parts. Rotations between positive and negative energy solutions were suppressed within the linear response module. The small-component basis set for the four-component relativistic HF and DFT calculations was generated using unrestricted kinetic balance, with restricted kinetic balance imposed in the canonical orthonormalization step.\cite{77} A Gaussian charge distribution was chosen as the nuclear model using the recommended values of ref. [77], except for the NR CCSD(T) calculations on Pd.

The finite-field CCSD(T) calculations for Pd were performed using the MOLPRO code.\cite{78} All explicitly occupied orbitals (3p, 4s, 4p) were correlated in the CCSD(T) calculations. The CCSD(T) polarizabilities were obtained with the symmetric five-point formula, by employing a step value of 0.001 a.u. for the perturbing dipole fields.

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Keywords: ab initio calculations · closed-shell atoms · density functional calculations · polarizability · quantum chemistry

12.2. Qualitatively Correct Charge-Transfer Excitation Energies in HeH$^+$ by TDDFT Due to Exact Exchange
Kohn-Sham Eigenvalue Differences

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**Key words:**
- charge-transfer excitation
- exact exchange kernel
- two-electron system
- spatially separated systems
- derivative discontinuities
Qualitatively Correct Charge-Transfer Excitation Energies in HeH\(^+\) by Time-Dependent Density-Functional Theory Due to Exact Exchange Kohn–Sham Eigenvalue Differences

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Abstract: Time-dependent density-functional theory in the response regime is shown to yield qualitatively correct charge-transfer excitation energies in the system HeH\(^+\) if the exact Kohn–Sham exchange potential is employed to determine the Kohn–Sham orbitals and eigenvalues entering the time-dependent density-functional calculation. The employed exact-exchange kernel is frequency-independent and, like conventional kernels in the local density approximation or in generalized gradient approximations, does not contribute to the charge-transfer excitation energy. This shows that it can be that not the exchange-correlation kernel, as generally believed, but the exchange-correlation potential plays the crucial role in the description of charge-transfer excitations.

One of the presently most widely used approaches to calculate electronic excitation energies of molecules or clusters is time-dependent density-functional theory (TDDFT) in the response regime.\(^1\)–\(^8\) Besides excitation energies, oscillator strengths and thus UV/vis spectra are also accessible. Furthermore, circular dichroism spectra can be calculated.

While current density-functional response methods,\(^9\)–\(^17\) that is, methods based on TDDFT in the response regime, are often very successful, they also exhibit a number of serious shortcomings due to the necessary approximations in the required exchange-correlation functionals. Excitations into states with Rydberg character are poorly described.\(^18\) This problem can be solved by determining the Kohn–Sham (KS) orbitals and eigenvalues that enter a density-functional response calculation with asymptotically corrected exchange-correlation potentials\(^19\)–\(^26\) or more fundamentally\(^27\) with an exact-exchange (EXX) KS method,\(^28\)–\(^31\) that is, a KS method that employs the exact local KS exchange potential. For other failures of current density-functional response methods, no convincing, generally applicable remedies are available at present. Excitation energies of molecules with long conjugated systems of \(\pi\) electrons\(^32\)–\(^36\) are systematically underestimated, and the description of two-electron excitations is problematic.\(^37\)

The perhaps most important deficiency of density-functional response methods employing presently available approximations for the exchange-correlation functionals is their incapability to correctly describe charge-transfer (CT) excitations.\(^16\)\(^,\)\(^40\)–\(^44\) Excitations with significant CT can be underestimated by several electron volts, and the behavior of CT excitations between two separated units with the distance of the units is described qualitatively wrong. CT excitation energies between neutral fragments, in particular, excitations from the highest occupied molecular orbital (HOMO) of one fragment to the lowest unoccupied molecular orbital (LUMO) of the other, should approach \((I - A)/R\) with \(I\) denoting the ionization energy of the donor, \(A\) denoting the electron affinity of the acceptor, and \(R\) standing for the distance of the units. Present density-functional response methods do not yield this \(-1/R\) behavior. Instead, the CT excitation energies, at relatively small distances \(R\) approach a constant given by the difference between the KS eigenvalues of the LUMO of the acceptor and those of the HOMO of the donor. HOMO–LUMO CT excitations from a neutral to a cationic unit, on the other hand, approach

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(I - A) at small distances $R$, while current density-functional response methods exhibit an erroneous $1/R$ behavior. In the limit of an infinite distance $R$, the current density-functional response methods yield CT excitation energies that equal the eigenvalue difference between the LUMO and the HOMO. This eigenvalue difference, however, in general, does not equal the CT excitation energy given by $(I - A)$ in this limit. While the negative of the HOMO eigenvalue equals the ionization energy $I^{55,56}$ in the exact formalism and represents a well-defined approximation for $I$ in practice, the negative of the LUMO eigenvalue differs from the electron affinity $A$ by the derivative discontinuity of the exchange-correlation energy at integer electron numbers $^{57,58,59}$ and therefore cannot serve as an approximation for $A$.

The failure of current density-functional response methods to describe CT excitations usually is attributed to shortcomings in the employed approximations for the exchange-correlation kernel, the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density. In particular, the neglect of the frequency dependency of the kernel, the adiabatic approximation, is made responsible for the failure to describe CT excitations. Here, we show that in certain cases problems in describing CT excitations are caused by shortcomings of the approximations of the exchange-correlation potential, not the kernel.

For the simple test system HeH$^+$, $^{40,50}$ we here show that a density-functional response method that employs the EXX KS potential and kernel and neglects correlation yields a qualitative correct behavior with the HeH$^+$ distance $R$ for the energy of the CT excitation from the He 1s orbital to the H$^+$ 1s orbital. To our knowledge, this is the first time that a density-functional response method has correctly described the distance behavior of a CT excitation without the introduction of special correction terms to enforce the correct behavior. $^{41,51}$ Even more important is the finding that the EXX kernel employed in the density-functional response calculation turns out to be not responsible for the correct distance behavior of the CT excitation. Indeed, in the system HeH$^+$, the exchange kernel does not contribute at all to the excitation energy at large distances $R$. The CT excitation energy like in conventional TDDFT methods using functionals within the local density-approximation (LDA) or generalized gradient approximations (GGA) equals the difference between the KS eigenvalue of the LUMO of the acceptor, the H$^+$ 1s orbital, and the HOMO of the donor, the He 1s orbital. However, in contrast to LDA or GGA eigenvalue differences, the EXX eigenvalue difference does not exhibit an unphysical $1/R$ behavior but correctly approaches a constant already at small distances, $R$. This means that, for HeH$^+$, the adiabatic approximation or, generally, approximations to the exchange-correlation kernel, in contrast to what is generally believed, are not responsible for the failure of conventional TDDFT methods, that is, density-functional response methods employing the LDA or GGA, to describe CT excitations.

Most density-functional response methods for excitation energies are based on the nonlinear eigenvalue equation 

$$[\epsilon^2 - 4\epsilon^{1/2}\mathbf{K}(\omega)^{1/2}]\mathbf{z}(\omega) = \omega^2 \mathbf{z}(\omega)$$

introduced by Casida. $^{5,13,52}$ The dimension of eq 1 is given by the product of the number of occupied KS orbitals times the number of unoccupied KS orbitals. In eq 1, the eigenvalue $\omega^2$ equals the square of the excitation frequency or energy $\omega$. The eigenvector $\mathbf{z}(\omega)$ determines the transition density $\rho(\omega, \mathbf{r})$ of the excitation via

$$\rho(\omega, \mathbf{r}) = \sum_{i} \sum_{\text{occ. unocc.}} \mathbf{z}_{ia}(\omega) \left( \frac{1}{\omega} \right) \phi_i(\mathbf{r}) \phi_a(\mathbf{r})$$

in terms of products of occupied KS orbitals times unoccupied KS orbitals, $\phi_i$ and $\phi_a$, respectively, with $\epsilon_{ia} = \epsilon_{ia} - \epsilon_i$ denoting the difference of the corresponding KS eigenvalues $\epsilon_a$ and $\epsilon_i$. The elements $K_{ia,jb}(\omega)$ of the matrix $\mathbf{K}(\omega)$ are given by

$$K_{ia,jb}(\omega) = \int d\mathbf{r} d\mathbf{r}' \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{xc}}(\omega, \mathbf{r}, \mathbf{r}') \phi_j(\mathbf{r}') \phi_b(\mathbf{r}')$$

and the elements $\epsilon_{ia, jb}$ of the diagonal matrix $\epsilon$ are given by $\epsilon_{ia, jb} = \delta_{ia,jb}(\epsilon_a - \epsilon_i)$. The indices $ia$ and $jb$ are superindices labeling the products of occupied times unoccupied KS orbitals. The sum of the Coulomb kernel $1/|\mathbf{r} - \mathbf{r}'|$ and the exchange-correlation kernel is denoted by $f_{\text{xc}}$. In practice, almost always the frequency dependence of the matrix $\mathbf{K}$ is neglected. That is, the adiabatic approximation is made, and the nonlinear eigenvalue, eq 1, turns into a linear one.

We now consider an intermolecular CT excitation that can be described as an excitation from an occupied orbital, $\phi_i$, of one molecule into an unoccupied orbital, $\phi_a$, of another molecule. At large intermolecular distances $R$, the spatial overlap of the two orbitals vanishes, and the product $\phi_i \phi_a$ approaches zero everywhere. As a result, one row and one column of the matrix $\mathbf{K}$ approach zero, and one eigenvector of eq 1 is a unit vector with an entry of one at the position $ia$. The corresponding eigenvalue is given by $\epsilon_{ia}^2$. This means that the CT excitation energy obtained with a conventional density-functional response method equals the corresponding KS eigenvalue difference $\epsilon_a - \epsilon_i$. The only way to obtain a CT excitation energy that differs from the corresponding KS eigenvalue difference seems to be seen when the kernel $f_{\text{xc}}$ approaches infinity in such a way that the matrix elements $K_{ia,jb}(\omega)$, eq 3, containing the vanishing product $\phi_i \phi_a$ approach finite values. This represents a complicated demand on the kernel that is believed to be intimately related to the frequency dependence of the kernel. Adiabatic LDA or GGA kernels are finite and clearly cannot exhibit the required behavior. Therefore, all density-functional response methods employing LDA or GGA kernels yield CT excitation energies that equal the corresponding KS eigenvalue differences.

For the special case of a nonspin-polarized two-electron system, the exact local KS exchange potential is known. It equals simply the negative of half of the Coulomb potential. For a nonspin-polarized two-electron system, the exchange kernel is also known exactly. $^{54}$ It equals the negative of half of the Coulomb kernel; that is, it is given by $-I/(2(|\mathbf{r} - \mathbf{r}'|))$. Thus, in this special case, the exchange kernel is frequency-independent, does not approach infinity except at $\mathbf{r} = \mathbf{r}'$. 


and thus does lead to vanishing matrix elements $K_{ia,jb}(\omega)$ in eqs 1 and 3 for indices $ia$ or $jb$ referring to a CT excitation. Therefore, time-dependent exact-exchange (TDEXX) calculations have to yield CT excitation energies that equal the corresponding KS eigenvalue difference for nonspin-polarized two-electron systems.

For a nonspin-polarized two-electron system, it is straightforward to turn any Hartree–Fock (HF) and any time-dependent Hartree–Fock (TDHF) method into an EXX KS and a TDEXX density-functional response method, respectively. It is merely necessary to multiply the terms originating from exchange in the HF and TDHF method by zero, that is, to neglect them, and to multiply the terms originating from the Coulomb potential and Coulomb kernel by one-half. We carried out such a modification in the program package TURBOMOLE\(^5\)\(^6\)\(^7\) and then performed HF/TDHF, EXX/TDEXX, LDA/TDLDA (LDA and time-dependent LDA), and PBE/TDPBE (GGA and time-dependent GGA with the exchange-correlation potential and kernel attributable to Perdew, Burke, and Ernzerhof)\(^5\)\(^3\) calculations for HeH\(^+\) and the CT excitation from the He 1s orbital to the H 1s orbital.

Five different basis sets, the aug-cc-pVXZ basis sets of Dunning\(^5\)\(^6\)\(^5\)\(^7\) with $X = D, T, Q, 5, 6$, were employed in the calculations. In Figure 1, results for the aug-cc-pV6Z basis set are shown, which are fully converged with respect to the basis set size. The TDHF energy for the considered CT excitation differs strongly from the corresponding HF eigenvalue difference. As expected, the TDHF CT energy exhibits a qualitatively correct behavior with the HeH\(^+\) distance $R$. TDHF considers the response of the first-order density matrix not the response of the density, like TDDFT. A representation of the response of the first-order density matrix in terms of products $\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})'$ of occupied times unoccupied orbitals does not vanish in CT cases due to the occurrence of the two different variables, $\mathbf{r}$ and $\mathbf{r}'$, in the products. Therefore, TDHF describes charge-transfer excitations qualitatively correctly.

Figure 1 shows that the TDPBE as well as the TDEXX energies for the considered CT excitation equal the corresponding KS eigenvalue differences, as could be expected from the discussion above. However, while the TDPBE CT excitation energies exhibit a qualitatively wrong $1/R$ behavior with the HeH\(^+\) distance $R$, TDEXX CT excitation energies exhibit the qualitative correct behavior. Indeed, the TDEXX results are identical to the TDHF ones. LDA/TDLDA results, which are not displayed here, show the same behavior as the PBE and TDPBE results.

The differences between LDA and PBE eigenvalue differences, on the one hand, and the TDEXX eigenvalues, on the other, can be explained as follows. For a HeH\(^+\) distance $R$ that is large compared to the spatial extent of the 1s orbitals of He and H\(^+\), the effective KS potential around the He atom equals that of an isolated He atom plus the constant $-1/R$, the constant being the term originating to leading order in the HeH\(^+\) distance $R$ from the electrostatic potential of the H\(^+\), that is, of a proton. The He 1s orbital eigenvalue therefore, to leading order in $R$, equals the eigenvalue of the 1s orbital of an isolated He atom minus $1/R$. This holds true for the LDA and the PBE as well as the EXX eigenvalues of the He 1s orbital. The eigenvalue of the H\(^+\) 1s orbital in the LDA and the PBE cases, to leading order in $R$, equals that of an isolated proton, that is, that of atomic hydrogen, for large $R$ values. The reason is that the effective KS potential of He is short-range because the LDA and PBE exchange-correlation potentials erroneously are short-range and because the Hartree potential and the electrostatic potential of the He nucleus cancel each other asymptotically. This means that the eigenvalue of the H\(^+\) 1s orbital in the LDA and the PBE cases is constant for large distances $R$. The difference between the H\(^+\) 1s eigenvalue and the He 1s eigenvalue therefore exhibits the erroneous $1/R$ behavior for large distances $R$.

In the EXX case, the effective KS potential of He, on the other hand, is long-range and correctly approaches $-1/r$ for large distances $r$, from the He nucleus because the exact-exchange KS potential exhibits such a $-1/r$ behavior. As a result, the He atom contributes, to leading order in $R$, a constant $-1/R$ to the effective KS potential around the H\(^+\). Therefore, the H\(^+\) 1s eigenvalue like the He 1s eigenvalue equals the eigenvalue of an isolated H\(^+\) minus $1/R$. In the difference between the H\(^+\) 1s and the He 1s eigenvalue, the $1/R$ terms cancel, and the eigenvalue difference at large distances $R$ is constant, as it should be. The wrong behavior of the LDA and PBE eigenvalue difference thus has its origin in the qualitatively wrong asymptotic behavior of LDA and PBE exchange potentials that are caused by unphysical Coulomb self-interactions of each electron that are not canceled completely by the approximate LDA and PBE exchange functionals. The fact that the LDA and PBE exchange-correlation potential and not the kernel causes the qualitatively wrong CT excitation energies is confirmed by carrying out density-functional response calculations employing the LDA or GGA kernel but EXX orbitals and eigenvalues. Such calculations yield de facto identical results as the EXX/TDEXX calculations.
Of course, other GGA functionals than the PBE lead to the same qualitatively wrong results for the considered CT excitation in HeH+. Moreover, CT excitation energies from neutral to positively charged units in other systems than HeH+, including systems with more than two electrons, are also described in the same way wrongly with LDA and GGA functionals in density-functional response methods.

The simple two-electron example of HeH+ certainly is a special case. Not only are the exchange potential and kernel exactly known in terms of the electron density in this case, but, moreover, in this special case, the negative of the eigenvalue of the LUMO, the 1s orbital of H+, exactly equals the electron affinity for large He H+ distances. This is not the case in general, and therefore EXX eigenvalue differences in general are not sufficient to describe CT excitations qualitatively correctly. Nevertheless, this special case does point to a new aspect of the CT problem of TDDFT, namely, that the KS eigenvalue differences at least in special cases may be essential for the behavior of excitation energies with the distance R. Indeed, in the special case of HeH+, the KS eigenvalue differences exclusively determine this behavior, while the exchange-correlation kernel does not contribute to it at all. This means for the CT problem that not only the exchange-correlation kernel is of importance but also the exchange-correlation potential in the KS calculation determining the KS eigenvalues, and their differences may be crucial.

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References

(37) An approach to treat the special case of an admixture of a two-electron excitation into a one-electron excitation separated, that is, not strongly interacting, with other excitations was recently introduced and applied in refs 38 and 39.
Charge Transfer Excitation Energies in HeH$^+$


(49) In ref 50, the system HeH$^+$ was considered within time-dependent density-matrix-functional theory.

12. Time-dependent density functional theory


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12.3. Blindness of the exact density response function to certain types of electronic excitations: Implications for TDDFT
Blindness of the Exact Density Response Function to Certain Types of Electronic Excitations: Implications for Time-Dependent Density-Functional Theory

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Examples of electronic excitations are presented and discussed that do not contribute to the sum-over-state expression of the frequency-dependent density-density response function and thus do not lead to poles of the latter. As a consequence, these excitations principally cannot be described by time-dependent density-functional theory (TDDFT) response methods or any other method relying on the poles of the density-density response function. For these excitations, the DFT response approach commonly used in molecular physics or quantum chemistry is shown to not properly represent a DFT method and to yield differences of Kohn-Sham eigenvalues as excitation energies. The discussed examples are simple valence-valence excitations in the neon atom and the nitrogen molecule.

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Methods based on time-dependent density-functional theory (TDDFT) in the response regime are widely used in physics and quantum chemistry to calculate excitation energies and oscillator strengths of molecules, clusters, and solids [1–6]. Indeed, for the interpretation of ultraviolet or visible and of circular dichroism spectra of molecules and the investigation of photophysical properties in general, DFT response methods have developed into a standard approach. While present TDDFT methods are very successful in many cases, they are also known to suffer from a number of serious deficiencies, in particular, the problem of describing charge transfer excitations [7], the systematic underestimation of excitation energies of molecules with long conjugated systems of π-electrons [8], or problems in the description of two-electron excitations and of excitonic effects. However, these shortcomings can be attributed to the presently employed approximations for the exchange-correlation (XC) kernel, in particular, the adiabatic approximation that presently is made de facto always. It is generally believed that if the exact frequency-dependent XC kernel were available, then methods based on TDDFT in the linear response regime would yield all excitation energies of electronic systems, be it atoms, molecules, clusters, or solids. Here, we show that this is not the case by presenting examples of valence-valence excitations in simple systems, like the neon atom, Ne, and the nitrogen molecule, N₂, that principally cannot be treated by TDDFT response methods or by any other approach that determines excitation energies from the poles of the density-density response function. The reason is that these excitations surprisingly do not contribute at all to the exact density-response density response function. In these cases, the DFT response method introduced by Casida [9–11], which, at present, is the one almost exclusively adopted to calculate excitation energies within TDDFT, is shown to not properly represent a DFT response method. While the considered blindness of TDDFT does not affect simulations of optical spectra, because the problematic excitations do not carry any oscillator strength, it is of relevance in the calculation of dark states, i.e., the states where theory is most needed.

DFT response methods determine excitation energies from the positions of the poles of the frequency-dependent density-density (potential-density) response function \(X(\omega, \mathbf{r}, \mathbf{r}')\) [1–6]. The latter is given by the sum-over-state expression

\[
X(\omega, \mathbf{r}, \mathbf{r}') = \sum_n \left[ \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_n \rangle \langle \Psi_n | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{E_0 - E_n + \omega + i\eta} \right]
\]

(1)

In Eq. (1), \(\Psi_0\) and \(\Psi_n\) denote the electronic ground state and the excited electronic states, respectively, that is, the solutions of the corresponding electronic many-body Schrödinger equation. The accompanying energy eigenvalues are designated by \(E_0\) and \(E_n\). The operator \(\hat{\rho}(\mathbf{r}) = \sum_{\mathbf{r}'=1}^N \delta(\mathbf{r} - \mathbf{r}')\) with \(N\) being the number of electrons is the density operator, \(\omega\) denotes the frequency, and \(\eta\) is a convergence factor that shall approach zero. The residue of the poles of \(X\) are proportional to \(\langle [\Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_n] \rangle^2\). As long as the matrix element \(\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_n \rangle\) differs from zero at some value of \(\mathbf{r}\), a pole in the response function emerges and DFT response methods can determine the excitation even if it is, e.g., dipole forbidden. However, if the matrix element \(\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_n \rangle\) equaled zero for all values of \(\mathbf{r}\) for an excitation, then the term corresponding to the excited state \(\Psi_n\) would vanish in the sum-over-state expression (1) of the response function and DFT response methods could not determine this excitation. This would mean, on the one hand, that an excitation into the state \(\Psi_n\) is not possible by any perturbation given by a local multiplicative potential \(\nabla^2\Phi\) and, on the other hand, that the excitation would not give rise to a linear response of the electron density. The crucial question arising now is: do such excitations exist in practice? The answer is yes. Examples are the 2\(p\) → 3\(p\) excitation from the \(^1S\) ground state into the \(^1P\) excited state.
of Ne or the $\pi \to \pi^*$ excitation from the $\Sigma_g^+$ ground state
into the $\Sigma_u^-$ excited state of $N_2$. Both excitations are simple
single valence-valence excitations.

For $N_2$ the matrix element $\langle \Psi_0^{\Sigma_g^+} | \hat{p}(r) | \Psi_0^{\Sigma_u^-}(\pi \to \pi^*) \rangle$
between the ground state $\Psi_0^{\Sigma_g^+}$ and the $\pi \to \pi^*$ excited
state $\Psi_0^{\Sigma_u^-}(\pi \to \pi^*)$ is zero for all values of $r$ due to
symmetry. The combination of $\Psi_0^{\Sigma_g^+}$ and $\Psi_0^{\Sigma_u^-}(\pi
\to \pi^*)$ in the matrix element transforms according to the irreducible
representation $\Sigma_u^-$ of the point group $D_{oh}$ of $N_2$. Thus, the matrix element $\langle \Psi_0^{\Sigma_g^+} | \hat{p}^{\text{pert}}(\omega) | \Psi_0^{\Sigma_u^-}(\pi \to \pi^*) \rangle$
with the local multiplicative operator $\hat{p}^{\text{pert}}(\omega) = \int dr \hat{p}(r) \hat{p}(r)$
corresponding to a local perturbing potential can differ from zero only if the potential
$\hat{p}^{\text{pert}}(\omega, r)$ contains a contribution of a function of symmetry $\Sigma_u^-$. However, functions of a single variable $r$ of symmetry
$\Sigma_u^-$ cannot exist, because a function of $r$ can not be rotational symmetric
around the $z$ axis and, at the same time, be antisymmetric with respect to a mirror plane
containing the $z$ axis. Thus, the matrix element $\langle \Psi_0^{\Sigma_g^+} | \hat{p}^{\text{pert}}(\omega) | \Psi_0^{\Sigma_u^-}(\pi \to \pi^*) \rangle$
zero for any arbitrary function $\hat{p}^{\text{pert}}(\omega, r)$. This means the matrix element
$\langle \Psi_0^{\Sigma_g^+} | \hat{p}(r) | \Psi_0^{\Sigma_u^-}(\pi \to \pi^*) \rangle$ has to be zero for all values
of $r$ and therefore the excitation from the ground state $\Psi_0^{\Sigma_g^+}$
to the excited state $\Psi_0^{\Sigma_u^-}(\pi \to \pi^*)$ does not contribute to the density-density response function $X$ of Eq. (1)
and cannot be treated by DFT response methods.

In a similar way, the matrix element $\langle \Psi_0^{\Sigma_g^+} | \hat{p}(r) | \Psi_1^{\Sigma_u^-}(2p \to 3p) \rangle$
between the ground state $\Psi_0^{\Sigma_g^+}$ and the $2p \to 3p$ excited state $\Psi_1^{\Sigma_u^-}(2p \to 3p)$
of Ne is zero for all values of $r$ due to symmetry. Somewhat
uncommon, we have included in the symmetry labels $\Sigma_g$
and $P_g$ of the states $\Psi_0^{\Sigma_g}$ and $\Psi_1^{\Sigma_u^-}(2p \to 3p)$ besides the
angular momentum $S$ or $P$ also the parity of the states,
gerade in both cases. The combination of $\Psi_0^{\Sigma_g}$
and $\Psi_1^{\Sigma_u^-}(2p \to 3p)$ in the matrix element transforms according
to an angular momentum of $P$ character and is of
gerade parity. However, there exist no functions of a single
variable $r$ that exhibit $P_g$ symmetry.

We now discuss how DFT response methods behave for such excitations that are outside their range. For simplicity, we will concentrate on non-spin-polarized systems and we
will assume real-valued KS orbitals. For systems with a
closed shell ground state, like Ne or $N_2$, it is always
possible to choose real-valued orbitals. The basic equation
time-dependent, more precisely, frequency-dependent
DFT response methods is given by [1–6]

$$
\int dr \left[ \delta(r - r') - \int d\omega' X_s(\omega, r, r') f_{\text{occ}}(\omega, r, r') \right] \rho(\omega, r') = \int d\omega' X_s(\omega, r, r') \hat{p}^{\text{pert}}(\omega, r').
$$

In Eq. (2), $\rho$ is the response of the electron density, $f_{\text{occ}}$ is the
Coulomb and exchange correlation kernel, the
frequency-dependent functional derivative of the sum of
Coulomb and XC potential with respect to the electron
density, and $X_s$ is the Kohn-Sham response function

$$
X_s(\omega, r, r') = \sum_{\text{occ}} \sum_{\text{unocc}} \varphi_i(r) \varphi_a(r') \lambda_{ia}(\omega) \varphi_i(r) \varphi_a(r')
$$

(3)

with $\lambda_{ia}(\omega) = 4e_{ia}/(\omega^2 - e_{ia}^2)$, with $e_{ia} = e_a - e_i$, and
with $\varphi_i$ and $\varphi_a$ denoting occupied and unoccupied Kohn-Sham
orbitals with eigenvalues $e_i$ and $e_a$. The orbitals $\varphi_i$
and $\varphi_a$ are pure spatial orbitals, spin is taken into account
via appropriate prefactors.

At frequencies approaching a pole of the density-density response function (1), the response $\rho(\omega, r)$ becomes infinite
and, for any finite right-hand side of Eq. (2), $\rho(\omega, r)$
approaches an eigenfunction of the operator in the square
brackets on the left hand side of the Eq. (2) with eigenvalue
zero. Excitation energies therefore can be determined as the
frequencies for which the latter operator has eigenvalues
equal to zero. Indeed, from Eq. (2) follows that the
product of the inverse of the operator in the square brackets
on the left-hand side of the Eq. (2) with the Kohn-Sham
response function $X_s$ represents the density-density response function $X$ of Eq. (1). If, however, an excitation
does not contribute to $X$ and thus does not lead to a pole of
it, then the operator in the square brackets on the left-hand
side of Eq. (2) does not have an eigenvalue equal to zero at the
frequency corresponding to the excitation energy. Such
an excitation energy thus can not be determined via Eq. (2).

In practice, DFT response calculations are not carried
out using Eq. (2) but on the basis of a matrix equation of the
dimension of products of occupied times unoccupied orbitals
that was introduced by Casida in Ref. [9]. This equation
was originally derived within the quantum mechanical
action formalism, which, however, is known to be problematic
from a formal point of view [12]. We hence reconsider
an alternative derivation given in Ref. [10].

From Eq. (2) in rearranged form and definition (3) follows that the response of the electron density can be written as

$$
\rho(\omega, r) = \sum_{\text{occ}} \sum_{\text{a}} x_{ia}(\omega) \varphi_i(r) \varphi_a(r) = Y^T(\omega) x(\omega)
$$

(4)

with the elements $Y_{ia}(r)$ of the vector $Y$ given by products
of occupied times unoccupied KS orbitals $\varphi_i$ and $\varphi_a$, respectively, i.e., by

$$
Y_{ia}(r) = \varphi_i(r) \varphi_a(r).
$$

(5)

The vector $x(\omega)$ collects the expansion coefficients
$x_{ia}(\omega)$ occurring in Eq. (4). The index $ia$ running over
occupied times unoccupied orbitals is a superindex labeling the elements of the vectors $Y(r)$ and $x$. The basic equation (2) can be rewritten as

$$Y^T(r)[1 - \lambda(\omega)K(\omega)]x(\omega) = Y^T(r)\lambda(\omega)v^{\text{pert}}(\omega) \tag{6}$$

with the matrix elements $K_{ia,jb}(\omega)$ of the coupling matrix $K(\omega)$ given by $K_{ia,jb}(\omega) = \int dr dr' \varphi_i(r)\varphi_a(r') f_{ia,c}(r, r')\varphi_c(r)\varphi_b(r')$, the elements $\lambda_{ia,jb}(\omega)$ of the diagonal matrix $\lambda(\omega)$ given by $\lambda_{ia,jb}(\omega) = \delta_{ia,jb}\lambda_i(\omega)$, and the elements $v^{\text{pert}}_{ia}(\omega)$ of the vector $v^{\text{pert}}(\omega)$ given by $v^{\text{pert}}_{ia}(\omega) = \int dr \varphi_i(r)v^{\text{pert}}(\omega, r)\varphi_a(r)$.

If the products $\varphi_i$ and $\varphi_a$ were linearly independent, then Eq. (6) would directly imply the matrix equation

$$[1 - \lambda(\omega)K(\omega)]x(\omega) = \lambda(\omega)v^{\text{pert}}(\omega). \tag{7}$$

However, the products $\varphi_i$ and $\varphi_a$ are, in general, linearly dependent. Nevertheless, it can be shown [10] that the matrix equation (7) is equivalent to Eq. (6) and thus to the basic Eq. (2). To that end, we show that each solution of the matrix equation (7) uniquely determines a solution of Eq. (2) and vice versa. Let us first consider the case of frequencies for which the operator, respectively, the matrix in the square brackets on the left-hand sides of Eqs. (2) and (7) are nonsingular, i.e., have no eigenfunctions or eigenvectors with eigenvalue zero. Then, substitution of a solution $x(\omega)$ of the matrix equation (7) into Eq. (4) determines a solution $\rho$ of Eq. (2) because multiplication of the matrix equation (7) by the left from $Y^T(r)$ turns it into Eq. (2). On the other hand, a solution $\rho$ of Eq. (2) leads to a solution $x(\omega) = \lambda(\omega)v^{\text{pert}}(\omega) + \lambda(\omega)y(\omega)$ of Eq. (7) with the elements $y_{ia}(\omega)$ of the vector $y(\omega)$ given by $y_{ia}(\omega) = \int dr dr' \varphi_i(r)\varphi_a(r') f_{ia,c}(r, r')\rho(r, r' \omega)$. Because $y(\omega) = K(\omega)[\lambda(\omega)v^{\text{pert}}(\omega) + \lambda(\omega)y(\omega)]$ if $\rho$ solves Eq. (2), for the considered case that both Eq. (2) and the matrix equation (7) are nonsingular, the solutions of both equations are unique, and we have thus established a one-to-one mapping between them.

Next, we consider the case of a frequency $\omega$ for which Eq. (2) and the matrix equation (7) both are singular, i.e., the case that the operator, respectively, the matrix in the square brackets on the left-hand sides have eigenvectors with eigenvalues equal to zero. By the same arguments as above, we can show that each solution of one of the equations determines a solution of the other. In this case, however, each of the equations has more than one solution or none, depending on the right-hand side. We now show that two different solutions of the matrix equation (7) determine two different solutions of Eq. (2) or vice versa. The difference $x(\omega) = x'(\omega) - x''(\omega)$ of two solutions of the matrix equation (7) obeys the homogeneous equation

$$[1 - \lambda(\omega)K(\omega)]x(\omega) = 0. \tag{8}$$

If the corresponding solutions $\rho'(\omega) = Y^T(r)x'(\omega)$ and $\rho''(\omega) = Y^T(r)x''(\omega)$ of Eq. (2) were equal then for the difference $x(\omega) = x'(\omega) - x''(\omega)$, the equation $0 = Y^T(r)x(\omega)$ would hold. Because the products $\varphi_i\varphi_a$ are linearly dependent, it is, in principle, possible that $Y^T(r)x(\omega)$ equals zero for a nonzero vector $x(\omega)$. However, as a result the product, $K(\omega)x(\omega)$ would equal zero due to the definition of $K(\omega)$ and the homogeneous equation (8) would turn into $x(\omega) = 0$ which is a contradiction to the condition that the two solutions $x'(\omega)$ and $x''(\omega)$ are different. This argument also guarantees that a solution of the homogeneous equation (8) cannot lead to the trivial solution $\rho = 0$ of the homogeneous equation corresponding to Eq. (2). Similarly, the difference $\rho' = \rho''$ between two different solutions $\rho'$ and $\rho''$ of Eq. (2) obeys the homogeneous equation corresponding to Eq. (2). If the two solutions $x'(\omega) = \lambda(\omega)v^{\text{pert}}(\omega) + \lambda(\omega)y(\omega)$ and $x''(\omega) = \lambda(\omega)v^{\text{pert}}(\omega) + \lambda(\omega)y(\omega)$ of the matrix equation (7) that are determined by the solutions $\rho'$ and $\rho''$ were equal, then $\lambda(\omega)y'(\omega) - y''(\omega) = 0$ which would imply $Y^T(r)\lambda(\omega)[y'(\omega) - y''(\omega)] = \int dr dr' X_c(\omega, r, r') f_{ia,c}(r, r')\rho(\omega, r) = 0$. With the latter equation, the homogeneous equation corresponding to Eq. (2) would turn into $\rho = 0$, contradiction to the condition that $\rho'$ and $\rho''$ are different. The former argument also shows that a nontrivial solution $\rho$ of the homogeneous equation corresponding to Eq. (2) cannot lead to a trivial solution of the homogeneous equation (8) with $x(\omega) = 0$. Finally, we have to exclude the possibility that the matrix equation (7) is singular while Eq. (2) is not. If the matrix equation (7) is singular, then it has an eigenvector $x(\omega)$ with eigenvalue zero, i.e., a solution to the homogeneous equation (8). This solution $x(\omega)$, however, determines a solution $\rho(r) = Y^T(r)x(\omega)$ of the homogeneous equation corresponding to Eq. (2) which means that Eq. (2) also has to be singular. Analogously, one can show that a singular Eq. (2) implies a singular matrix equation (7).

Having shown that the matrix equation (7) is equivalent to the basic equation (2), the former can be used to actually calculate electronic excitation energies. This is done by finding the frequencies for which the homogeneous equation (8) has nontrivial solutions. In practice, Eq. (8) is multiplied by $\lambda(\omega)^{-1}e^{1/2}$ to yield the nonlinear eigenvalue equation

$$[\epsilon^2 + 4e^{1/2}K(\omega)e^{1/2}]z(\omega) = \omega^2z(\omega) \tag{9}$$

with $z(\omega) = e^{-1/2}x(\omega)$ and the diagonal matrix $\epsilon$ with elements $\epsilon_{ia,jb} = \delta_{ia,jb}(\epsilon_i - \epsilon_j)$. If the adiabatic approximation is employed for the XC kernel, then the matrix $\mathbf{K}$ becomes independent of $\omega$ and Eq. (9) turns into a standard eigenvalue problem.

The eigenvalue problem (9) first suggested by Casida [9] is the basis of de facto [13] all TDDFT methods to determine excitation energies of molecules or clusters. However, it is now only equivalent to the original DFT response equation (2) for those frequencies for which the latter is defined, that is for frequencies $\omega$ that do not correspond to a difference of eigenvalues, i.e., $\epsilon_i - \epsilon_j$. The critical point is now that the eigenvalue equation (9) per se is well.
defined for those frequencies. However, at those frequencies, it does not represent the basic DFT response equation (2), i.e., not a TDDFT equation. Therefore, if the eigenvalue problem (9) yields an eigenvalue $\omega^2$ that equals the square of an eigenvalue difference, then the corresponding excitation energy not necessarily is a proper TDDFT excitation energy but may be a spurious excitation. Indeed, we will show that the above discussed excitations that cannot be determined via DFT response methods lead to such spurious excitations.

In the case of $N_2$, the twofold degenerate $\pi$-orbitals $\pi(\theta, r) \cos(\phi)$ and $\pi(\theta, r) \sin(\phi)$ [equivalent to the complex-valued orbitals $\pi(\theta, r) \exp(i \phi)$ and $\pi(\theta, r) \exp(-i \phi)$] and the twofold degenerate $\pi^*$ orbitals $\pi^*(\theta, r) \cos(\phi)$ and $\pi^*(\theta, r) \sin(\phi)$ give rise to four products of occupied times unoccupied orbitals. By $r$, $\theta$, and $\phi$, spherical coordinates are denoted. The linear combination of products given by $\pi(\theta, r) \cos(\phi) \pi^*(\theta, r) \cos(\phi)$ and $\pi(\theta, r) \sin(\phi) \pi^*(\theta, r) \cos(\phi)$ equals zero. We now construct a vector $\mathbf{z}$ with values of $1/\sqrt{2}$ and $-1/\sqrt{2}$ at the positions of the products $\pi(\theta, r) \times \cos(\phi) \pi^*(\theta, r) \sin(\phi)$ and $\pi(\theta, r) \sin(\phi) \pi^*(\theta, r) \cos(\phi)$, respectively, and zero elsewhere. Because the eigenvalue difference corresponding to the two considered products of occupied times unoccupied states are equal and due to the definition of the matrix $\mathbf{K}$, the product $\mathbf{z}^\dagger \mathbf{K} \mathbf{z}$ equals zero and the vector $\mathbf{z}$ is an eigenvector of the eigenvalue equation (9) with an eigenvalue that equals the square of an eigenvalue difference, i.e., the eigenvalue difference between the $\pi$ and $\pi^*$ orbitals. As shown above, this eigenvalue difference corresponding to a pole of the density-density response function (1).

In a similar way, the nine products of real-valued $2p$ with $3p$ orbitals, $R_i(1/r)x_i$, $R_i(1/r)y_i$, $R_i(1/r)z_i$ with $i = 2p$, $3p$, in $Ne$ give rise to three linearly independent vectors $\mathbf{z}$ that correspond to a response of the density equal to zero and that are spurious eigenvectors of Eq. (9) not corresponding to a pole of the density-density response function (1).

With the program package TURBOMOLE [15], we calculated excitation energies and corresponding orbital eigenvalue differences for the $2p \rightarrow 3p$ excitations in $Ne$ and the $\pi \rightarrow \pi^*$ excitations in $N_2$ by Hartree-Fock and time-dependent Hartree-Fock (TDDHF) and by DFT and the TDDFT method based on Eq. (9) introduced by Casida [9]. The DFT calculations were carried out with LDA (local density approximation) and with PBE (Perdew, Burke, Ernzerhof) [16] XC potentials and kernels. For $N_2$, a bond distance of 1.0977 Å was used. The calculations for $N_2$ were carried out with the aug-cc-pVTZ basis set of Dunning [17] while for $Ne$ the aug-cc-pVTZ basis set was further augmented by 3 diffuse $s$ and $p$ functions. For $N_2$ and for $Ne$ in the LDA as well as in the PBE case, we calculated excitation energy exactly equals the corresponding orbital eigenvalue difference whereas the other excitation energies and all TDDHF excitation energies differ from the corresponding orbital eigenvalue differences, see Ref. [18]. Thus, as expected, excitations into the $Ne^1P(2p \rightarrow 3p)$ state and the $N_2 \sum_{\pi} (\pi \rightarrow \pi^*)$ state cannot be described by TDDFT are reflected by spurious eigenvalues of Eq. (9) that equal the corresponding orbital eigenvalue differences or more precisely the squares of the latter. TDDH, on the other hand, does not suffer from such problems because it is based on the response of the density matrix represented in products of occupied times unoccupied orbitals with different coordinates $r$ and $r'$. Similarly, also time-dependent current-density-functional theory would be able to treat the above discussed excitations because the latter contribute to the current-current response function. The results of this work therefore motivate the development of generally applicable time-dependent current-density-functional methods that so far are not available.

The authors gratefully acknowledge the funding of the German Research Council (DFG), through the Cluster of Excellence “Engineering of Advanced Materials” (www.eam.uni-erlangen.de).

[18] See EPAPS Document No. E-PRLTAO-103-018952 for a table containing the $2p \rightarrow 3p$ excitation energies in $Ne$ and the $\pi_\sigma \rightarrow \pi_\sigma^*$ excitation energies in $N_2$. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
Excitation energies for the transitions $2p \rightarrow 3p$ in the neon atom and $\pi_u \rightarrow \pi_g$ in the $N_2$ molecule calculated by time-dependent Hartree-Fock (TDHF) and by time-dependent density functional theory using exchange-correlation potentials and kernels according to the (adiabatic) local density approximation (LDA) and to Perdew, Burke and Ernzerhof (PBE) [1].

TABLE I. Singlet-singlet excitation energies and corresponding orbital eigenvalue differences $\Delta \varepsilon$ of Ne and $N_2$ calculated with HF/TDHF (column HF), LDA/time-dependent LDA (columns LDA), and of Ne and $N_2$ calculated with HF/TDHF (column HF), LDA/time-dependent LDA (columns LDA), and PBE/time-dependent PBE (column PBE). Those excitation energies that do not represent proper TDDFT excitation energies but correspond to spurious eigenvalues of Eq. (9) are equal to eigenvalue differences and are printed in bold. The calculations for $N_2$ were carried out with the standard aug-cc-pVTZ basis set [2] while for Ne the aug-cc-pVTZ basis has been further augmented by 3 diffuse s- and p-functions using the progression ratios of the respective last two s- and p-functions in the standard basis set. All values are in eV.

<table>
<thead>
<tr>
<th>Excitations</th>
<th>Ne $2p \rightarrow 3p$ excitations</th>
<th>$N_2 \pi_u \rightarrow \pi_g$ excitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \varepsilon$</td>
<td>HF 25.42</td>
<td>LDA 13.70</td>
</tr>
<tr>
<td>$^1D$</td>
<td>20.13</td>
<td>13.70</td>
</tr>
<tr>
<td>$^1P$</td>
<td>20.16</td>
<td>13.70</td>
</tr>
<tr>
<td>$^1S$</td>
<td>20.56</td>
<td>13.70</td>
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<tr>
<td>$\Delta \varepsilon$</td>
<td>19.92</td>
<td>9.69</td>
</tr>
<tr>
<td>$^1\Sigma_u^-$</td>
<td>7.94</td>
<td>9.69</td>
</tr>
<tr>
<td>$^1\Delta_u$</td>
<td>8.76</td>
<td>10.23</td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>14.03</td>
<td>13.63</td>
</tr>
</tbody>
</table>

$^a$ Ne: Reference [3], $N_2$: Reference [4]

12. Time-dependent density functional theory


12.4. Charge-transfer excitation energies with a TDDFT method suitable for orbital-dependent exchange-correlation kernels

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Charge-transfer excitation energies with a time-dependent density-functional method suitable for orbital-dependent exchange-correlation kernels

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A time-dependent density-functional (TDDFT) response equation for the effective Kohn-Sham potential instead of the electron densities is presented that enables the use of orbital-dependent exchange-correlation kernels. In combination with the frequency-dependent exact-exchange kernel the present approach describes long-range charge-transfer excitations qualitatively correct in contrast to standard TDDFT methods, as shown by formal analysis and applications to molecular systems. Even charge-transfer excitations obtained with the adiabatic frequency-independent exact-exchange kernel exhibit a long-range dependence with the distance of the charge transfer, which, however, is too weak by a factor of 2. This indicates that it is not the frequency dependence of the kernel alone that leads to a correct description of charge-transfer excitations.

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I. INTRODUCTION

Density-functional (DFT) response methods, i.e., methods based on time-dependent density-functional theory (TDDFT) in the response regime, are widely used to calculate excitation energies of molecules and generally of response properties of electronic systems [1–3]. Despite their great success, present DFT response methods suffer from a number of severe shortcomings, with the most important one being the incapability to treat excitations of charge-transfer (CT) character [4–8]. In recent years a number of correction schemes were developed in order to fix the latter problem and to obtain qualitatively correct CT excitations [4,9–16] employing, e.g., hybrid methods that adopt nonlocal exchange from the Hartree-Fock theory in the time-dependent formalism [4,10,17,18] or methods with approximate exchange-correlation (xc) kernels that contain terms designed to enforce a qualitatively correct behavior of long-range charge-transfer excitation energies [11–14].

It is an interesting question of how far a correct description of CT excitations requires frequency-dependent xc kernels. For certain two-electron systems, it has recently been shown [19] that qualitatively correct CT excitation energies are obtained without the necessity to use frequency-dependent xc kernels. In Refs. [12,13], on the other hand, it has been demonstrated that the frequency dependence of the exact xc kernel is crucial for the description of CT excitations between open-shell fragments of a supersystem, e.g., in a diatomic molecule that dissociates into its constituting atoms. In Ref. [20] it was even conjectured that TDDFT has to be extended to time-dependent current-density-functional theory [21–24] in order to correctly describe CT excitations. It is known that the time-dependent Hartree-Fock (TDHF) is able to describe CT excitations and thus it may be expected that the same holds true also for TDDFT in the exact-exchange only approximation [time-dependent exact exchange (TDEXX)] [25–29]. The exact-exchange (EXX) TD-DFT kernel is frequency dependent [27–29]. Previous implementations of adiabatic and nonadiabatic TDEXX methods [30,31] relying on expansions of the Kohn-Sham (KS) response function in auxiliary basis sets suffered from numerical instabilities and, so far, it could not be investigated in how far TDEXX is capable to describe CT excitations.

Here, as a first result, we present a TDDFT response equation for the effective KS potential instead of the electron density that leads to a DFT response method that, in contrast to present methods, is well suited for the use of orbital-dependent exchange-correlation functional methods, because it completely avoids numerically prohibitive inverse response functions. Then as a second result we show that this method in combination with the exact frequency-dependent exchange kernel describes CT excitations qualitatively correct.

For notational simplicity we consider closed-shell systems and choose real-valued orbitals throughout this work. At present, most TDDFT calculations in the response regime are based on the equation

\[ [ε^2 + 4ε^{1/2}K(ω)ε^{1/2}]ζ_i(ω) = Ω_i^2ζ_i(ω) \]  (1)

introduced by Casida [2,32–34]. The dimension of Eq. (1) is given by the product of the number of occupied times the number of unoccupied KS orbitals. In Eq. (1) the eigenvalue \( Ω_n^2 \) equals the square of the excitation energy of the nth excited state. The eigenvectors \( ζ_i(ω) \) determine the density-density (potential-density) response function

\[ χ(r,r',ω) = \sum_{n} \sum_{ia,jb} Ω_n^2 ζ_a^i(ω)ζ_n^*ζ_n^jbΦ_{ia}(r)Φ_{jb}(r') \]  (2)

terms of products \( Φ_{ia}(r) = Φ_i(r)ϕ_a(r) \) of occupied times unoccupied KS orbitals \( ϕ_i \) and \( ϕ_a \), respectively. The elements \( K_{ia,jb}(ω) \) of the matrix \( K(ω) \) are given by

\[ K_{ia,jb}(ω) = \int drdr' Φ_{ia}(r)Φ_{ia}(r')Φ_{jb}(r') \]  (3)

and the elements of the diagonal matrix \( ε \) by \( ε_{ia,jb} = δ_{ia,jb}(ε_ia − ε_jb) \) with \( ε_ia \) and \( ε_jb \) denoting the orbital energies of the occupied and the virtual orbitals \( ϕ_i \) and \( ϕ_a \), respectively. The indices \( ia \) and \( jb \) are superindices labeling the products of occupied times unoccupied KS orbitals. The sum of the Coulomb kernel \( 1/|r − r'| \) and the xc kernel \( f_{xc} \), the frequency-dependent functional derivative of the KS xc po-
tential with respect to the electron density, is denoted by \( f_{xc} \).

At present, the xc kernel \( f_{xc} \) in Eqs. (1) and (3) is almost exclusively approximated by taking the functional derivative of xc potentials in the local-density approximation or in generalized gradient approximations. This includes the adiabatic approximation, i.e., the neglect of the frequency dependence of \( f_{xc} \). We now consider a CT excitation between two molecular fragments at increasing distance \( R \). In a one-electron picture, this excitation is described by an excitation of an electron from the highest occupied molecular orbital (HOMO) \( \varphi_i \) of one fragment to the lowest unoccupied molecular orbital (LUMO) \( \varphi_a \) of the other. The spatial overlap between \( \varphi_i \) and \( \varphi_a \) vanishes with the distance \( R \) and therefore all matrix elements \( K_{ia,ia}(omega) \) carrying the index \( ia \) of the two involved orbitals, i.e., all matrix elements with \( ic=ia \) or \( jb=ia \), vanish for any finite kernel. As a result the corresponding row and column of the matrix \( K(omega) \) of Eq. (1) vanishes and therefore Eq. (1) has an eigenvalue \( \omega_i^2=\varepsilon_{ia}^2 \), which means that Eq. (1) yields a CT excitation energy equal to the KS eigenvalue difference \( \varepsilon_{ia}-\varepsilon_{ia} \).

For two initially neutral fragments the true CT excitation energy behaves like \( I-A-1/R \) for large distances \( R \) of the fragments with \( I \) denoting the ionization energy of the donor and \( A \) denoting the electron affinity of the acceptor. Present DFT response methods do not yield this \( 1/R \) behavior and furthermore the difference \( \varepsilon_{ia}-\varepsilon_{ia} \) is a poor approximation for \( I-A \) because the negative of \( \varepsilon_{ia} \) differs from the electron affinity \( A \) by the derivative discontinuity of the xc energy at integer particle number, which is completely neglected in present methods. The only way to obtain a CT excitation energy that differs from the KS eigenvalue difference \( \varepsilon_{ia}-\varepsilon_{ia} \) is that the TDDFT kernel \( f_{xc} \) approaches infinity in such a way that matrix elements \( K_{ia,ia}(omega) \) of Eq. (3) with \( ic=ia \) and/or \( jb=ia \) remain finite instead of approaching zero for an increasing distance \( R \) of the fragments \([11]\).

II. FORMALISM

The EXX kernel \( f_{ex} \) obeys the equation \([27–29]\)

\[
f_{ex}(\textbf{r}, \textbf{r}', \omega) = \int d\textbf{r}'' d\textbf{r}''' \chi_s^{-1}(\textbf{r}, \textbf{r}'', \omega) h_s(\textbf{r}'', \textbf{r}'''', \omega) \chi_s^{-1}(\textbf{r}'', \textbf{r}''', \omega).
\]

(4)

In Eq. (4) \( h_s \) is an orbital-dependent function given in Refs. \([27–29]\) and discussed later on and \( \chi_s \) is the KS response function

\[
\chi_s(\textbf{r}, \textbf{r}', \omega) = \sum_{\text{occ}} \sum_{\text{unocc}} \varphi_{ia}(\textbf{r}) \lambda_{ia}(\omega) \varphi_{ia}(\textbf{r}').
\]

(5)

with \( \lambda_{ia}(\omega)=4\varepsilon_{ia}/(\omega^2-\varepsilon_{ia}^2) \). The EXX kernel is a orbital-dependent kernel. Other orbital-dependent kernels derived from orbital-dependent approximations of the xc potential will obey equations differing from Eq. (4) only in that the function \( h_s \) is replaced with some other functions. The present DFT response method derived in the following is therefore of very general use.

Solving Eq. (4) is numerically highly problematic due to the occurrence of the inverse KS response functions \( \chi_s^{-1} \)[35,36]. Solving Eq. (1) together with Eq. (4) for an orbital-dependent kernel therefore does not seem to be an advisable option.

We develop our present method starting from the basic equation \([3]\)

\[
\int d\textbf{r}' \left[ \delta(\textbf{r} - \textbf{r}') - \int d\textbf{r}'' \chi_s(\textbf{r}, \textbf{r}'', \omega) f_{xc}(\textbf{r}'', \textbf{r}'', \omega) \right] \rho^{(1)}(\textbf{r}', \omega) = \int d\textbf{r}' \chi_s(\textbf{r}, \textbf{r}', \omega) \nu^{(1)}(\textbf{r}', \omega)
\]

(6)

of DFT response theory which can be derived \([32]\) directly from the Runge-Gross theorem without referring to the formally problematic \([37]\) action formalism. By \( \nu^{(1)} \) the frequency-dependent perturbation of the external potential of the electronic system is denoted. We furthermore note that the response of the electron density in TDDFT can be expressed by

\[
\rho^{(1)}(\textbf{r}, \omega) = \int d\textbf{r}' \chi_s(\textbf{r}, \textbf{r}', \omega) \nu^{(1)}(\textbf{r}', \omega)
\]

(7)

with \( \nu^{(1)} \) denoting the linear response of the effective KS potential that corresponds according to the Runge-Gross theorem \([1]\) to the perturbation \( \epsilon^{(1)} \).

Neglect of the correlation contribution to \( f_{xc} \) separation of the Coulomb and exchange contributions, and insertion of Eqs. (4) and (7) into the basic equation (6) yields

\[
\int d\textbf{r}' \left[ \chi_s(\textbf{r}, \textbf{r}', \omega) - \int d\textbf{r}'' d\textbf{r}''' \chi_s(\textbf{r}, \textbf{r}'', \omega) h_s(\textbf{r}'', \textbf{r}''', \omega) \chi_s^{-1}(\textbf{r}'', \textbf{r}''', \omega) \right] \nu^{(1)}(\textbf{r}', \omega) = \int d\textbf{r}' \chi_s(\textbf{r}, \textbf{r}', \omega) \nu^{(1)}(\textbf{r}', \omega),
\]

(8)

which is the central equation of this work. Equation (8), in contrast to the original equation (6), is an equation for the response \( \nu^{(1)} \) of the effective KS potential and not the response \( \rho^{(1)} \) of the electron density. Its great advantage is that it no longer contains the exchange kernel but the function \( h_s \) and therefore does not require the solution of the numerically problematic equation (4).

The function \( h_s \) shall be expressed later on as

\[
h_s(\textbf{r}, \textbf{r}', \omega) = \sum_{ia,jb} \varphi_{ia}(\textbf{r}) \lambda_{ia}(\omega) X_{ia,jb}(\omega) \lambda_{jb} \varphi_{jb}(\textbf{r}').
\]

(9)

With Eq. (9), Eq. (8) can be rewritten in the matrix form

\[
\mathbf{W}^{T}(\omega) \left[ \epsilon^2 - 4\epsilon^{1/2} [C + \mathbf{X}(\omega)] \epsilon^{1/2} \right] \varphi(\omega)
\]

\[
= \mathbf{W}^{T}(\omega) \epsilon^{1/2} \nu^{(1)}(\omega)
\]

(10)

with the elements \( W_{ia,ia}(\omega) \) of the vector \( \mathbf{W}(\omega) \) given by \( W_{ia,ia}(\omega)=\lambda_{ia}(\omega) \varphi_{ia}(\textbf{r}) \), the elements \( \nu^{(1,ia)}(\omega) \) of the vector \( \nu^{(1)}(\omega) \) given by \( \langle \varphi_{ia} | \nu^{(1)}(\omega) | \varphi_{ia} \rangle \), the vector \( \mathbf{X}(\omega)=\epsilon^{-1/2} \lambda(\omega) \nu^{(1)}(\omega) \), and the elements of the matrix \( C \) given by \( C_{ia,jb}=(ij|ab) \) with \( (st|uv) \).

\[
= \int d\textbf{r}'' \varphi(\textbf{r}) \varphi(\textbf{r}') \varphi(\textbf{r}) \varphi(\textbf{r}') / |\textbf{r} - \textbf{r}'|.
\]
If the functions $W_{ia}(\mathbf{r})$ were linearly independent then Eq. (10) would imply the matrix equation
\[
\{\omega^2 1 - \varepsilon^2 - 4\varepsilon^{1/2}[C + X(\omega)]\varepsilon^{1/2}\} z(\omega) = 4\varepsilon^{1/2} x^{(1)}(\omega),
\]
(11)

As usual in DFT response methods, excitation energies are determined by searching those values of $\omega$ that lead to a matrix $\{\omega^2 1 - \varepsilon^2 - 4\varepsilon^{1/2}[C + X(\omega)]\varepsilon^{1/2}\}$ with an eigenvalue equaling zero, which implies an infinite response of the electron density. This leads to the eigenvalue equation
\[
\{\varepsilon^2 + 4\varepsilon^{1/2}[C + X(\omega)]\varepsilon^{1/2}\} z(\omega) = \omega^2 z(\omega),
\]
(12)

which equals Eq. (1), but instead of the matrix $K$ the sum of the matrices $C$ and $X$ occurs in Eq. (12). The matrix $C$ equals the contribution in the matrix $K$ that originates from the Coulomb kernel, while the contribution originating from the xc kernel is replaced with the matrix $X$. The functions $W_{ia}(\mathbf{r})$, in general, are linearly dependent because the products of occupied times unoccupied orbitals contained in them are linearly dependent. Thus Eqs. (11) and (12), at first, do not represent proper DFT response equations. In order to turn them into proper DFT response equations, a projection on a set of linearly independent linear combinations of the products $W_{ia}(\mathbf{r})$ has to be carried out.

To that end those eigenvectors of the overlap matrix of the functions $W_{ia}(\mathbf{r})$ that have eigenvectors unequal to zero or in practice eigenvalues above a certain threshold, here $10^{-12}$, are determined, and Eqs. (11) and (12) are projected onto the space defined by these eigenvectors. Results for small molecules, to be published elsewhere, showed that this projection has de facto no effect on the energies of regular valence excitations and therefore can be avoided in practice. For CT excitations the overlap matrix of the functions $W_{ia}(\mathbf{r})$ first has to be rescaled in such a way that all diagonal elements are equal to 1, because functions $W_{ia}(\mathbf{r})$ corresponding to CT excitations vanish. In the examples considered below such a rescaled overlap matrix had eigenvalues above the threshold of $10^{-12}$ indicating that no projection was necessary.

The function $h_{ia}$ of Eq. (4) (see Refs. [27–29]) can be partitioned into two parts $h_{ia}^x$ and $h_{ia}^y$. The first part $h_{ia}^x$ has the form of Eq. (9) with matrix elements $X_{ia,jb}^x$ given by
\[
X_{ia,jb}^x(\omega) = \frac{1}{4} \left[ 1 + \frac{\omega^2}{E_{ia}E_{jb}} \right] [-\langle ia|jb \rangle + \delta_{ia} \delta_{ja} - \delta_{ia} \delta_{ja}] \\
- \frac{1}{4} \left[ 1 - \frac{\omega^2}{E_{ia}E_{jb}} \right] (ij|ab),
\]
(13)

with $s_{ia} = \langle \varphi_i|\tilde{\varphi}_{ia}^{NL} - \tilde{\varphi}_{ia}\rangle$. In Eq. (13) $\tilde{\varphi}$ is the local KS exchange operator, while $\tilde{\varphi}^{NL}$ is a nonlocal exchange operator of the form of the Hartee-Fock exchange operator but constructed from KS orbitals, i.e., an exchange operator with the kernel $\Sigma(\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}'))/|\mathbf{r} - \mathbf{r}'|$. The second part $h_{ia}^y$ of the function $h_{ia}$ is a sum of terms of the form $\varphi_i(\mathbf{r})\lambda_{ia}X_{ia,jb}^y(\omega)\varphi_j(\mathbf{r}')$ with the indices $s$ and $t$ referring either to two occupied or to two unoccupied orbitals. In order to cast the contribution $h_{ia}^y$ in the form of Eq. (9), the products of two occupied or two unoccupied orbitals are expanded in products of occupied times unoccupied orbitals. It turns out that the contribution of $h_{ia}^y$ to results of valence or Rydberg excitations of small molecules, to be published elsewhere, as well as to the CT excitations considered below, is negligible. Therefore this contribution shall not be discussed any further here, although it is, of course, taken into account in the calculations.

We are now analyzing the asymptotic behavior of the CT excitation from the HOMO $\varphi_i$ of one fragment to the LUMO $\varphi_a$ of the other by considering the dominating contribution of the diagonal elements $ia,ia$ in Eq. (12). (This single pole approximation is only made here in the formal analysis, not in the calculations.) We take into account that the overlap between $\varphi_i$ and $\varphi_a$ and thus the Coulomb integral $\langle ii|aa \rangle$ approach zero. Then from Eqs. (12) and (13) one obtains for the CT excitation energy $\omega_{CT}$
\[
\omega_{CT}^2 = \omega_{ia}^2 + \left( \frac{\omega^2}{E_{ia}} + \frac{\omega^2}{E_{ia}} \right) \Delta_{ia} - \langle ia|ia \rangle,
\]
(14)

with $\Delta_{ia} = \langle \varphi_i|\varphi_{ia}^{NL} - \tilde{\varphi}_{ia}\rangle - \langle \varphi_i|\varphi_{ia}^{NL} - \tilde{\varphi}_{ia}\rangle$ being the exchange contribution to the derivative discontinuity [38]. The matrix element $\langle \varphi_i|\varphi_{ia}^{NL} - \tilde{\varphi}_{ia}\rangle$ equals zero because $\varphi_i$ is the HOMO [39]. Given that the right-hand side (rhs) of Eq. (14) for the CT energy $\omega_{CT}$ is frequency dependent, we consider three different cases:

1. adiabatic case ($\omega=0$):
\[
\omega_{CT}^{adiab} = \omega_{ia} \sqrt{1 + \frac{\Delta_{ia} - \langle ia|ia \rangle}{E_{ia}}},
\]
(15)

2. fully nonadiabatic case ($\omega=\omega_{CT}$):
\[
\omega_{CT} = \omega_{ia} \sqrt{\frac{E_{ia} + \Delta_{ia} - \langle ia|ia \rangle}{E_{ia} - \Delta_{ia} + \langle ia|ia \rangle}},
\]
(16)

3. partially nonadiabatic case ($\omega=\omega_{CT}^{partial}$):
\[
\omega_{CT}^{partial} = \omega_{ia} + \Delta_{ia} - \langle ia|ia \rangle = \omega_{ia} + \Delta_{ia} - 1/R. \quad (17)
\]

Equation (17) is obtained by inserting $\omega=\omega_{CT}^{adiab}$ i.e., the rhs. of Eq. (15), into Eq. (14). In Eq. (17) it is exploited that the integral $\langle ia|ia \rangle$ approaches $1/R$ for large distances $R$ between the fragments. The rhs. of Eq. (17) is readily interpreted because $\omega_{CT}^{adiab}$ approximates the difference $-\Delta_{ia}$ of the ionization potential and the electron affinity. If we expand the rhs. of Eqs. (15) and (16) in a Taylor series up to first order with respect to $\Delta_{ia} - \langle ia|ia \rangle$, we then obtain $\omega_{CT}^{adiab} = E_{ia} + (1/2)\Delta_{ia} - 1/(2R)$ and $\omega_{CT} = E_{ia} + \Delta_{ia} - 1/R$, respectively. Thus in first order the fully nonadiabatic case equals the partially adiabatic case and both yield a CT excitation energy that behaves correctly with $R$ and contains a term approximating the difference between the ionization energy and the electron affinity. Because the exchange contribution $\Delta_{ia}$ overestimates the true derivative discontinuity, the quantity $\Delta_{ia} - \langle ia|ia \rangle$ is not that small that the Taylor series of the rhs. of Eq. (16) is completely converged in first order. Therefore the fully nonadiabatic case shall lead to results differing somewhat from the partially nonadiabatic one. The Taylor series of the adiabatic case shows that it can be expected to lead to CT excitations that are too small and exhibit a too weak $R$ dependence due to the factor of $1/2$ in front of $\Delta_{ia} - 1/R$.
III. EXAMPLES

We considered CT excitations in three systems, He$_2$, HeBe, and H$_2$+C$_2$H$_2$ (ethylene) and carried out calculations with the presented exact-exchange DFT response method and with standard TDDFT employing Perdew-Burke-Ernzerhof (PBE) [40] xc potentials and kernels. Furthermore we performed TDHF and, as a reference, equation-of-motion coupled-cluster singles doubles (EOM-CCSD) [41] calculations. In all cases CT excitation were considered for increasing distances $R$ between the fragments. For the H$_2$+C$_2$H$_2$ dimer a geometry with a parallel orientation of the molecules was chosen with monomer bond lengths of $d$(H-H) = 1.401 04$a_0$, $d$(C-C) = 2.272 58$a_0$, and $d$(C-H) = 1.970 42$a_0$.

For He$_2$ and HeBe Dunning's augmented correlation consistent polarized valence quadruple zeta (aug-cc-pVQZ) basis sets [42,43] were used for the PBE, the TDHF, and the EOM-CCSD calculations; while for H$_2$+C$_2$H$_2$ the augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) basis sets from Dunning [42] and Kendall et al. [43] were used correspondingly. The ground-state EXX calculations have been carried out using the scheme described in Ref. [36] employing large even tempered balanced orbital and auxiliary basis sets. The local exact KS exchange potentials obtained from these calculations were then used to generate EXX orbitals and eigenvalues with the aug-cc-pVQZ and the aug-cc-pVTZ basis sets, respectively, in a self-consistent KS calculation, in which only the Coulomb potential was updated during the self-consistency process. The EXX orbitals and eigenvalues as well as the corresponding matrix elements with the exact KS exchange potential then entered the TDEXX calculations. All calculations were performed with the MOLPRO quantum chemistry program [44] with exception of the PBE calculations which were done using the TURBOMOLE package [45].

He$_2$ is a symmetric system and thus does not exhibit regular CT excitations. However, it was shown recently [6,7] that the CT problem of TDDFT is actually a more general problem that occurs whenever excitations between separated fragments are considered. In He$_2$, two CT-like excitations occur that are symmetry-determined combinations of two CT excitations, namely, CT excitations from the 1$s$ orbital of the helium atom 1 (2) into the 2$s$ orbital of the helium atom 2 (1). The energies of both CT-like excitations approach $I−A−1/R$ like usual CT excitations with $I$ and $A$ being the ionization potential and the electron affinity of the helium atom. The eigenvectors $\mathbf{z}$ of Eq. (12) corresponding to both CT-like excitations are dominated not just by one but two entries corresponding to the two involved products of occupied times unoccupied orbitals [1$s$ orbital on helium 1 (2) times 2$s$ orbital on helium 2 (1)]. Nevertheless the analysis given in Eqs. (14)–(17) turns out to still hold true for eigenvalue differences $\varepsilon_{1a}$ and matrix elements $\Delta_\omega$ and $(ia|ia)$ referring to either of the products. (The quantities $\varepsilon_{1a}$, $\Delta_\omega$, and $(ia|ia)$ are identical for the two involved pairs of occupied times unoccupied orbitals.)

In Fig. 1 the results of the various calculations for He$_2$ are displayed. As expected TDDFT using PBE functionals yields too small CT excitation energies which are de facto identical to the corresponding eigenvalue differences (not displayed) and do not exhibit the correct behavior with the He-He distance $R$. The CT excitation energies obtained with the presented exact-exchange DFT response method in the adiabatic case (labeled ATDEXX) differ from the corresponding eigenvalue differences, are larger than the PBE energies, and show some dependence on the He-He distance $R$. The CT energies, however, are still too small compared to the EOM-CCSD reference and the $R$ dependence is too small by roughly a factor of 1/2. This is in line with the above analysis within the single pole approximation. We emphasize that the ATDEXX results show that even a frequency-independent kernel can lead to CT energies differing from the corresponding eigenvalues differences. The partially nonadiabatic exact-exchange kernel leads to CT energies [labeled TDEXX($\omega = \omega_{\text{adiab}}$)] that are almost identical to the TDHF ones, exhibit a qualitatively correct behavior, and lie close to the EOM-CCSD reference. The CT excitations obtained with the fully nonadiabatic exact-exchange kernel are a bit higher than those from the partially nonadiabatic case. This reflects the fact that the above discussed Taylor series of the excitation energies in the single pole approximation contains non-negligible higher-order terms.

Figure 2 presents the lowest CT excitation in the HeBe dimer from the He(1$s$) to the Be(2$p_{\alpha}$) state for the various methods. As in the He$_2$ example discussed above, the PBE functional largely underestimates the CT excitation and approaches a constant already at a small internuclear distance. On the other hand, both TDEXX and TDEXX($\omega = \omega_{\text{adiab}}$) yield a CT excitation curve that is close to the TDHF curve. Figure 2 demonstrates that this also holds for smaller distances where the excitation is no longer of pure CT character. As in the case of He$_2$ the correlation effects captured in the EOM-CCSD calculations lead to a slight downward shift of the CT curve of about 0.025 hartree on average.

In case of the H$_2$+C$_2$H$_2$ dimer we considered the excitation of the HOMO $\pi$ orbital of ethylene to the LUMO $\sigma_\pi$ orbital on H$_2$. Note that the presence of the H$_2$ molecule destroys the degeneracy of the $\pi$ orbitals of ethylene and the HOMO orbital is always the one which is lying in the plane of the total system. Figure 3 shows the corresponding exci-
tation energies for the various methods with a function of the distance between the centers of mass of the two molecules. Again, as with H$_2$ and HeBe, the partially nonadiabatic TDEXX excitation curve closely resembles the TDHF one. In contrast, however, to H$_2$ and HeBe the EOM-CCSD method yields a small positive correlation contribution to the charge-transfer excitation.

IV. SUMMARY

In summary, we have shown that based on an equation for the response of the effective KS potential [Eq. (8)] instead of the response of the electron density, numerically stable density-functional response methods with orbital-dependent kernels are feasible. At the exact exchange level, i.e., by employing the frequency-dependent exact-exchange kernel, it turned out to be possible to describe CT excitations within a TDDFT framework. We note that the presented exact-exchange DFT response approach fundamentally differs from TDHF because it is a nonlinear approach due to its frequency-dependent kernel. Whether the nonlinearity of the TDEXX approach leads to the occurrence of additional excitations, e.g., two-electron excitations that cannot be described in the TDHF method, is currently investigated [46]. The relation of the presented TDEXX approach to the TDHF method will be considered elsewhere [46] analyzing among other points in detail the role of the frequency dependence of the exact-exchange kernel. CT excitation energies obtained with an adiabatic TDEXX approach exhibit a distinct long-range behavior with the distance $R$ of the fragments involved in the CT which, however, is too weak by a factor of 2. This indicates that it is not the frequency dependence of the kernel alone that leads to a correct description of charge-transfer excitations.

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12. Time-dependent density functional theory

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12.5. Molecular excitation spectra by TDDFT with the nonadiabatic exact exchange kernel

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Molecular Excitation Spectra by TDDFT
With the Nonadiabatic Exact Exchange Kernel

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ABSTRACT: A time-dependent density functional theory (TDDFT) method using the nonadiabatic exact-exchange kernel is discussed. Compared to previous TDDFT methods with orbital-dependent kernels, the presented time-dependent exact exchange (TDEXX) approach avoids a numerical unstable inversion of the Kohn–Sham response function. If the complete frequency dependency of the exact-exchange kernel is taken into account, then the proposed method yields the long-range distance behavior of charge-transfer (CT) excitation energies qualitatively correctly. The relation between time-dependent Hartree–Fock and TDEXX approaches is analyzed. This analysis shows by formal arguments why the TDEXX method is capable to correctly treat CT excitations and conversely shows that the problems to describe CT excitations with conventional TDDFT methods based on generalized gradient approximations (GGAs) has its origin in the shortcomings of the GGA exchange functionals. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 110: 2202–2220, 2010

Key words: time-dependent density functional theory; exact-exchange kernel; charge-transfer excitations; nonadiabatic

1. Introduction

Theoretical methods based on density-functional theory (DFT) are widely used to study the electronic structure of atoms, molecules, atomic clusters, and condensed matter [1–4]. Conventional DFT methods like those based on the local density approximation (LDA) [2–6] or generalized gradient approximations (GGAs) [2–4, 7–9] use approximate functionals for the exchange-correlation (xc) energy that are integrals over functions of the electron density or, in the case of GGAs, of the electron density and its gradient. Electronic excitations and the energies of excited states can be treated via time-dependent density-functional theory (TDDFT) [10, 11], in particular density-functional response methods, relying also on functionals within the
LDA or GGA. However, despite the evident success achieved, conventional DFT methods are not accurate enough for many questions of interest. Let us concentrate here on the shortcomings of TDDFT methods. One weakness of conventional TDDFT methods, i.e., methods based on the LDA or GGAs, is that they cannot correctly describe excitations into states with Rydberg character [12], which, e.g., often are present as low-lying excited states in organic molecules. Another important shortcoming of conventional TDDFT methods is that charge-transfer (CT) excitations are described qualitatively wrong [13–19]. CT excitation energies can be underestimated by as much as a few electronvolts, and the excited-state energy curves do not exhibit the correct 1/R asymptotic behavior, where R corresponds to the distance between the positive and negative charges of the CT state. The latter problems have their origin in shortcomings of the employed xc functionals for which, for instance, the 1/R failure can be explained as an electron-transfer self-interaction error [19].

A strategy to overcome the shortcomings of conventional TDDFT methods is to develop and use better approximate xc functionals, in particular better xc potentials and, crucial for TDDFT methods in the response regime, better xc kernels. In recent years, a new generation of DFT methods emerged that uses functionals that not only depend on the electron density and its gradients but also on Kohn–Sham (KS) orbitals. Such functionals are referred to as orbital-dependent functionals (ODFs) [20]. Examples are functionals that contain the kinetic energy density, meta-GGA functionals [21–28], or functionals that contain the exchange energy density, hyper-GGA functionals [22, 29–37], and local hybrid functionals [33, 38–40]. Other examples are methods that treat the exchange interactions exactly, see later on, or that take into account correlation via perturbation theory approaches [41–51] or via the random phase approximation [52–62]. Because the orbitals are functionals of the electron density, ODFs lie within the realm of DFT. ODF-based TDDFT schemes and TDDFT/TDHF hybrid schemes were developed that qualitatively correctly describe low-energy molecular excited states [17, 63–70], e.g., hybrid functionals that adopt the nonlocal Hartree–Fock exchange operator in the TDDFT framework [17, 69, 71].

Considering DFT in general, the evaluation of ODFs for the xc energy poses no principal difficulty. However, if within DFT for electronic ground states the KS equations [70] are solved, then not only the xc energy but also the xc potential, the functional derivative of the xc energy with respect to the electron density [20, 41, 42, 72, 73], is required during the self-consistency process to obtain the orbitals. In contrast to the case of GGA functionals, the evaluation of functional derivatives for ODFs is problematic because the dependence of the orbitals on the density a priori is not known and the functional derivative of an ODF with respect to the electron density cannot simply be taken via the chain rule. Within TDDFT, the situation is even more difficult because there in addition to the xc potential, the xc kernel is also required, the frequency-dependent functional derivative of the xc potential with respect to the electron density.

We now consider the exchange component of the total xc energy. Its functional dependence on the KS orbitals is exactly known as ODF. For a closed shell system, the KS exchange energy in terms of the orbitals has exactly the same form as the Hartree–Fock (HF) exchange energy, i.e., the exchange energy is given by the well-known expression for the exchange energy of a single Slater determinant. One should note, however, that the values of the KS and HF exchange energies are different because the expression is evaluated for different orbitals, i.e., for KS or for HF orbitals, respectively. The HF and KS exchange potentials, on the other hand, have completely different forms. The nonlocal HF exchange potential is determined as functional derivative of the exchange energy with respect to occupied orbitals, whereas the local multiplicative KS exchange potential is defined as functional derivative of the exchange energy with respect to the electron density. This means the difference between the HF method and an exact exchange-only KS method [20, 41, 72–77], further denoted as exact exchange (EXX) method, is the type of the functional derivative of the exchange energy taken to obtain the exchange potential.

While HF and EXX total energies and the single-particle energies of occupied states differ only to a small extent [78], the unoccupied KS orbitals and eigenvalues are completely different from the HF ones [20, 72, 75–77]. As KS orbitals and eigenvalues are the input quantities for the calculation of response properties, in particular, of excitation energies via TDDFT in the response regime [6, 10, 11], it is crucial that the correct functional derivative with respect to the electron density is taken, if orbitals are determined that shall be used in a TDDFT approach. Unoccupied HF orbitals mostly have positive eigenvalues, and therefore are of little physical meaning.
The eigenvalue spectra of conventional LDA or GGA methods is qualitatively wrong because of the presence of the unphysical Coulomb self-interactions in these methods and, e.g., do not exhibit Rydberg series. Consequently, TDDFT methods based on LDA or GGA functionals yield very poor excitation energies for transitions into states with Rydberg character. EXX methods, on the other hand, yield physically meaningful eigenvalue spectra that contain Rydberg series [62, 79, 80], and as a result, the orbitals as well as TDDFT methods based on them describe Rydberg states very well [79, 80]. This means in order to solve the problem of conventional TDDFT methods to describe states with Rydberg character, it is enough to improve the KS calculation that preceeds the actual TDDFT calculation and generates the KS orbitals and eigenvalues by using an exchange potential in this KS calculation that correctly cancels the self-interactions present in the Coulomb potential. An improvement of the xc kernel of the TDDFT response calculation is not required for this purpose. This demonstrates that it is of importance to use KS xc potentials accounting for exact exchange interactions.

For the calculation of the functional derivative of an ODF with respect to the electron density, the optimized effective potential (OEP) approach [20, 41, 42, 72, 73] is widely used. Numerically stable OEP methods for atoms based on representations of orbitals and potentials on spatial grids [72, 73, 81] as well as for periodic systems based on plane wave basis sets are known [82–84] since quite a while. OEP methods for molecules using Gaussian basis sets were recently proposed [74, 85]. However, such Gaussian basis set OEP methods turned out to be computationally demanding and suffered from numerical instabilities [74, 76, 78, 86–88], the origin of which is closely related to the KS response function which has to be effectively inverted when solving the OEP equation. Various attempts to develop numerically stable OEP methods for molecules were made in recent years [74, 77, 79, 80, 85–87, 89–95]. For instance, the origin of instabilities of OEP methods was analyzed in Ref. [76, 88], and a numerically stable Gaussian basis set OEP method was developed in Ref. [77]. Gaussian basis set TDDFT methods for molecules, using ODFs, in particular time-dependent DFT methods accounting for exact exchange, i.e., methods that use the exact frequency-dependent exchange kernel [96–100], and that shall be denoted as TDEXX methods, are numerically even more demanding than EXX KS methods or OEP methods in general. The reason is that in TDEXX methods not only one but two KS response functions occur which have to be effectively inverted [85, 99–101]. Moreover, the frequency dependent instead of the static KS response function is required. First straightforward implementations of TDEXX methods using Gaussian basis sets suffered from numerical instabilities [102, 103]. Using the theoretical analysis of Refs. [101, 104, 105], the basic TDDFT response equation was reformulated in such a way that inverse KS response functions no longer occur in TDEXX methods, or generally in TDDFT methods using ODFs [101]. In this way, the source of the numerical instabilities could be removed. The resulting TDEXX approach that takes into account exchange exactly and is based on the frequency-dependent exact exchange kernel [74, 78, 96, 99, 101] is numerically stable and can correctly describe charge-transfer excitations similarly as the TDHF method [78], but in contrast to TDDFT methods based on the LDA or GGAs [13–18]. Except for the special case of two-electron systems, where it has recently been shown [105] that qualitatively correct CT excitation energies can be obtained without the use of a frequency-dependent kernel, it has been demonstrated that the frequency-dependent kernel is crucial for the description of CT excitations between open-shell fragments of a dissociating molecule [66, 106].

A charge-transfer electronic excitation in the single pole approximation [101] can be described as a quantum transition from an occupied orbital $i$ mainly localized in one spacial part of the system into an unoccupied state $a$, localized in another region. When the overlap between the initial and final states vanishes, then, in the case of ‘traditional’ LDA or GGA functionals, matrix elements of the xc kernel containing the product of the two involved orbitals $i$ and $a$ vanish and the CT transition frequency or energy equals the difference of corresponding single-particle energies. Moreover, TDDFT based on ‘traditional’ LDA or GGA functionals does not yield the expected $1/A−1/R$ dependence of the CT energy [19, 65, 66, 78, 106] on the distance between the molecular fragments, while the employment of the exact frequency-dependent exchange kernel within the TDEXX method leads to the proper asymptotic dependence.

In this work, the aforementioned alternative approach for the TDEXX problem is reconsidered. Within this method, the linear response equation is solved not with respect to the electron density but with respect to the effective potential and as result does not require a numerically demanding inversion of the KS response function [101]. Moreover,
in combination with the frequency-dependent exact exchange kernel, the method provides an accurate description of CT excitations. We present results of the method for the nitrogen molecule N₂ and the ethylene molecule C₂H₄. As a central part of this article, the relation between TDHF and TDEXX is discussed. The analysis explains why excitation spectra obtained via TDHF and via the considered TDEXX method are almost identical. Moreover, this analysis shows by formal arguments why the TDEXX is capable to correctly treat CT excitations and conversely shows that the problems to describe CT excitations using conventional TDDFT methods based on GGAs has its origin in the shortcomings of the GGA exchange functionals.

For the sake of simplicity, systems with closed-shell ground-state electronic configurations are considered in this work. The indexes i, j, k are used for occupied orbitals, a, b, c designate unoccupied single-particle states, respectively, and p, q, r general orbitals. The atomic system of units (\(\hbar = e = m_c = 1\)) is used throughout the text.

## 2. OEP-EXX Potential

Let us consider a nonspin-polarized, closed-shell system with \(N = 2N_{\text{occ}}\) particles with real-valued doubly occupied orbitals with spin to be implicitly taken into account by appropriate prefactors. Restricting ourselves to the single-reference framework, the system shall be described either within the Hartree–Fock or the Kohn–Sham approach. In the first case, the many-particle wave function is approximated by a single Slater determinant, namely the HF determinant \(\psi_{\text{HF}}\) constructed by orthonormal single-particle HF orbitals \(\{\psi_{\text{HF}}\}\) that are the eigenfunctions of the HF equation

\[
\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \nu_1(\mathbf{r})\right] \psi_{\text{HF}}(\mathbf{r}) = \varepsilon_{\text{HF}} \psi_{\text{HF}}(\mathbf{r})
\]

which can be rewritten in operator form as

\[
\hat{H}_{\text{HF}} \psi_{\text{HF}}(\mathbf{r}) = \left[\hat{T} + \hat{\nu}_{\text{ext}} + \hat{\nu}_1 + \hat{\varepsilon}_{\text{NL}}\right] \psi_{\text{HF}}(\mathbf{r}) = \varepsilon_{\text{HF}} \psi_{\text{HF}}(\mathbf{r})
\]

with the Hartree potential

\[
\nu_1(\mathbf{r}) = 2 \sum_{i}^{\text{occ}} \int \rho_{\text{HF}}^{\text{occ}}(\mathbf{r}, \mathbf{r}') \psi_{\text{HF}}^\ast(\mathbf{r}') \psi_{\text{HF}}(\mathbf{r}') \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}
\]

and the nonlocal exchange operator defined according to

\[
\int d\mathbf{r} \varepsilon_{\text{NL}}^N(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') = -\sum_{i}^{\text{occ}} \int d\mathbf{r} \frac{\psi_{\text{HF}}^\ast(\mathbf{r}') \psi_{\text{HF}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{\text{HF}}(\mathbf{r}).
\]

Alternatively, within the KS approach, the KS wave function \(\psi_{\text{KS}}\) is introduced, which, for closed systems, again is a single determinant. The KS determinant, by definition, yields the same electron density as the true many-electron wave function. The KS orbitals \(\{\psi_{\text{KS}}\}\) building the KS determinant \(\psi_{\text{KS}}\) are eigenfunctions of the single-particle KS equation

\[
\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \nu_1(\mathbf{r}) + \nu_s(\mathbf{r}) + \nu_c(\mathbf{r})\right] \psi_{\text{KS}}(\mathbf{r}) = \varepsilon_{\text{KS}} \psi_{\text{KS}}(\mathbf{r})
\]

or, similarly, in operator form

\[
\hat{H}_{\text{KS}} \psi_{\text{KS}} = [\hat{T} + \hat{\nu}_{\text{ext}} + \hat{\nu}_1 + \hat{\nu}_s + \hat{\nu}_c] \psi_{\text{KS}} = \varepsilon_{\text{KS}} \psi_{\text{KS}}
\]

with

\[
\nu_s(\mathbf{r}) = 2 \sum_{i}^{\text{occ}} \int d\mathbf{r} \frac{\psi_{\text{KS}}(\mathbf{r}) \psi_{\text{KS}}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = \int d\mathbf{r} \rho_{\text{KS}}(\mathbf{r})
\]

In the following, we concentrate on the exchange potential, the correlational potential \(\nu_c(\mathbf{r})\) shall not be considered further here.

The exact KS exchange potential \(\nu_s(\mathbf{r})\) is a local multiplicative potential and obeys the OEP-EXX equation [20, 41, 42, 72, 73]

\[
\int d\mathbf{r} \chi_s(\mathbf{r}, \mathbf{r}') \nu_s(\mathbf{r}') = \ell(\mathbf{r})
\]

with the static KS response function \(\chi_s(\mathbf{r}, \mathbf{r}')\) given by

\[
\chi_s(\mathbf{r}, \mathbf{r}') = 4 \sum_{a}^{\text{unocc}} \sum_{i}^{\text{occ}} \frac{\psi_{\text{KS}}^\ast(\mathbf{r}) \psi_{\text{KS}}^\ast(\mathbf{r}) \psi_{\text{KS}}(\mathbf{r}) \psi_{\text{KS}}(\mathbf{r})}{\varepsilon_i^{\text{KS}} - \varepsilon_a^{\text{KS}}}
\]

and the right-hand side of (8) defined as
\[ t(r) = 4 \sum_{\text{occ}} \sum_{\text{unocc}} \phi_{i}^{\text{KS}}(r) \psi_{i}^\text{KS}(r) \frac{\epsilon_{i}^{\text{KS}} - \epsilon_{a}^{\text{KS}}}{\epsilon_{i}^{\text{KS}}} \]

Equation (8) can be rewritten in the compact form as
\[ 0 = \sum_{\alpha} \Theta_{\alpha}(r) \frac{1}{\epsilon_{\alpha}^{\text{KS}} - \epsilon_{a}^{\text{KS}}} \Delta V_{x,\alpha} \quad (10) \]
with the vector \( \Delta V_{x} \) defined by its elements
\[ \Delta V_{x,\alpha} = \langle \psi_{a}^{\text{KS}} | \phi_{\alpha}^{\text{NL}} - \hat{\delta}_{x} \psi_{i}^{\text{KS}} \rangle \quad (11) \]
and the vector \( \Theta_{\alpha}(r) \) defined by its elements
\[ \Theta_{\alpha}(r) = \langle \psi_{i}^{\text{KS}}(r) | \psi_{a}^{\text{KS}}(r) \rangle \quad (12) \]
where \( \alpha \) is considered as a superindex labeling the elements of the vectors \( \Theta_{\alpha}(r) \) and \( \Delta V_{x} \).

If the products \( \Theta_{\alpha}(r) = \langle \psi_{i}^{\text{KS}}(r) | \psi_{a}^{\text{KS}}(r) \rangle \) were linear independent then Eq. (10) would imply that \( \Delta V_{x} = 0 \), i.e., the matrix elements would satisfy the condition
\[ \Delta V_{x,\alpha} = \langle \psi_{a}^{\text{KS}} | \phi_{\alpha}^{\text{NL}} - \hat{\delta}_{x} \psi_{i}^{\text{KS}} \rangle = 0 \quad (13) \]
This would mean that the exchange-only KS and the HF determinants would be equivalent. To prove this statement, we add the operator
\[ \hat{\delta}_{x} \]
to the exchange-only (i.e., assuming \( \hat{\delta}_{c} \equiv 0 \)) KS Hamiltonian operator (5), i.e., the KS Hamiltonian operator resulting if \( \hat{\delta}_{c} \) is neglected. The resulting Hamiltonian operator \( \hat{F}_{\text{KS}}^{\text{EXX}} + \hat{\delta}_{x} \hat{\delta}_{x} \) is represented in the basis of the exchange-only KS orbitals, denoted as EXX (exact exchange) orbitals, leading to
\[ \begin{pmatrix} e^{\text{EXX},\text{occ}} & 0 \\ 0 & e^{\text{EXX},\text{unocc}} \end{pmatrix} + \begin{pmatrix} \Delta V_{x,\text{occ}} & 0 \\ 0 & \Delta V_{x,\text{unocc}} \end{pmatrix} \quad (15) \]
with the diagonal matrices \( e^{\text{EXX},\text{occ}} \) and \( e^{\text{EXX},\text{unocc}} \) containing the KS eigenvalues \( \epsilon_{i}^{\text{KS}} \) and \( \epsilon_{a}^{\text{KS}} \) of the occupied and unoccupied EXX orbitals, respectively. The matrix elements of the matrices \( \Delta V_{x,\text{occ}} \) and \( \Delta V_{x,\text{unocc}} \) are given by
\[ \Delta V_{x,ij}^{\text{occ}} = \langle \psi_{i}^{\text{EXX}} | \phi_{\alpha}^{\text{NL}} - \hat{\delta}_{x} \psi_{i}^{\text{EXX}} \rangle \quad (16) \]
\[ \Delta V_{x,ab}^{\text{unocc}} = \langle \phi_{a}^{\text{EXX}} | \phi_{\alpha}^{\text{NL}} - \hat{\delta}_{x} \phi_{b}^{\text{EXX}} \rangle \quad (17) \]
Note that there are no matrix elements coupling occupied and unoccupied KS orbitals, i.e., no matrices \( \Delta V_{x,\text{occ},\text{unocc}} \) or \( \Delta V_{x,\text{unocc},\text{occ}} \) because those matrix elements were assumed to be zero in Eq. (13), and \( \Delta V_{x,\text{unocc},\text{occ}} \) would correspond to \( \Delta V_{x} \) from Eq. (10) interpreted as matrix. This means that if we diagonalize the above Hamiltonian operator matrix (15) then the eigenstates will be obtained by unitary transformations within the occupied and within the unoccupied EXX orbitals, respectively, and the Slater determinant formed by those eigenstates resulting from the unitary transformation of occupied EXX orbitals is the same as the one resulting from the occupied EXX orbitals itself. The Hamiltonian operator obtained by adding \( \hat{\delta}_{x} \) to the exchange-only KS Hamiltonian operator has the form of the Fock operator (4), however, constructed from EXX orbitals. Because all terms in this Hamiltonian operator are invariant with respect to unitary transformations of the occupied orbitals among themselves the Hamiltonian operator remains unchanged if we replace the EXX orbitals by those ones that diagonalize the Hamiltonian operator (15). In this way, we have generated orbitals that are eigenstates of a Hamiltonian operator of the form of the Hartree–Fock operator which can be constructed using these orbitals. In other words, the new orbitals obtained are HF orbitals, and the Hamiltonian operator corresponding to the matrix (15) is the Hartree–Fock operator represented in the basis of the EXX orbitals. In practice, it turns out that the differences between the EXX and the HF determinants \( \Psi_{\text{HF}}^{\text{EXX}} \) and \( \phi_{\text{KS}}^{\text{EXX}} \), indeed, are very small, i.e., EXX and HF determinants are almost identical and their overlap is thus almost equal to one, i.e., the equation
\[ \langle \Psi_{\text{HF}}^{\text{EXX}} | \phi_{\text{KS}}^{\text{EXX}} \rangle = 1 \quad (18) \]
is obeyed very closely. In Table I, this is demonstrated by displaying the overlap \( \langle \Psi_{\text{HF}}^{\text{EXX}} | \phi_{\text{KS}}^{\text{EXX}} \rangle \) for a number of small molecules. It is thus a reasonable approximation to neglect the matrix elements \( \langle \phi_{\text{EXX}}^{\text{EXX}} | \phi_{\text{EXX}}^{\text{EXX}} \rangle \) between occupied and unoccupied EXX orbitals.

For later use, we now introduce matrices \( U_{\text{occ}} \) and \( U_{\text{unocc}} \) that transform EXX into HF orbitals and vice versa. To that end, we collect the eigenvectors of the matrix (15) in the columns of the matrix
\[ U = \begin{pmatrix} U_{\text{occ}} & 0 \\ 0 & U_{\text{unocc}} \end{pmatrix} \quad (19) \]
TABLE I
Deviation from unity of the overlap between the
HF determinant and the EXX and PBEx
(Perdew–Burke–Ernzerhof exchange density
functional) [107] determinants in units of 10−3.

<table>
<thead>
<tr>
<th>System</th>
<th>EXX</th>
<th>PBEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.01</td>
<td>1.94</td>
</tr>
<tr>
<td>H2O</td>
<td>0.12</td>
<td>2.72</td>
</tr>
<tr>
<td>NH3</td>
<td>0.20</td>
<td>2.51</td>
</tr>
<tr>
<td>CH4</td>
<td>0.36</td>
<td>1.83</td>
</tr>
<tr>
<td>CO</td>
<td>0.45</td>
<td>4.11</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.69</td>
<td>3.19</td>
</tr>
<tr>
<td>H2CO</td>
<td>0.69</td>
<td>4.73</td>
</tr>
</tbody>
</table>

The uncontracted triple zeta basis sets from [77, 108] were used.

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\[
\sum_{c} U_{ac}^{\text{unocc}} U_{bc}^{\text{unocc}} = \sum_{c} U_{ac}^{\text{occ}} U_{bc}^{\text{occ}} = \delta_{ab}
\]

is obtained.

3. Exact-Exchange TDDFT

Within the linear response (LR) TDDFT framework, excitation energies \( \Omega_n \) of electronic systems are given by the equation

\[
[e^2 + 4e^{1/2}K(\omega)e^{1/2}z_n = \Omega_n^2 z_n
\]

introduced by Casida [6, 10, 101, 109, 110]. The dimension of Eq. (25) is given by the product of the number of occupied times the number of unoccupied KS orbitals. In Eq. (25), the eigenvalue \( \Omega_n^2 \) equals the square of the excitation energy of the nth excited state. The eigenvectors \( z_n(\omega) \) determine the density–density (potential-density) response function

\[
\chi(r, r', \omega) = \sum_{n} \sum_{ia,jb} \frac{4(e_{ia}^2e_{jb}^{1/2})}{\omega^2 - \Omega_n^2} z_{i,ia}z_{j,ib}\phi_{ia}^{KS}(r)\phi_{jb}^{KS}(r')
\]

Here,

\[
K_{ia,jb}(\omega) = \int dr dr' \phi_{ia}^{KS}(r)\phi_{jb}^{KS}(r)f_{\text{aux}}(\omega, r, r') \phi_{ia}^{KS}(r')\phi_{jb}^{KS}(r')
\]

is the matrix representation of the sum of Coulomb and exchange-correlation kernel, which is frequency dependent [10, 98, 100], and

\[
e_{ia}^{KS} = \delta_{ia} + e_{ia}^{KS} = \delta_{ia} + (e_{ia}^{KS} - e_{ia}^{KS}),
\]

with \( e_{ia}^{KS} \) and \( e_{ia}^{KS} \) being eigenvalues of occupied and virtual KS orbitals, respectively. We here approximate \( f_{\text{aux}} \) as \( f_{\text{aux}} \), that is, we neglect the correlation contribution to the kernel but we treat the exchange contribution exactly. The Coulomb kernel is given as

\[
f_{cd}(r, r') = \frac{1}{|r - r'|}
\]

that is, its contribution to the kernel matrix elements is

\[
K_{ia,jb} = \int dr dr' \phi_{ia}^{KS}(r)\phi_{ia}^{KS}(r)\phi_{jb}^{KS}(r')\phi_{jb}^{KS}(r')
\]

\[
|r - r'|
\]
with

$$
\langle \alpha \beta | \gamma \delta \rangle = \int d\mathbf{r} d\mathbf{r}' \frac{\psi_\alpha(\mathbf{r}) \psi_\gamma(\mathbf{r}) \psi_\beta(\mathbf{r}') \psi_\delta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.
$$

The exchange kernel obeys the integral equation [74, 100]

$$
\hat{f}_e(\omega, \mathbf{r}, \mathbf{r}') = \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_e^{-1}(\omega, \mathbf{r}, \mathbf{r}_1) \hat{h}_e(\omega, \mathbf{r}_1, \mathbf{r}_2) \chi_e^{-1}(\omega, \mathbf{r}_2, \mathbf{r}')
$$

(32)

with the frequency-dependent KS response function given by

$$
\chi_e(\omega, \mathbf{r}, \mathbf{r}') = \sum_{i, a} \sum_{\text{occ}} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r}) \frac{4 \epsilon_a}{\omega^2 - \epsilon_a^2} \sum_{\text{occ}} \phi_a^{KS}(\mathbf{r}') \phi_i^{KS}(\mathbf{r}')
$$

$$
= \sum_i \sum_{a, \text{occ}} \Theta_{ia}(\mathbf{r}) \lambda_{ia}(\omega) \Theta_{ia}(\mathbf{r}')
$$

(33)

with

$$
\lambda_{ia}(\omega) = \frac{4 \epsilon_a}{\omega^2 - \epsilon_a^2}
$$

(34)

and the function $h_e(\omega, \mathbf{r}_1, \mathbf{r}_2)$ given by KS orbitals and eigenvalues.

The function $h_e$ is quite complicated and consists of various parts according to

$$
\hat{h}_e = \hat{h}^{(1)} + \hat{h}^{(2)} + \hat{h}^{(3)}.
$$

(35)

The contribution $h^{(1)}_e$ to the kernel is given by [100]

$$
\hat{h}^{(1)}_e(\omega, \mathbf{r}, \mathbf{r}') = \sum_{i, a} \sum_{\text{occ}} \sum_{\text{occ}} \frac{-4 \epsilon_a \epsilon_b - 4 \omega^2}{(\epsilon_a^2 - \omega^2)(\epsilon_b^2 - \omega^2)} \langle ia|jb\rangle^{KS} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r}) \phi_j^{KS}(\mathbf{r}') \phi_b^{KS}(\mathbf{r}')
$$

$$
+ \sum_{i, a, b} \frac{-4 \epsilon_a \epsilon_b + 4 \omega^2}{(\epsilon_a^2 - \omega^2)(\epsilon_b^2 - \omega^2)} \langle ia|jb\rangle^{KS} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r}) \phi_j^{KS}(\mathbf{r}') \phi_b^{KS}(\mathbf{r}')
$$

$$
\times \langle \alpha \beta | \gamma \delta \rangle
$$

(36)

and can be rewritten as

$$
\hat{h}^{(1)}_e(\omega, \mathbf{r}, \mathbf{r}') = -2 \sum_{i, a, b} \sum_{\text{occ}} \sum_{\text{occ}} \frac{\phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r})}{\epsilon_a - \omega} \frac{1}{\epsilon_a + \omega} \langle ia|jb\rangle^{KS}
$$

$$
\times \langle \alpha \beta | \gamma \delta \rangle
$$

$$
- 2 \sum_{i, a, b} \frac{\phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r})}{\epsilon_a - \omega} \frac{1}{\epsilon_a + \omega} \langle jb|ia\rangle^{KS}
$$

$$
\times \langle \alpha \beta | \gamma \delta \rangle
$$

$$
- 2 \sum_{i, a, b} \frac{\phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r})}{\epsilon_a - \omega} \frac{1}{\epsilon_a + \omega} \langle ab|ia\rangle^{KS}
$$

$$
\times \langle \alpha \beta | \gamma \delta \rangle
$$

$$
- 2 \sum_{i, a, b} \frac{\phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r})}{\epsilon_a - \omega} \frac{1}{\epsilon_a + \omega} \langle ab|ia\rangle^{KS}
$$

$$
\times \langle \alpha \beta | \gamma \delta \rangle
$$

$$
\times \frac{1}{\epsilon_b + \omega} \phi_j^{KS}(\mathbf{r}') \phi_b^{KS}(\mathbf{r}')
$$

(37)

The second term $h^{(2)}_e$ reads as [100]

$$
\hat{h}^{(2)}_e(\omega, \mathbf{r}, \mathbf{r}') = -2 \sum_{i, a} \sum_{\text{occ}} \left[ \phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r}) \frac{1}{\epsilon_a + \omega} \Delta V_{occ}^{occ}
$$

$$
\times \frac{1}{\epsilon_i + \omega} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}')
$$

$$
+ \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}) \frac{1}{\epsilon_i - \omega} \Delta V_{occ}^{unocc}
$$

$$
\times \frac{1}{\epsilon_i + \omega} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}')
$$

$$
+ 2 \sum_{i, a, b} \sum_{\text{occ}} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS}(\mathbf{r}) \phi_j^{KS}(\mathbf{r}) \frac{1}{\epsilon_i + \omega} \Delta V_{unocc}^{occ}
$$

$$
\times \frac{1}{\epsilon_b + \omega} \phi_j^{KS}(\mathbf{r}') \phi_b^{KS}(\mathbf{r}')
$$

$$
\times \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}) \frac{1}{\epsilon_i - \omega} \Delta V_{unocc}^{unocc}
$$

$$
\times \frac{1}{\epsilon_i + \omega} \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}')
$$

$$
+ \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}) \frac{1}{\epsilon_i + \omega} \Delta V_{unocc}^{occ}
$$

$$
\times \phi_i^{KS}(\mathbf{r}) \phi_a^{KS} (\mathbf{r}') \phi_j^{KS}(\mathbf{r}) \phi_b^{KS}(\mathbf{r}')
$$

(38)

where the matrix elements $\Delta V_{occ}^{occ}$ and $\Delta V_{unocc}^{unocc}$ are defined by (16) and (17), respectively.

The last term $\hat{h}^{(3)}_e$ [100] of $h_e$ contains matrix elements $\langle \psi_a^{KS} | \hat{\Omega}_{NL} - \hat{V}_x | \psi_b^{KS} \rangle$ that vanish if the condition (13) is assumed, i.e., if it is assumed that the HF and KS determinants are identical. If not neglected then these terms contribute very little [101]. For the further discussion, we will neglect $\hat{h}^{(3)}_e$.

Equation (32) shows that the construction of the exact-exchange kernel requires to apply twice the inverse of the frequency-dependent KS response...
function (33), which is not only computationally expensive but even more importantly leads to numerical instabilities [101–104].

4. An Alternative Form of the TDDFT-EXX Equation

We now consider a time-dependent density-functional response equation which is an alternative to the one usually used. Designating an external frequency-dependent perturbation potential by $\delta \nu_{ext}(r, \omega)$, the standard time-dependent density-functional response is given by

$$\int \left[ \delta(r - r') - \int dr'' dr'' \chi_a(r, r'', \omega) f_{ia}(r'', \omega) \right] \delta \rho(r, \omega) = \int dr' \chi_a(r, r', \omega) \delta \nu_{ext}(r', \omega) \quad (39)$$

where $f_{ia}$ is defined by Eqs. (29) and (32), and the response of the electron density by invoking the Runge-Gross theorem [111] can be expressed as

$$\delta \rho(r, \omega) = \int dr' \chi_a(r, r', \omega) \delta \nu_{ext}(r', \omega) \quad (40)$$

with $\delta \nu_a(r, \omega)$ being the response of the effective KS potential $\nu_a(r) = \nu_{ext}(r) + \nu_{1}(r) + \nu_{0}(r)$ [see Eq. (5)] to the external perturbation $\delta \nu_{ext}(r, \omega)$. Insertion of (40), (29), and (32) into (39) yields

$$\int dr \left[ \chi_a(r, r', \omega) - \int dr'' dr'' \chi_a(r, r'', \omega) \chi_a(r', r'', \omega) \right] = \int dr' \chi_a(r, r', \omega) \delta \nu_{ext}(r', \omega) \quad (41)$$

The frequency-dependent function $h_\omega$ in Eqs. (37) and (38) can be rewritten in the following form

$$h_\omega(r, r', \omega) = \sum_{i,j} \phi_i(r) \phi_j(r') \lambda_{ij} \chi_{ia, jb}(\omega) \lambda_{jb} \phi_i(r') \phi_j(r') \quad (42)$$

if the term $h^{(3)}$ of the function $h_\omega$ is neglected. In this case, the elements $X_{ia, jb}(\omega)$ are given as the sum of two terms $X^{(1)}_{ia, jb}(\omega)$ and $X^{(2)}_{ia, jb}(\omega)$ corresponding to $h^{(1)}_\omega$ and $h^{(2)}_\omega$:

$$X^{(1)}_{ia, jb}(\omega) = -\frac{1}{4} \left[ 1 + \frac{\omega^2}{\epsilon_{ia} \epsilon_{jb}} \right] (ia|jb) + \left[ 1 - \frac{\omega^2}{\epsilon_{ia} \epsilon_{jb}} \right] (ja|ib) \quad (43)$$

and

$$X^{(2)}_{ia, jb}(\omega) = \frac{1}{4} \left[ 1 + \frac{\omega^2}{\epsilon_{ia} \epsilon_{jb}} \right] \left( \delta_{ij} \Delta V_{unocc}^{\omega} - \delta_{ab} \Delta V_{occ}^{\omega} \right) \quad (44)$$

Note that in contrast to the original Eq. (39), the new Eq. (41) is an equation for the response $\delta \nu_a(r, \omega)$ of the effective KS potential and not for the response $\delta \rho(r, \omega)$ of the electron density. The advantage of Eq. (41) is that it no longer contains the exchange kernel $f_\omega$ but the function $h_\omega$ and therefore does not require the numerically problematic inversion of the response function (32).

Now Eq. (41) can be rewritten [101] as

$$\sum_i \Theta_i(r) \lambda_i(\omega) \left( \nu_i - \sum_j |C_{i,jb} - X_{i,jb}(\omega)| \lambda_{jb} \nu_j \right) = \sum_i \Theta_i(r) \lambda_i(\omega) \nu_{ext}^i \quad (45)$$

with $\Theta_i(r)$ defined in (12) and $C_{i,jb}$ defined as

$$C_{i,jb} = (ij|ab) \quad (46)$$

and with the definitions

$$\nu_i = \int dr \phi_i(r) \delta \nu_a(r, \omega) \phi_i(r)$$

$$\nu_{ext}^i = \int dr \phi_i(r) \delta \nu_{ext}(r, \omega) \phi_i(r) \quad (47)$$

We now cast Eq. (45) into a matrix eigenvalue equation of the same form as (25). To that end, we rewrite Eq. (45) as

$$\sum_i \Theta_i(r) \lambda_i(\omega) \nu_i - \frac{1}{4} \left[ \sum_j \left[ \delta_{ij} \omega^2 - \epsilon_i^2 \right] \left( \delta_{ij} \Delta V_{unocc}^{\omega} - \delta_{ab} \Delta V_{occ}^{\omega} \right) + 4 \epsilon^2 \left( C_{i,jb} - X_{i,jb}(\omega) \right) \nu_j \nu_j \right] = \sum_i \Theta_i(r) \lambda_i(\omega) \nu_{ext}^i \quad (48)$$

Introducing the auxiliary vectors $w(r, \omega)$ and $z(\omega)$ defined by

$$w(r, \omega) = e^{-1/2} \lambda(\omega) \Theta(r) \quad (49)$$

$$z(\omega) = e^{-1/2} \lambda(\omega) \nu'(\omega) \quad (50)$$
one can rewrite the Eq. (48) in the matrix form
\[
\mathbf{w}^T \omega^2 \mathbf{1} - \mathbf{e}^2 - 4 \mathbf{e}^{1/2} [\mathbf{C} + \mathbf{X}(\omega)] \mathbf{e}^{1/2} \mathbf{z}(\omega) = \mathbf{w}^T \mathbf{e}^{1/2} \mathbf{v}^{\text{ext}}(\omega). \tag{51}
\]

The vectors \( \mathbf{w} \) and \( \mathbf{v}^{\text{ext}} \) and the matrices \( \mathbf{e} \), \( \mathbf{C} \), \( \mathbf{X} \) are defined by their matrix elements given in Eqs. (47), (28), (46), (43), and (44), respectively, the matrix elements \( \lambda_{ab}(\omega) = \delta_{ab} \lambda_\omega(\omega) \) of the diagonal matrix \( \lambda(\omega) \) are defined in Eq. (34).

If the functions \( \mathbf{w}_n(r, \omega) \) were linearly independent \[101\] then Eq. (51) would reduce to
\[
(\omega^2 \mathbf{1} - \mathbf{e}^2 - 4 \mathbf{e}^{1/2} [\mathbf{C} + \mathbf{X}(\omega)] \mathbf{e}^{1/2} \mathbf{z}(\omega) = 4 \mathbf{e}^{1/2} \mathbf{v}^{\text{ext}}(\omega) \tag{52}
\]

The functions \( \mathbf{w}(r, \omega) \) actually are not linearly independent. Nevertheless, for the moment we pretend they were. Later on, we will briefly consider the effect of the fact that the functions \( \mathbf{w}(r, \omega) \) are linearly dependent.

As usual in the TDDFT linear response methods \[10, 11, 19\], excitation energies are determined by searching those values of \( \omega \) that yield an infinite vector \( \mathbf{z}(\omega) \) for a finite right-hand side of (52), i.e., an infinite response of the electron density corresponding to a pole of the density–density response function. This leads to the TDEXX eigenvalue equation
\[
(\mathbf{e}^2 + 4 \mathbf{e}^{1/2} [\mathbf{C} + \mathbf{X}(\omega)] \mathbf{e}^{1/2}) \mathbf{z}(\omega) = \Omega_n^2 \mathbf{z}(\omega) \tag{53}
\]
which is equivalent to the standard equation (25) if the matrix \( \mathbf{K}(\omega) \) that is defined by (27, 30, 32) is given by the sum of the matrices \( \mathbf{C} \) and \( \mathbf{X}(\omega) \). The matrix \( \mathbf{C} \) takes into account the contribution to the matrix \( \mathbf{K}(\omega) \) that originates from the Coulomb kernel (29), while the matrix \( \mathbf{X}(\omega) \) takes into account the contribution originating from the exact frequency-dependent exchange kernel. As mentioned earlier, the correlation contribution to the kernel is neglected.

To compare later on the TDEXX approach with the TDHF method, we rewrite (53) in the form
\[
\left( \mathbf{e} + \frac{1}{2} \mathbf{G}(\omega) \right) \left( \frac{1}{2} \mathbf{G}(\omega) \right) \mathbf{z}(\omega) = \Omega_n \mathbf{z}(\omega) \tag{54}
\]
that corresponds to the form of the TDHF equation. The matrix \( \mathbf{G}(\omega) \) in Eq. (54) is defined as
\[
\mathbf{G}(\omega) = 4(\mathbf{C} + \mathbf{X}(\omega)) \tag{55}
\]
and the vectors \( \mathbf{x}_n \), \( \mathbf{y}_n \), and \( \mathbf{z}_n \) are related by
\[
x_n = \frac{1}{2} (1 + \Omega_n) \mathbf{e}^{1/2} \mathbf{z}_n,
\]
\[
y_n = \frac{1}{2} (1 - \Omega_n) \mathbf{e}^{1/2} \mathbf{z}_n,
\]
and
\[
\mathbf{z}_n = \mathbf{e}^{-1/2} (\mathbf{x}_n + \mathbf{y}_n). \tag{57}
\]

As mentioned earlier, the functions \( \mathbf{w}(r) \) are not linearly independent. Therefore, Eq. (53) is not fully equivalent to Eq. (51) and therefore formally does not represent a proper density-functional response equation. To turn, in a formally strictly correct way, Eq. (51) into a matrix equation it has to be projected onto the space spanned by the products \( \delta_{\lambda \omega} \mathbf{e}^{1/2} \mathbf{v}^{\text{ext}}(\omega) \) building the vector \( \mathbf{w}(r) \) \[101\]. In this case, a matrix equation similar to Eq. (53) results, which, however, contains in addition projection matrices. We checked the effect of including such projection matrices and it turned out to be negligible for the low-lying excitations. We therefore do not consider such a projection any further in this work.

5. Relation Between TDHF and TDEXX

5.1. TRANSFORMATION OF HF INTO EXX ORBITALS IN THE TDHF EQUATION

When discussing the relation between TDEXX and TDHF, we neglect the difference between EXX and HF determinants, i.e., we assume that we can neglect the matrix elements \( \langle \phi_{\text{EXX}}^{\text{NL}} | \mathbf{e} | \phi_{\text{EXX}}^{\text{NL}} \rangle = \delta_{\lambda \omega} \mathbf{e}_{\lambda \omega}^{\text{HF}} \) between occupied and unoccupied EXX orbitals. The aforementioned comparison between EXX and HF determinants, see Table I, shows that this is justified.

The TDHF matrix equation with a dimension \( 2N_{\text{occ}}N_{\text{unocc}} \) equal to twice the product of the numbers \( N_{\text{occ}} \) times \( N_{\text{unocc}} \) of occupied and unoccupied orbitals, respectively, reads as \[10, 112, 113\]
\[
\begin{pmatrix}
\mathbf{e}^{\text{HF}} + \mathbf{A}^{\text{HF}} \mathbf{B}^{\text{HF}} \\
\mathbf{e}^{\text{HF}} + \mathbf{A}^{\text{HF}}
\end{pmatrix}
\begin{pmatrix}
\mathbf{x}\rangle^{\text{HF}} \\
\mathbf{y}\rangle^{\text{HF}}
\end{pmatrix}
= \Omega_n \begin{pmatrix}
\mathbf{x}_n^{\text{HF}} \\
\mathbf{y}_n^{\text{HF}}
\end{pmatrix} \tag{58}
\]
with the matrices \( \mathbf{e}^{\text{HF}} \), \( \mathbf{A}^{\text{HF}} \), and \( \mathbf{B}^{\text{HF}} \) defined as
\[
\epsilon_{\alpha \beta}^{\text{HF}} = \delta_{\alpha \beta} (\epsilon_{\alpha}^{\text{HF}} - \epsilon_{\beta}^{\text{HF}}) \equiv \epsilon_{\alpha}^{\text{HF}},
\]
\[
A_{\alpha \beta}^{\text{HF}} = 2 \langle \alpha \beta \rangle^{\text{HF}} - \langle \alpha \alpha \rangle^{\text{HF}} - \langle \beta \beta \rangle^{\text{HF}},
\]
\[
B_{\alpha \beta}^{\text{HF}} = 2 \langle \beta \alpha \rangle^{\text{HF}} - \langle \alpha \beta \rangle^{\text{HF}}. \tag{59}
\]
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In the considered case of closed-shell systems with real-valued orbitals, the matrices $\epsilon^{\text{HF}}$, $\mathbf{A}^{\text{HF}}$, and $\mathbf{B}^{\text{HF}}$ are hermitian and symmetric. The labels “HF” in (58) indicate that the matrix elements (59) and all quantities refer to Hartree–Fock orbitals $|\psi^{\text{HF}}\rangle$, i.e., the eigenfunctions of Eq. (2). The TDHF excitation energies are given by $\Omega^{\text{HF}}$.

Next, we define a unitary transformation matrix $\mathbf{V}$ of dimension $N_{\text{occ}}N_{\text{unocc}}$ as direct product of the unitary matrices $\mathbf{U}^{\text{occ}}$ and $\mathbf{U}^{\text{unocc}}$ (19, 21, 22) by

$$\mathbf{V} = \mathbf{U}^{\text{occ}} \otimes \mathbf{U}^{\text{unocc}}$$

or, equivalently, with respect to the matrix elements by

$$V_{ia,jb} = U_{ij}^{\text{occ}} U_{jb}^{\text{unocc}}$$

Because the matrices $\mathbf{U}^{\text{occ}}$ and $\mathbf{U}^{\text{unocc}}$ are unitary, see Eqs. (23) and (24), also the transformation matrix $\mathbf{V}$ is unitary as follows directly from

$$\sum_{ia} V_{ia,jb} V_{ia,kr} = \sum_{ia} U_{ia}^{\text{occ}} U_{jb}^{\text{unocc}} U_{ic}^{\text{occ}} U_{kc}^{\text{unocc}} = \delta_{jb} \delta_{kc} \equiv \delta_{kc,kr}$$

$$\sum_{ja} V_{ia,jb} V_{ja,kr} = \sum_{ja} U_{ia}^{\text{occ}} U_{jb}^{\text{unocc}} U_{ja}^{\text{occ}} U_{ja}^{\text{unocc}} = \delta_{jb} \delta_{jc} \equiv \delta_{ja,kc}$$

Taking into account Eq. (20), we can transform the diagonal matrix $\epsilon^{\text{HF}}$ containing on its diagonal the differences of occupied and unoccupied HF eigenvalues according to

$$\mathbf{V} \epsilon^{\text{HF}} \mathbf{V}^T = \epsilon^{\text{EXX}} + \Delta^{\text{EXX}}$$

with the matrix $\Delta^{\text{KS}}$ defined by its matrix elements

$$\Delta^{\text{EXX}}_{ia,ib} = \delta_{ij} \Delta V^{\text{unocc}}_{ab} - \delta_{ab} \Delta V^{\text{occ}}_{ai}$$

with $\Delta V^{\text{occ}}_{ab}$ and $\Delta V^{\text{unocc}}_{ab}$ given by Eqs. (16) and (17). The diagonal matrix $\epsilon^{\text{EXX}}$ contains on its diagonal differences of occupied and unoccupied EXX eigenvalues $\epsilon^{\text{EXX}}_a$ and $\epsilon^{\text{EXX}}_i$, respectively, i.e., its eigenvalues are given by

$$\epsilon^{\text{EXX}}_{ia,ib} = \delta_{ij} \delta_{ab} (\epsilon^{\text{EXX}}_a - \epsilon^{\text{EXX}}_i) \equiv \epsilon^{\text{EXX}}_{ia,ib}$$

Similarly, the coupling matrices $\mathbf{A}^{\text{HF}}$ and $\mathbf{B}^{\text{HF}}$ (59) satisfy the relations

$$\mathbf{V} \mathbf{A}^{\text{HF}} \mathbf{V}^T = \mathbf{A}^{\text{EXX}}$$

$$\mathbf{V} \mathbf{B}^{\text{HF}} \mathbf{V}^T = \mathbf{B}^{\text{EXX}}$$

The matrix elements of $\mathbf{A}^{\text{EXX}}$ of $\mathbf{B}^{\text{EXX}}$ in terms of orbitals have the same form as the matrices $\mathbf{A}^{\text{HF}}$ of $\mathbf{B}^{\text{HF}}$, see Eq. (59), however, the orbitals used to evaluate the matrix elements are EXX instead of HF orbitals, i.e.,

$$A^{\text{EXX}}_{ia,ib} = 2 (i |a|b) - (i |a|b)_{\text{EXX}}$$

$$B^{\text{EXX}}_{ia,ib} = 2 (i |a|b)_{\text{EXX}} - (i |a|b)_{\text{EXX}}.$$ (67)

If we transform the TDHF equation (58) using the matrix $\mathbf{V}$ according to

$$\begin{pmatrix} \mathbf{V} & 0 \\ 0 & \mathbf{V} \end{pmatrix} \begin{pmatrix} \epsilon^{\text{HF}} + \mathbf{A}^{\text{HF}} \\ \mathbf{B}^{\text{HF}} \end{pmatrix} \begin{pmatrix} \mathbf{V}^T & 0 \\ 0 & \mathbf{V}^T \end{pmatrix}$$

$$= \begin{pmatrix} \epsilon^{\text{EXX}} + \Delta^{\text{EXX}} + \mathbf{A}^{\text{EXX}} \\ \mathbf{B}^{\text{EXX}} \end{pmatrix} \begin{pmatrix} \mathbf{V}^{\text{EXX}} & 0 \\ 0 & \mathbf{V}^{\text{EXX}} \end{pmatrix}$$

$$= \Omega^{\text{HF}} \begin{pmatrix} \mathbf{x}^{\text{EXX}} \\ \mathbf{y}^{\text{EXX}} \end{pmatrix}$$

(68)

and use (63, 66) we obtain the TDHF equation expressed in terms of EXX orbitals

$$\begin{pmatrix} \epsilon^{\text{EXX}} + \Delta^{\text{EXX}} + \mathbf{A}^{\text{EXX}} \\ \mathbf{B}^{\text{EXX}} \end{pmatrix} \begin{pmatrix} \mathbf{x}^{\text{EXX}} \\ \mathbf{y}^{\text{EXX}} \end{pmatrix} = \Omega^{\text{HF}} \begin{pmatrix} \mathbf{x}^{\text{EXX}} \\ \mathbf{y}^{\text{EXX}} \end{pmatrix}$$

(69)

with

$$\begin{pmatrix} \mathbf{x}^{\text{EXX}} \\ \mathbf{y}^{\text{EXX}} \end{pmatrix} = \begin{pmatrix} \mathbf{V} & 0 \\ 0 & \mathbf{V} \end{pmatrix} \begin{pmatrix} \mathbf{x}^{\text{HF}} \\ \mathbf{y}^{\text{HF}} \end{pmatrix}.$$ (70)

Equation (69) enables one to effectively carry out TDHF calculations with EXX orbitals. An advantage of doing this may be that unoccupied EXX orbitals and their eigenvalues have a physical meaning. As a result, the vectors $\mathbf{x}^{\text{EXX}}$ and $\mathbf{y}^{\text{EXX}}$ can straightforwardly be used to characterize excitations, whereas this is problematic on the basis of the vectors $\mathbf{x}^{\text{HF}}$ and $\mathbf{y}^{\text{HF}}$, because the latter, in particular if large basis sets are used and excitations with Rydberg character are considered, contain a large number of contributions which cannot be assigned to physically meaningful transitions into unoccupied orbitals.

5.2. TDDFT-EXX TRANSFORMATION: ADIABATIC CASE

The matrix equation (69) can be decomposed into two coupled systems of linear equations. (For simplicity, the labels “KS” indicating that the matrix
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elements were calculated using EXX orbitals \( \{ \phi^{\text{EXX}} \} \) shall be omitted, i.e., \( \varepsilon \equiv \varepsilon^{\text{KS}} \), \( \Lambda \equiv \Lambda^{\text{KS}} \), \( \Lambda \equiv \Lambda^{\text{KS}} \) etc.

\[
\begin{align*}
(e + \Delta + A + B)(x_n + y_n) &= \Omega_n(x_n - y_n) \\
(e + \Delta + A - B)(x_n - y_n) &= \Omega_n(x_n + y_n)
\end{align*}
\]  

(71) \hspace{1cm} (72)

Equation (72) can be rewritten as

\[
(x_n - y_n) = \Omega_n(e + \Delta + A - B)^{-1}(x_n + y_n)
\]

(73)

and after substitution into the right-hand side of (71) one obtains

\[
(e + \Delta + A - B)(e + \Delta + A + B)(x_n + y_n) = \Omega_n^2(x_n + y_n)
\]

(74)

or

\[
(e + \Delta + A + B)(x_n + y_n) = \Omega_n^2(e + Q)^{-1}(x_n + y_n)
\]

(75)

with the “perturbation” matrix

\[
Q = \Delta + A - B.
\]

(76)

If the perturbation matrix is set to zero then we can rewrite Eq. (75) as

\[
(e^2 + e^{1/2}[\Delta + A + B]e^{1/2})e^{-1/2}(x_n + y_n) = \Omega_n^2e^{-1/2}(x_n + y_n)
\]

(77)

If we now take into account that

\[
\Delta + A + B = 4(C + X(\omega = 0))
\]

(78)

then we can write Eq. (77) as

\[
(e^2 + 4e^{1/2}[C + X(0)]e^{1/2})z_n = \Omega_n^2z_n
\]

(79)

with

\[
z_n = e^{-1/2}(x_n + y_n).
\]

(80)

This means we have recovered the TDEXX equation (53) in the adiabatic limit, that is the TDEXX equation for \( \omega = 0 \), i.e., the TDEXX equation with the adiabatic, frequency-independent exact-exchange kernel.

5.3. SMALL PERTURBATION: NONADIABATIC AND HALF-ADIABATIC CASES

In this subsection, we treat the \( Q \) (76) as a small perturbation. This means we exploit the relation

\[
Q = \Delta + A - B \ll \varepsilon
\]

(81)

which seems to be always true in practice, at least in all cases we considered so far. This means the inverse matrix on the right-hand side of (75) can be approximated by the first two terms of its Taylor series

\[
(Q + \varepsilon)^{-1} \approx e^{-1} - \varepsilon^{-1}Qe^{-1} + O(Q^2)
\]

(82)

Insertion of relation (82) into Eq. (75) leads to

\[
(e + \Delta + A + B + \Omega_n^2e^{-1}Qe^{-1})(x_n + y_n) = \Omega_n^2e^{-1}(x_n + y_n)
\]

(83)

or

\[
(e^2 + e^{1/2}[\Delta + A + B + \Omega_n^2e^{-1}Qe^{-1}]e^{1/2})e^{-1/2}(x_n + y_n)
\]

(84)

which reduces to the TDEXX equation (53) if we take into account that

\[
\Delta + A + B + \omega^2e^{-1}Qe^{-1} = (1 + e^{-1}\omega^2e^{-1})(\Delta + A) + (1 - e^{-1}\omega^2e^{-1})B
\]

(85)

and define again \( z_n = e^{-1/2}(x_n + y_n) \).

In summary, we have shown that the TDHF method leads to the considered TDEXX method if we assume that HF and EXX determinants are identical and if we replace the matrix \( (e + Q)^{-1} \) by its Taylor series up to first order in the perturbation matrix \( Q \). Consequently, the considered TDEXX method leads to the TDHF method if \( (e^{-1} - \varepsilon^{-1}Qe^{-1}) \) is replaced by \( (e + Q)^{-1} \) and HF and EXX determinants are assumed to be identical.

One important consequence of this result, following from the fact that TDHF describes CT excitations qualitatively correct, is that it shows by formal analytic arguments that CT excitations can be qualitatively correctly described by TDDFT response methods and that it is the approximation of the exchange kernel in conventional GGA-based TDDFT methods that is responsible for the problems of these methods to describe CT excitations.
The TDEXX equation needs to be solved iteratively with respect to the frequency $\omega$ that enters the kernel matrix $X(\omega)$. For each excitation, the frequency $\omega$ eventually needs to be identical to the considered excitation energy, i.e., $\omega = \Omega_i$. This means that the TDEXX equation is a nonlinear equation.

If the frequency $\omega$ is not determined completely self-consistent for each excitation but instead is set to the excitation energy resulting in the adiabatic TDEXX case, then we obtain an approach we shall denote half-adiabatic TDEXX method. The iterative determination of the frequency $\omega$ usually starts with $\omega = 0$, i.e., the adiabatic case. In the half-adiabatic TDEXX method, the iterative determination of $\omega$ is stopped after the first iteration step. The results we obtained with the half-adiabatic TDEXX method often agree even better with the TDHF results, than the fully “nonadiabatic,” i.e., the fully frequency-dependent, TDDFT method. A reason for this finding may be that errors introduced by the replacement of the total energy derivative discontinuity with respect to the frequency $\omega$ eventually needs to be identical to the contribution of the total energy derivative discontinuity with respect to the frequency $\omega$.

### 6. Charge-Transfer Excitation Energies With the TDEXX Method

Let us first analyze the asymptotic behavior of the CT excitation from the donor HOMO $\psi_i$ of one fragment to the acceptor LUMO $\psi_i$ of the other by considering the dominating contribution of the diagonal elements $ia, ia$ in Eq. (53) and neglecting the other excitations in the system. This single-pole approximation is assumed in the formal analysis, not in the calculations. With increase of the distance $R$ between the donor and acceptor atoms, the overlap between $\psi_i$ and $\psi_i$, and consequently the Coulomb matrix element $(ii|ia)$ approaches zero. Then from Eqs. (53) and (43) one obtains for the CT excitation energy $\Omega_{CT}$:

$$\Omega_{CT} = \varepsilon_{ia}^2 + \left(\varepsilon_{ia} + \frac{\Delta_{ia}}{\varepsilon_{ia}}\right)(\Delta_{ia} - \langle ia|ia\rangle) \quad (86)$$

with $\Delta_{ia} = \langle \psi_i | \hat{P}_{NL} | \psi_i \rangle - \langle \psi_i | \hat{V}_{NL} | \psi_i \rangle = \langle \psi_i | \hat{P}_{NL} | \psi_i \rangle - \hat{V}_i | \psi_i \rangle$ being the exchange contribution to the total energy derivative discontinuity with respect to the number of particles [42, 114], where the matrix element $\langle \psi_i | \hat{P}_{NL} | \psi_i \rangle - \hat{V}_i | \psi_i \rangle$ equals zero because $\psi_i$ is the HOMO [41, 115]. Depending on the frequency $\omega$ as a parameter of the TDEXX exact-exchange kernel $X(\omega)$ (43, 44, 53), one should consider three cases corresponding to adiabatic, half-adiabatic, and completely self-consistent nonadiabatic approaches. Given that the CT energy $\Omega_{CT}$ in Eq. (86) is frequency dependent, these three different cases considered lead to the following results [101] in the single pole approximation:

1. ATDEXX: adiabatic case ($\omega = 0$):

$$\Omega_{CT}^{(0)} = \varepsilon_{ia} + \frac{\Delta_{ia} - \langle ia|ia\rangle}{\varepsilon_{ia}} \quad (87)$$

2. TDEXX: half-adiabatic case ($\omega = \Omega_{CT}^{(1)}$):

$$\Omega_{CT}^{(1)} = \varepsilon_{ia} + \Delta_{ia} - \langle ia|ia\rangle \quad (88)$$

3. TDEXX: nonadiabatic case ($\omega = \Omega_{CT}$):

$$\Omega_{CT} = \varepsilon_{ia} + \frac{\Delta_{ia} - \langle ia|ia\rangle}{\varepsilon_{ia} - \Delta_{ia} + \langle ia|ia\rangle} \quad (89)$$

In the asymptotic limit of a large distance $R$ between the fragments, the integral $(\langle ii|ia\rangle)$ approaches $1/R$, and expanding the right-hand side of (87) and (89) in a Taylor series up to first order with respect to $(\Delta_{ia} - \langle ia|ia\rangle)/\varepsilon_{ia}$ one finally obtains

1. ATDEXX: adiabatic case ($\omega = 0$):

$$\Omega_{CT}^{(0)} \approx \varepsilon_{ia} + \frac{\Delta_{ia} - 1/R}{2}$$

2. TDEXX: half-adiabatic case ($\omega = \Omega_{CT}^{(1)}$):

$$\Omega_{CT}^{(1)} \approx \varepsilon_{ia} + \Delta_{ia} - 1/R \quad (91)$$

3. TDEXX: nonadiabatic case ($\omega = \Omega_{CT}$):

$$\Omega_{CT} \approx \varepsilon_{ia} + \Delta_{ia} - 1/R$$

where the right-hand side of Eqs. (91) and (92) is readily interpreted because $\varepsilon_{ia} - \varepsilon_i + \Delta_{ia}$ approximates the difference $I - A$ of the ionization potential and electron affinity. It can be observed that in first order, the fully nonadiabatic case equals the half-adiabatic case and both yield a CT excitation energy that behaves correctly with $R$ and contains a term approximating the difference between the ionization energy and electron affinity. One should note that the exchange contribution $\Delta_{ia}$ overestimates the true derivative discontinuity and therefore the quantity $(\Delta_{ia} - \langle ia|ia\rangle)/\varepsilon_{ia}$ is not that small.
the Taylor series of the right-hand side of (89) is completely converged in first order. Therefore, the fully nonadiabatic case shall lead to results differing somewhat from the partially nonadiabatic one due to the contribution of the high-order expansion terms. Correspondingly, the Taylor series of the adiabatic case (90) shows that it can be expected to lead to CT excitations that are too small and exhibit a too weak \( R \) dependence due to the factor of 1/2 in front of \( \Delta_{\omega} - 1/R \). This fact illustrates the important role of the frequency-dependent component of the exchange kernel in the calculations of molecular excitation spectra within the TDEXX approach.

### 7. Computational Details

We have calculated excitation energies within the TDEXX method for three molecular systems, namely the \( \text{H}_2-\text{CO} \) dimer, the \( \text{N}_2 \) molecule, and the \( \text{C}_2\text{H}_4 \) (ethylene) molecule. In the case of the \( \text{H}_2-\text{CO} \) dimer, a parallel orientation of the \( \text{H}_2 \) and the \( \text{CO} \) molecule has been used with a distance axis that goes perpendicularly through the bond centers of each molecular bond. The bond lengths used are \( \text{H}_2: 1.394 \ a_0 \), \( \text{CO} : 2.152 \ a_0, \text{N}_2: 2.068 \ a_0, \) and \( \text{C}_2\text{H}_4: 2.519 \ a_0 \) (C–C) and \( 2.043 \ a_0 \) (C–H). In case of the ethylene molecule, a \( \text{H}–\text{C}–\text{H} \) bond angle of \( 117.347^\circ \) has been used.

The calculations of the excitation energies were done in two steps: first stable OEP-EXX calculations were performed for each system with the method and the balanced triple-zeta orbital and auxiliary basis sets described in Ref. [77]. The local EXX exchange potential, which is represented in the corresponding auxiliary basis set, obtained from these calculations has then been used in subsequent ground-state EXX calculations for smaller basis sets, i.e., it has been kept fixed during the self-consistent iterations and only the Coulomb potential was variationally optimized. The EXX orbitals and eigenvalues calculated with these smaller basis sets were then used to determine the excitation energies with the TDEXX method described in Section 4.

For the \( \text{H}_2-\text{CO} \) dimer, the cc-pVTZ basis set from Dunning and coworkers [108, 116] has been used for the TDEXX calculations, whereas for \( \text{N}_2 \) and \( \text{CO} \), we have used three types of basis sets with increasing quality, namely the aug-cc-pVTZ basis set from Dunning and coworkers [108, 116], the uncontracted C,N [14s9p3d], H [9s5p1d] basis sets from Hirata et al. [102], and the uncontracted basis sets from Ref. [77] augmented with two additional diffuse s- and p-type basis functions for each atom.

In addition to the calculation of the ‘full nonadiabatic’ (53) TDEXX (\( \omega = \Omega_n \)) excitation energies we have also done the calculations with five approximate TDEXX approaches:

- EXX(unc): uncoupled TDEXX method with the coupling matrix \( K(\omega) \) in (25) being set to zero, i.e., within the single-particle EXX approach.
- ATDEXX: adiabatic TDEXX method with the frequency-dependent part of the EXX kernel (43, 44) neglected.
- TDEXX(\( \omega_{\text{adiab}} \)): half-adiabatic TDEXX method in which the eigenvalues of the full TDEXX hessian matrix are determined for the frequencies obtained from the ATDEXX approach (\( \omega = \Omega_n^{\text{adiab}} \)).
- TDHF(EXX): hybrid method based on the TDDFT-EXX equation (69) defined in the Section 5.1.
- EXX/ALDA: TDDFT approach using EXX orbitals and eigenvalues and the adiabatic local density approximation (ALDA) exchange-correlation kernel [117].

For comparison we have also calculated the excitation energies with TDHF, TDDFT using the Perdew–Burke–Ernzerhof exchange-correlation functional and kernel (PBE) [107] and, in case of the \( \text{H}_2-\text{CO} \) dimer, equation-of-motion coupled cluster singles doubles (EOM-CCSD) [118]. All calculations were performed using the Molpro quantum chemistry package [121] with exception of the TDDFT/PBE calculations which were done using the Turbomole program [122].

### 8. Results and Discussion

#### 8.1. CT Excitation in the \( \text{H}_2-\text{CO} \) Dimer

In the \( \text{H}_2-\text{CO} \) dimer, we have considered the CT excitation from the HOMO orbital of the \( \text{CO} \) molecule to the LUMO (\( \sigma_u \)) orbital of \( \text{H}_2 \). The asymptotic behavior of the excitation energy has been studied by calculations performed for different distances between the bond centers of the molecules.

The corresponding excitation energy curves are shown in Figure 1. One can see that the ATDEXX method does not possess the correct \( 1/R \) distance behavior of the TDHF curve but exhibits the asymptotic dependence of \( 1/(2R) \), in line with the single-pole approximation analysis (90) of Section 6. On the other hand, the full nonadiabatic TDEXX curve overestimates the TDHF values. The reason for this is that...
TDDFT WITH THE NONADIABATIC EXACT EXCHANGE KERNEL

FIGURE 1. CO(HOMO) → H2(LUMO) charge-transfer excitation energies calculated using time-dependent Hartree–Fock (TDHF), different time-dependent exact exchange methods (ATDEXX for \( \omega = 0 \), TDEXX for \( \omega = \Omega^{(0)} \) and TDEXX for \( \omega = \Omega \)), time-dependent DFT with Perdew-Burke-Ernzerhof xc potential and kernel [107] (PBE), and equation-of-motion coupled cluster singles and doubles (EOM-CCSD). The geometry corresponds to a parallel orientation of the H2–CO dimer with a distance axis that goes perpendicularly through the bond centers of each molecular bond. The distance between the H2 and CO molecule is measured by the distance between the bond centers of both molecules. Calculations were done using the cc-pVTZ basis set from Dunning and coworkers [108, 116].

shown in the plot, as expected does not possess any distance behavior and largely underestimates the magnitude of the CT excitation. Actually it was found that the TDDFT-PBE CT excitation energy is identical to the eigenvalue difference between the CO-HOMO and the H2-LUMO orbital [14, 19, 65]. The EOM-CCSD curve possesses the same distance behavior as the TDHF and TDEXX(\( \omega_{\text{adiab}} \)) plot but lies slightly lower. This relative energy shift arises from the many-particle correlations that are not taken into account within the TDHF and the TDEXX approaches.

8.2. VALENCE EXCITATIONS IN THE N2 AND THE C2H4 MOLECULES

It is important to note that the theoretical approach being discussed can be used not only for

FIGURE 2. Frequency dependence of the \( ^1\Delta_u \) and \( ^1\Pi_g \) excitation energies of the N2 molecule calculated using the time-dependent exact exchange (TDEXX) approach for exchange kernels \( l_k(\omega) \) with varying frequencies \( \omega \). The corresponding time-dependent Hartree–Fock (TDHF) results are shown by thin solid lines. The half-adiabatic TDEXX (\( \omega = \Omega^{(0)} \)) excitation energies are marked by white circles, whereas the full TDEXX excitation energies correspond to intersections with the bisectrix (\( \Omega(\omega) = \omega \)) are given by the dotted line. Calculations were done using the aug-cc-pVQZ basis set from Dunning and coworkers [108, 116].
the case of CT excitations in molecules. In Figure 2, we represent the dependencies of the excitation energies on the frequency \( \omega \) in the exchange kernel \( f_x(\omega) \) for the two low excited states \( ^1\Delta_u \) and \( ^1\Pi_u \) of the \( \text{N}_2 \) molecule using the Dunning’s aug-cc-pVTZ basis set [108, 116]. On the same plot, the values of the corresponding TDHF transition energies are presented. As one can see, the values \( \Omega^{(\omega)} \) obtained are in a good agreement with the TDHF frequencies shown by the thin solid lines for both transitions. One should pay attention to the fact that within the proposed approach for the description of excited states in many-electron systems that accounts only for exchange interactions using a frequency-dependent kernel, one cannot expect to obtain valence excitation energies that surpass the accuracy of TDHF. In particular, within the TDEXX framework, the inter-electron correlations that affect the optical properties of a many-particle system [10, 111, 116] were not taken into account.

In Table II, the transition energies (in eV) for four excited states in the \( \text{N}_2 \) molecule are presented. The frequencies obtained within the TDEXX approach are compared with TDHF calculations, with TDDFT using PBE and LDA functionals, the adiabatic OEP (AOEP) results from Hirata et al. [102] and with experimental data [102, 119]. The TDEXX calculations were performed using three different basis sets with increasing quality to analyze the basis set dependence of each excitation. As seen in Table II, all excitations considered are well converged already with the standard aug-cc-pVTZ basis set with exception of the \( \Sigma^+_u \) transition, which is overestimated by about 0.7 eV with TDHF/aug-cc-pVTZ if compared with the large uncontracted basis set result given in the third row of the table. Because of this we will only consider the results with the largest basis set in the further discussion.

As seen in the table, the results for \( ^1\Pi_u, ^1\Delta_u \), and \( \Sigma^+_u \) by TDEXX and TDHF are in good agreement with one another for both the TDEXX and the TDEXX(\( \omega \)adab) methods, which means that the frequency dependence of the excitation energies is relatively weak for the transitions considered here (see also Fig. 2).

A good agreement with TDHF is also found for the hybrid TDHF(EXX) method while the EXX/ALDA excitation energies show clear differences from the TDEXX results. This illustrates the important role of the exchange-correlation kernel for the considered transitions and this can also be seen by a comparison of the TDEXX excitation energies with the EXX(unc) results in Table II that are equal to the corresponding orbital energy differences.

### Table II

Singlet excitation energies of the \( \text{N}_2 \) molecule (in eV).

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>( \Pi_g )</th>
<th>( \Sigma_u )</th>
<th>( \Delta_u )</th>
<th>( \Sigma^+_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDHF</td>
<td>1(^b)</td>
<td>9.76</td>
<td>7.94</td>
<td>8.76</td>
<td>14.71</td>
</tr>
<tr>
<td></td>
<td>2(^c)</td>
<td>9.80</td>
<td>7.93</td>
<td>8.77</td>
<td>14.03</td>
</tr>
<tr>
<td></td>
<td>3(^d)</td>
<td>9.76</td>
<td>7.94</td>
<td>8.75</td>
<td>13.99</td>
</tr>
<tr>
<td>EXX(unc)</td>
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<td>10.19</td>
<td>10.19</td>
<td>12.86</td>
</tr>
<tr>
<td></td>
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<td>10.18</td>
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<tr>
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<td>10.18</td>
<td>10.18</td>
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<td>—</td>
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</tr>
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<td>—</td>
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<tr>
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<td>3</td>
<td>9.86</td>
<td>—</td>
<td>8.34</td>
<td>13.34</td>
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<td>—</td>
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<td>—</td>
<td>8.74</td>
<td>13.95</td>
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<td>EXX/ALDA</td>
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<td>—</td>
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<td>—</td>
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<td>—</td>
<td>10.70</td>
<td>12.69</td>
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<td>10.09</td>
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<td>—</td>
<td>10.09</td>
<td>10.32</td>
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<td>—</td>
<td>10.09</td>
<td>10.24</td>
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<tr>
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<td>—</td>
<td>10.26</td>
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<td>—</td>
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<td>Expt.(^g)</td>
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<td>9.31</td>
<td>9.92</td>
<td>10.27</td>
<td>12.2</td>
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</table>

\(^a\)This excitation cannot be described by the TDDFT method in the response regime [104].
\(^b\)aug-cc-pVTZ basis set.
\(^c\)Uncontracted [14s9p3d] basis set from Hirata et al. [102].
\(^d\)Uncontracted [14s9p5d3f] basis set from Ref. [77] + two diffuse s,p-functions.
\(^e\)Ref. [102].
\(^f\)6-311+(3s,3p)G** (cartesian d-functions).
\(^g\)Ref. [119].
TABLE III
Singlet excitation energies of the C2H4 molecule (in eV).

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>B_{3u}</th>
<th>B_{1u}</th>
<th>B_{1g}</th>
<th>B_{2g}</th>
<th>A_{g}</th>
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<td>TDHF</td>
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<td>7.38</td>
<td>7.73</td>
<td>7.90</td>
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<tr>
<td></td>
<td>2\textsuperscript{b}</td>
<td>7.11</td>
<td>7.37</td>
<td>7.70</td>
<td>7.86</td>
<td>8.07</td>
</tr>
<tr>
<td></td>
<td>3\textsuperscript{c}</td>
<td>7.12</td>
<td>7.37</td>
<td>7.71</td>
<td>7.87</td>
<td>8.07</td>
</tr>
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\textsuperscript{a} aug-cc-pVTZ basis set.
\textsuperscript{b} Uncontracted [14s9p3d] basis set from Hirata et al. [102].
\textsuperscript{c} Uncontracted C[14s9p5d3f],H[8s5p3d] basis set from Ref. [77] + two diffuse s,p-functions.
\textsuperscript{d} Ref. [74].
\textsuperscript{e} Sadlej basis set, C(10s6p4d)/[5s3p2d], H(6s4p)/[3s2p].
\textsuperscript{f} Ref. [120].

Suppose that this discrepancy results from different procedures used for the ground-state EXX calculations and also from numerical instabilities caused by the auxiliary basis set approach of the AOEP method used in Ref. [102].

In Table III, the five lowest excitation energies of the ethylene molecule are shown for various approaches. As in the previous case of N_{2}, the presented results illustrate the importance of the basis set quality. For instance, for the A_{g} excitation, the energy reduces by \sim 0.5 eV with increasing quality of the basis set size for all methods. One can see that there is almost no coupling matrix effect to all excitations with exception of the B_{1u} transition, i.e., for all other excitations considered the differences between the approaches taking into account the TDEXX kernel and the single-particle ("uncoupled") EXX case is very small. For the lowest excitations presented the EXX(unc) results are in a good agreement with the experimental data shown in the last line in Table III, with exception of the B_{1u} case, where the difference with the experimental frequency amounts to \sim 1.7 eV. This discrepancy is largely corrected in all TDEXX approaches. In particular, within the nonadiabatic approaches, TDEXX and TDEXX(ω_{adiab}), the deviation from the experimental value is reduced to \sim 0.3 eV only.

While in the case of the lowest excitation energies of the C_{2}H_{4} molecule, the various TDEXX approaches (including TDHF(EXX) and EXX/ALDA) yield very close results, one can observe clear differences to both TDDFT-LDA and TDDFT-PBE data shown in Table III. In fact, for all five excitations, the energies obtained within the TDEXX and TDHF frameworks are closer to the experimental data than those from the standard TDDFT approaches. This is in contrast to the case of the N_{2} molecule where a good agreement between the PBE results and the experiment was found (Table II).

Finally, it should be noted that the hybrid TDHF(EXX) approach introduced in the Section 5 of this work reproduced the TDHF results with a good accuracy for all excitations that were calculated (Tables II and III). This in addition to the overlap values presented in Table I demonstrates the validity of the approximation (18), i.e., the approximation that EXX and HF determinants are almost identical, on which the hybrid TDHF(EXX) method is based on.

9. Summary

In summary, we have discussed a TDDFT response method that takes into account exchange interactions exactly by using the exact nonadiabatic, i.e., frequency-dependent, exchange kernel. It was shown that based on an equation for the response of the effective KS potential, Eq. (41), instead of the response of the electron density, Eq. (39), numerically stable density-functional response methods with orbital-dependent kernels are feasible. This alternative formulation of the TDDFT response problem avoids numerically demanding inversions of KS response functions. At the exact-exchange level, i.e., by using the frequency-dependent exact-exchange kernel, it turned out to be possible to describe CT excitations within a TDDFT framework. We note that the presented exact-exchange
DFT response approach fundamentally differs from TDHF because it is a nonlinear approach due to its frequency-dependent kernel. Technically, this is a disadvantage because a solution of the equation requires more effort due to the described iteration process. On the other hand, this has the formal advantage that the number of possible solutions is not restricted to the dimension of the TDEXX matrix equation, i.e., the number of possible solutions is not restricted to the product of the numbers of occupied and unoccupied orbitals. Because there are more excitations than there are products of occupied times unoccupied orbitals, there is at least the chance that TDEXX methods might yield solutions not accessible in conventional TDDFT response methods. Whether this is actually the case needs to be considered in further investigations.

The relation of the presented TDEXX approach to the TDHF method and the role of the frequency dependence of the exact-exchange kernel was analyzed. It was shown that CT excitation energies obtained within an adiabatic TDEXX approach exhibit a distinct long-range behavior with the distance \( R \) between the fragments involved in the CT, which, however, is a factor of two too small. This demonstrates the importance of a proper treatment of the frequency in the exchange kernel for a correct description of charge-transfer excitations. It was shown that the TDHF and the TDEXX method are closely related. Indeed, one can obtain one from the other by a transformation if differences between the HF and EXX determinants are neglected and differences of matrix elements are assumed to be small when compared with eigenvalues differences between occupied and unoccupied orbitals. This explains from a formal point of view why TDEXX methods are able to describe CT excitations qualitatively correctly. The results for typical valence-type excitations of \( \text{N}_2 \) and \( \text{C}_2\text{H}_4 \) molecules demonstrate that the TDEXX methods based on nonadiabatic exchange kernels generally yield excitation energies close to those obtained with the TDHF method. A further improvement of the method that should account for correlation interactions is therefore required to be able to predict excitation energies that are closer to experimental results.

**Acknowledgments**

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**References**

TDDFT WITH THE NONADIABATIC EXACT EXCHANGE KERNEL

12. **Time-dependent density functional theory**

IPATOV, HEßELMANN, AND GÖRLING

12.6. Efficient exact-exchange TDDFT methods and their relation to TDHF

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- time-dependent Hartree-Fock
- exact exchange kernel
- Rydberg excitation
- valence excitation
- ethylene
- acetaldehyde
- pyridine
- response function
Efficient exact-exchange time-dependent density-functional theory methods and their relation to time-dependent Hartree–Fock

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A recently introduced time-dependent exact-exchange (TDEXX) method, i.e., a response method based on time-dependent density-functional theory that treats the frequency-dependent exchange kernel exactly, is reformulated. In the reformulated version of the TDEXX method electronic excitation energies can be calculated by solving a linear generalized eigenvalue problem while in the original version of the TDEXX method a laborious frequency iteration is required in the calculation of each excitation energy. The lowest eigenvalues of the new TDEXX eigenvalue equation corresponding to the lowest excitation energies can be efficiently obtained by, e.g., a version of the Davidson algorithm appropriate for generalized eigenvalue problems. Alternatively, with the help of a series expansion of the new TDEXX eigenvalue equation, standard eigensolvers for large regular eigenvalue problems, e.g., the standard Davidson algorithm, can be used to efficiently calculate the lowest excitation energies. With the help of the series expansion as well, the relation between the TDEXX method and time-dependent Hartree–Fock is analyzed. Several ways to take into account correlation in addition to the exact treatment of exchange in the TDEXX method are discussed, e.g., a scaling of the Kohn–Sham eigenvalues, the inclusion of (semi)local approximate correlation potentials, or hybrids of the exact-exchange kernel with kernels within the adiabatic local density approximation. The lowest lying excitations of the molecules ethylene, acetaldehyde, and pyridine are considered as examples.


I. INTRODUCTION

Methods based on time-dependent density-functional theory (TDDFT), more precisely time-dependent density-functional response methods, at present, are probably the most widely used methods to describe electronically excited states of molecules. Despite their widespread usage conventional TDDFT response methods, i.e., TDDFT response methods based on approximate exchange-correlation functionals employing the local density approximation (LDA) or generalized gradient approximations (GGAs), suffer from a whole list of severe shortcomings.

(i) Excitations with charge-transfer character cannot be described correctly. Charge-transfer excitations are calculated at much too low energies and therefore appear in the wrong region of the excitation spectrum. In case of charge transfer excitations between two fragments the behavior of the charge-transfer excitation energy with the distance of the fragments is qualitatively wrong. This not only makes the calculation of charge-transfer excitations impossible with conventional TDDFT response methods but also can impair the description of simple valence-valence excitations because the charge-transfer excitations erroneously occur in the same energy region and may even interact with the former or with excitations of some charge-transfer character.

(ii) Excitations into states with Rydberg character cannot be calculated exactly. This problem arises from the fact that the orbital and eigenvalue spectrum of conventional Kohn–Sham (KS) methods is qualitatively wrong and does not contain Rydberg orbitals. Because KS orbitals and eigenvalues are the input data of density-functional response methods it is not surprising that conventional TDDFT response methods cannot describe Rydberg excitations. Indeed, excitation energies from density-functional response methods in many cases, including the case of Rydberg excitations, can be considered as KS eigenvalue differences plus a correction given by the density-functional response method.

(iii) Excitation energies of long chain-like aromatic molecules are systematically underestimated by conventional TDDFT response methods.

(iv) Excitation energies that, in a one-electron picture, can be characterized as two-electron excitations, cannot be treated in conventional TDDFT response methods. It has, however, been reported that standard TDDFT methods, to some extent, are capable to describe double excited states in contrast to the configuration interaction singles method. Nevertheless, there has been quite some effort in recent years to extend TDDFT methods to multielectron excitations.

(v) Even for simple valence-valence excitation energies the accuracy of conventional TDDFT response methods is quite limited, deviations from experiment of up to half an electron volt are not uncommon if nonhybrid functionals are used. With hybrid functionals this problem is often less severe, however, even with hybrid functionals the high lying core excitations are considerably underestimated due to self-interaction errors.

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One way to overcome some of the problems of conventional TDDFT response methods is to go beyond LDA and GGA exchange-correlation functionals, and to turn to density-functional methods with orbital-dependent functionals, in particular to methods that treat the exchange exactly. Such exact-exchange (EXX) KS and TDDFT response methods must not be confused with Hartree–Fock (HF) and time-dependent Hartree–Fock (TDHF) methods. In HF as well as EXX methods exchange is treated exactly according to the respective definitions. However, these definitions are different. This most obviously shows up in the exchange potential which is a nonlocal potential in the case of HF and a local multiplicative potential in the case of EXX. A recently introduced time-dependent exact-exchange (TDEXX) response method, i.e., a density-functional response method that is based on EXX orbitals and eigenvalues and employs the exact frequency-dependent exchange kernel, solves the problems (i), (ii), and (iii) of the above list. The exchange-correlation kernel is the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density and is the density-functional occurring in linear density-functional response methods. In conventional density-functional response methods the frequency dependence of the kernel is neglected (an approximation called the adiabatic approximation) and the kernel is obtained simply as the derivative of LDA and GGA exchange-correlation potentials with respect to the electron density.

The problem of treating two-electron excitations, problem (iv) of the above list, is not solved by the recently introduced TDEXX response methods. However, in many cases this problem does not show up and an efficient TDDFT response method that solves all the other listed shortcomings would be a great step forward. In the recently introduced TDEXX response method electron correlation was completely neglected, although it is straightforward to include correlation at the LDA or GGA level. Excitation energies from an exchange-only TDEXX response method are similar to those from TDHF. TDHF like TDEXX does not suffer from shortcomings (i), (ii), and (iii). However, both TDHF and exchange-only TDEXX excitations energies are not very accurate, indeed, for valence-valence excitations they are often less accurate than conventional TDDFT excitations energies. A further disadvantage of the recently presented TDEXX procedure is that it is computationally much more demanding than TDHF and conventional TDDFT methods because it does not only require the determination of the lowest eigenvalues of a linear eigenvalue problem. Instead, due to the frequency dependence of the exact-exchange kernel, separately for each excitation, a nonlinear eigenvalue problem has to be iteratively solved.

In order to turn the TDEXX procedure of Refs. 37–39 into an efficient, generally applicable, and sufficiently accurate approach, two tasks have to be tackled. The efficiency has to be increased and the accuracy has to be improved. In this work we focus, for the most part, on the first task and introduce a linear TDEXX procedure that requires similar computational effort than conventional TDDFT or TDHF response methods. To this end, firstly, we convert the basic nonlinear TDEXX eigenvalue problem into a linear generalized eigenvalue problem. Then, in a second step, we present strategies to solve this generalized eigenvalue problem by efficient procedures like the Davidson algorithm, which is frequently employed in conventional TDDFT and TDHF methods. Indeed, the presented TDEXX procedure can be straightforwardly implemented in any computer code containing a TDHF module. With the TDEXX procedure presented here, one of the two above tasks on the way to an efficient, generally applicable, and accurate TDDFT method has been solved. Some information concerning the second task, the improvement of accuracy, is given in this work by considering how modifications of the KS eigenvalue spectrum and the inclusion of correlation at the LDA and GGA level in the KS potential and in the kernel of the actual TDDFT calculation influences the performance of TDEXX response methods.

The reformulation of the TDEXX equation introduced here facilitates a comparison of TDEXX and TDHF methods. We therefore discuss the relations between the two methods.

The article is organized as follows. In Sec. II on formalism, we first briefly review the derivation of a response equation for the effective KS potential that is better suited to deal with orbital-dependent exchange-correlation kernels than the standard TDDFT response equation for the electron density. Then the TDEXX equation underlying the TDEXX procedure of Ref. 37 is reconsidered. Next, the original TDEXX equation is reformulated, efficient methods to solve it are presented, and the relation to the basic equation of TDHF is discussed. Section III describes the computational details. In Sec. IV results for the test molecules ethylene, acetaldehyde, and pyridine are presented and the influence of modifications of the KS eigenvalue spectrum and the inclusion of LDA and GGA correlation is briefly investigated. In Sec. V concluding remarks are made.

II. FORMALISM

A. Response equation for the effective Kohn–Sham potential, TDEXX

We consider the linear response \( \rho^{(1)}(\omega, \mathbf{r}) \) of the electron density of an electronic system that is initially in its ground state to a time-dependent external perturbation \( v^{(1)}(\omega, \mathbf{r}) \) of frequency \( \omega \). The perturbation \( v^{(1)}(\omega, \mathbf{r}) \) has to be a local multiplicative potential in order to stay within the formal framework of density-functional theory. Within the time-dependent KS formalism this linear response of the electron density is determined with the help of the KS model system and is given by

\[
\rho^{(1)}(\omega, \mathbf{r}) = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') v^{(1)}(\omega, \mathbf{r}') .
\]  

In Eq. (1) \( \chi_s \) is the KS response function

\[
\chi_s(\omega, \mathbf{r}, \mathbf{r}') = \sum_{i} \sum_{\alpha} \phi_{i\alpha}(\mathbf{r}) \lambda_{i\alpha}(\omega) \phi_{i\alpha}(\mathbf{r}')
\]

containing products \( \phi_{i\alpha}(\mathbf{r}) = \phi_i(\mathbf{r}) \phi_{\alpha}(\mathbf{r}) \) of occupied times unoccupied KS orbitals \( \phi_i \) and \( \phi_{\alpha} \), respectively. Throughout the manuscript we consider non-spin-polarized electronic
systems with real-valued KS orbitals. The factors $\lambda_{ia}(\omega)$ in the KS response function $\chi_s$, Eq. (2), are given by

$$\lambda_{ia}(\omega) = 4s_{ia}/(\omega^2 - s_{ia}^2),$$

with $s_{ia} = e_a - e_i$ denoting differences of the KS eigenvalues $e_a$ and $e_i$ of unoccupied and occupied KS orbitals, respectively. Throughout, indices $i, j$ denote occupied and indices $a, b$ denote unoccupied orbitals.

The first order change $v_1^{(1)}(\omega, \mathbf{r}')$ of the effective KS potential occurring in Eq. (1) corresponds to the applied external perturbation $v_1^{(1)}(\omega, \mathbf{r}')$. This first order change of the effective KS potential is given by

$$v_1^{(1)}(\omega, \mathbf{r}') = v_1^{(1)}(\omega, \mathbf{r}') + \int d\mathbf{r}'' f_{\text{HC}}(\omega, \mathbf{r}', \mathbf{r}'') \rho_1^{(1)}(\omega, \mathbf{r}''),$$

with $f_{\text{HC}}$ denoting the sum of the Coulomb (Hartree) kernel

$$f_{\text{HC}}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

and the exchange-correlation kernel $f_{\text{xc}}$, which is the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density. By inserting Eq. (4) into Eq. (1) and rearranging terms, the basic equation of time-dependent density-functional response theory is obtained,1,2

$$\int d\mathbf{r}' \left[ \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}'' \chi_s(\omega, \mathbf{r}, \mathbf{r}') f_{\text{HC}}(\omega, \mathbf{r}', \mathbf{r}'') \right] \times \rho_1^{(1)}(\omega, \mathbf{r}') = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') v_1^{(1)}(\omega, \mathbf{r}') = 0.$$  

Equation (5) can be directly derived45 from the Runge–Gross theorem,46 the basic theorem underlying TD-DFT, without recourse to the action formalism, which requires great caution from a formal point of view47,48 in the context of density-functional response theory.

From now on, we will concentrate on the exchange contribution $f_e$ of the exchange-correlation kernel and neglect the correlation contribution. However, including the latter contribution at the LDA or GGA level is straightforward. The exact frequency-dependent exchange kernel obeys the integral equation

$$f_e(\omega, \mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' d\mathbf{r}''' \chi_s^{-1}(\omega, \mathbf{r}, \mathbf{r}'') \times h_s(\omega, \mathbf{r}'', \mathbf{r}''') \chi_s^{-1}(\omega, \mathbf{r}'', \mathbf{r}').$$

The function $h_s$ in Eq. (6) (see Appendix A or Refs. 38 and 40–43) can be decomposed into two contributions. The dominant one is given by

$$h_s(\omega, \mathbf{r}, \mathbf{r}') = \sum \varphi_{ia}(\mathbf{r}) \lambda_{ia}(\omega) X_{ia,jb}(\omega) \lambda_{jb}(\omega) \varphi_{jb}(\mathbf{r}'),$$

12. Time-dependent density functional theory

with

$$X_{ia,jb}(\omega) = \frac{1}{2} (A_{ia,jb} + B_{ia,jb} + \Delta_{ia,jb}) + \omega^2 \frac{1}{2} \delta_{ia}^{-1} \psi^{(1)}(\omega)$$

and

$$A_{ia,jb} = 2 (a|i) (j|b),$$

$$B_{ia,jb} = 2 (a|b) (j|i),$$

$$\Delta_{ia,jb} = \delta_{ij} (\varphi_a | \psi^{(NL)} - \hat{v}_s | \varphi_b) - \delta_{ab} (\varphi_i | \psi^{(NL)} - \hat{v}_s | \varphi_j),$$

$$C_{ia,jb} = (a|i) (j|b),$$

with integrals of the type $(a|b)$ being defined according to

$${\int d\mathbf{r} d\mathbf{r}' \varphi_a(\mathbf{r}) \varphi_b(\mathbf{r}) \varphi_j(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|}$$

and $v_1^{(1)}$ being the non-local exchange operator defined by $\sum \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$. The second contribution to the function $h_s$ (see Eq. (A5) in Appendix A), in a previous work,37 turned out to have a negligible effect on the considered excitation energies because it contains the matrix elements $\langle \varphi_i | \hat{v}_s | \varphi_a \rangle$ between occupied and unoccupied EXX orbitals that are very small due to the similarity of the HF and EXX determinants49 and therefore shall not be taken into account any further. The specific form of Eqs. (7) and (8) expresses the dominant contribution to the function $h_s$ was chosen because this form facilitates a reformulation of the TDEXX equation of Refs. 37–39, which is the crucial point of this work (see Sec. II B). The complete function $h_s$ can be found in Appendix A and Refs. 38, 40–43.

If Eq. (6) is inserted into the basic Eq. (5), and if Eq. (1) is taken into account, then a frequency-dependent response equation37

$$\int d\mathbf{r} \left[ \chi_s(\omega, \mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' d\mathbf{r}''' \chi_s(\omega, \mathbf{r}', \mathbf{r}'') \chi_s(\omega, \mathbf{r}'', \mathbf{r}''') \right] \times \rho_1^{(1)}(\omega, \mathbf{r}') = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') v_1^{(1)}(\omega, \mathbf{r}')$$

for the change $v_1^{(1)}$ of the effective KS potential is obtained.

The crucial advantage of Eq. (13) compared to Eq. (5) is that it contains the function $h_s$ instead of the kernel $f_e$. The function $h_s$ is explicitly known in terms of the KS orbitals and its eigenvalues whereas the kernel $f_e$ can only be obtained by solving the integral Eq. (6). Attempts to solve this equation, however, suffered from severe numerical instabilities even in the adiabatic, i.e., zero frequency, limit.44,46

Equation (13) can be written in the form

$$W(\mathbf{r}) \frac{1}{2} [\mathbf{e}^2 - 2 + e^{1/2} (\mathbf{C} + X(\omega)) e^{1/2}] z(\omega)$$

$$W(\mathbf{r}) \mathbf{e}^{1/2} v^{(1)}(\omega)$$

with the matrix elements of the diagonal matrix $\mathbf{e}$ given by $e_{ia,jb} = \delta_{ia,jb} e_i = \delta_{ia,jb} (e_a - e_i)$, the matrix elements of
the diagonal matrix \( \lambda(\omega) \) given by \( \lambda_{ia, jb}(\omega) = \delta_{ia, jb} \lambda_{ia}(\omega) \) with \( \lambda_{ia}(\omega) \) defined in Eq. (3), the elements \( W_{ia}(\mathbf{r}) \) of the vector \( \mathbf{W}(\mathbf{r}) \) given by \( W_{ia}(\mathbf{r}) = \epsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \phi_{ia}(\mathbf{r}) \), the elements \( \psi_{ia}(\omega) \) of the vector \( \psi^{(1)}(\omega) \) given by \( \langle \phi_{ia} \mid \psi^{(1)}(\omega) \rangle \phi_{ia} \), and the elements of the matrices \( \mathbf{C} \) and \( \mathbf{X}(\omega) \) defined in Eqs. (12) and (8), respectively. The vector \( \mathbf{z}(\omega) \) is related by

\[
\mathbf{z}(\omega) = \mathbf{e}^{-1/2} \lambda(\omega) \psi^{(1)}(\omega)
\]

(15)
to the vector \( \psi^{(1)}(\omega) \) with vector elements \( \psi_{ia}(\omega) \) given by \( \langle \phi_{ia} \mid \psi^{(1)}(\omega) \rangle \phi_{ia} \). The dimension of the above matrices and vectors equals the number of products of occupied times unoccupied orbitals, the index \( ia \) represents a superindex labeling the products. If the products of occupied times unoccupied orbitals, or more precisely the products \( W_{ia}(\mathbf{r}) = \epsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \phi_{ia}(\mathbf{r}) \) were linear independent then Eq. (14) would imply the matrix equation

\[
[\omega^2 \mathbf{1} - \mathbf{e}^{-1/2} \mathbf{C} + \mathbf{X}(\omega) \mathbf{e}^{1/2}] \mathbf{z}(\omega) = 4 \mathbf{e}^{1/2} \lambda^{(1)}(\omega).
\]

(16)
The products \( \epsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \phi_{ia}(\mathbf{r}) \) actually are not linear independent. Therefore, from a formal point of view, Eq. (16) should be projected onto the space spanned by the products \( \epsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \phi_{ia}(\mathbf{r}) \). It turned out that such a projection has only a negligible effect on low-lying excitations. Moreover, we show below, how it can be checked that a solution of Eq. (16) is not affected by the linear dependence of the products of occupied times unoccupied orbitals.

By solving Eq. (16) the vector \( \mathbf{z}(\omega) \) can be obtained, which determines the linear response \( \rho^{(1)}(\omega, \mathbf{r}) \) of the electron density to a frequency-dependent external perturbation \( \psi^{(1)}(\omega, \mathbf{r}) \) according to

\[
\rho^{(1)}(\omega, \mathbf{r}) = \sum_{ia} \sum_{\text{occupied}} \phi_{ia}(\mathbf{r}) \lambda_{ia}^{-1/2} \left( \phi_{ia} \psi^{(1)}_{ia}(\omega) \langle \phi_{ia} \rangle \phi_{ia} \right) = \sum_{ia} \sum_{\text{occupied}} \phi_{ia}(\mathbf{r}) \lambda_{ia}^{-1/2} \phi_{ia}(\mathbf{r}).
\]

(17)
The first line of Eq. (17) directly follows from Eqs. (1) and (2), the second line with Eq. (15). More important than calculating the frequency-dependent linear response of the electron density is to determine excitation energies. To that end, those frequencies are determined for which the linear response of the electron density becomes infinite. For these frequencies Eq. (16) becomes singular, i.e., for these frequencies the matrix in the square parenthesis on the left hand side of Eq. (16) has eigenvalues equal to zero. These frequencies and thus the electron density becomes infinite. For these frequencies which determines the linear response

\[
(\omega, \text{occupied}) = \sum_{\text{occupied}} \phi_{ia}(\mathbf{r}) \psi^{(1)}_{ia}(\omega)
\]

(18)
in order to obtain eigenvalues \( \Omega_n \) and eigenvectors \( \mathbf{z}_n \). If the frequency \( \omega \) equals an eigenvalue \( \Omega_n \), then Eq. (16) becomes singular and this frequency \( \omega = \Omega_n \) is an excitation frequency of the considered electronic system. This means, in order to calculate the \( n \)th excitation energy with Eq. (18), the frequency \( \omega \) has to be adjusted such that it equals the \( n \)th eigenvalue \( \Omega_n \) (see Sec. II.B.). The eigenvectors \( \mathbf{z}_n(\omega = \Omega_n) \) characterize the excitations and, if properly normalized (see Appendix B), yield the corresponding oscillator strength \( f_n \) according to

\[
f_n = \frac{4}{3} \sum_{\mu, \nu, \zeta} (d_{\mu\nu\zeta})^2 \lambda^{(1)}(\omega, \mathbf{z}_n)^2,
\]

(19)
with the elements \( d_{\mu\nu\zeta} \) of the vectors \( \mathbf{d}_\mu \) with \( \mu = x, y, z \) given by \( \langle \phi_{\mu x} \mid \langle \mathbf{z}_n \rangle \rangle \phi_{\mu x} \rangle \), and \( \langle \phi_{\mu y} \mid \langle \mathbf{z}_n \rangle \rangle \phi_{\mu y} \rangle \), and \( \langle \phi_{\mu z} \mid \langle \mathbf{z}_n \rangle \rangle \phi_{\mu z} \rangle \) respectively. Equation (18) is the equation that underlies the work on the TDEEX response methods of Refs. 37 and 38.

In order to check if solutions \( \mathbf{z}(\omega) \) of Eq. (16) or the eigenvectors \( \mathbf{z}_n(\omega) \) of Eq. (18) are affected by linear dependencies of products \( \psi_{ia} \) of occupied times unoccupied orbitals we consider a singular-value decomposition

\[
\mathbf{S} = (\mathbf{U} \mathbf{U}^0) \begin{pmatrix} 8 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} (\mathbf{U}^T \mathbf{U})
\]

(20)
of the overlap matrix \( \mathbf{S} \) of pairs \( \psi_{ia} \) with \( \psi_{jb} \) of products of occupied times unoccupied orbitals with matrix elements \( S_{ia,jb} = \int d\mathbf{r} \psi_{ia}(\mathbf{r}) \psi_{jb}(\mathbf{r}) \). The diagonal matrix \( \mathbf{s} \) shall contain those eigenvalues of the overlap matrix \( \mathbf{S} \) that are greater than zero. The corresponding eigenvectors, the columns of the matrix \( \mathbf{U} \), define the space spanned by the products of occupied times unoccupied orbitals \( \psi_{ia} \). The diagonal matrix \( \mathbf{s} \) contains the eigenvalues of \( \mathbf{S} \) that are zero or, in practice, below a given numerical threshold. The corresponding eigenvectors, the columns \( \mathbf{u}_n \) of the matrix \( \mathbf{U}^0 \), contain the coefficients of linear combinations of products \( \psi_{ia} \) that are identical to zero or, in practice, are close to zero,

\[
\sum_{ia} \mathbf{u}_{ia}^0 \psi_{ia}(\mathbf{r}) = 0.
\]

(21)
A solution \( \mathbf{z}(\omega) \) of Eq. (16) is related by Eq. (15) with the vector \( \psi^{(1)}(\omega) \) with vector elements \( \psi_{ia}(\omega) = \langle \phi_{ia} \mid \psi^{(1)}(\omega) \rangle \phi_{ia} \rangle = \int d\mathbf{r} \psi^{(1)}_{ia}(\omega, \mathbf{r}) \psi_{ia}(\mathbf{r}). \) We now consider a vector \( \mathbf{t}_i^0 \) given by

\[
\mathbf{t}_i^0 = \mathbf{U}_i^0 \mathbf{v}^{(1)}(\omega) = \mathbf{U}_i^0 \lambda^{-1}(\omega) \mathbf{e}^{1/2} \mathbf{z}(\omega).
\]

(22)
If the vector \( \mathbf{t}_i^0 \) does not equal the zero vector, i.e., if it contains elements \( t_{i\ell}^0 \neq 0 \), then the solution \( \mathbf{z}(\omega) \) of Eq. (16) is not physically meaningful because the elements \( t_{i\ell}^0 \) equal

\[
t_{i\ell}^0 = \mathbf{U}_i^0 \mathbf{v}^{(1)}(\omega) \mathbf{U}_\ell^0 \int d\mathbf{r} \psi^{(1)}_{ia}(\omega, \mathbf{r}) \psi_{ia}(\mathbf{r})
\]

\[
= \int d\mathbf{r} \left[ \sum_{ia} \mathbf{u}_{ia}^0 \psi_{ia}(\mathbf{r}) \right] \psi^{(1)}_{ia}(\omega, \mathbf{r})
\]

\[
= 0,
\]

(23)
i.e., equal integrals that must be zero, because it is integrated over the local multiplicative potential \( v^{(1)}_{ia}(\omega, \mathbf{r}) \) times linear combinations of products \( \psi_{ia} \) that are zero according to Eq. (21). This means physical meaningful solutions of Eq. (16) must obey the criterion

\[
\sum_{\ell} \mathbf{t}_{i\ell}^2 = 0
\]

(24)
or, in practice, the left-hand side of Eq. (24) must lie below a given threshold. Because the vectors \( \psi_i^{1/2}(\omega) = \lambda^{-1}(\Omega) e^{i/2} z(\omega) \) are not normalized, a threshold defined relative to the norm of the vectors seems reasonable. We, therefore, besides the vector \( t^0 \) of Eq. (22), calculate a vector \( t \) according to

\[
t = \left( U^T \right) \lambda^{-1}(\omega) e^{i/2} z(\omega)
\]

and take the measure

\[
\frac{\sum n (t^0_n)^2}{\sum n (t_n)^2}
\]

as criterion to judge whether solutions \( z(\omega) \) are affected by linear dependencies of products of occupied times unoccupied orbitals. Similarly, eigenvectors of \( z(\omega) = \Omega_n \) of Eq. (18) can be analyzed with the help of vectors

\[
t_n = U^T \lambda^{-1}(\Omega_n) e^{i/2} z_n (\Omega_n)
\]

and

\[
t = \left( U^T \right) \lambda^{-1}(\Omega_n) e^{i/2} z_n (\Omega_n).
\]

In order to avoid that products \( \varphi_{ia} \) that have a small norm fall below the threshold identifying products as being close to zero, we renormalize the overlap matrix according to

\[
\tilde{S} = \sigma S \sigma^T,
\]

with the diagonal matrix \( \sigma \) containing matrix elements \( \sigma_{ia,ia} = 1/\sqrt{S_{ia,ia}} \). In this case, Eq. (27) assumes the form

\[
t_0 = U^T \lambda^{-1}(\Omega_n) e^{i/2} z_n (\Omega_n)
\]

and Eqs. (22), (25), and (28) need to be analogously modified. It will be shown in Sec. IV that the eigenvectors \( x_n(\Omega_n) \) of all excitations studied in this work are only very slightly affected by linear dependencies of products of occupied times unoccupied orbitals according to the measure (26) evaluated on the basis of the overlap matrix \( \tilde{S} \). Therefore, the use of the unprojected Eq. (18) seems to be justified.

**B. Reformulation of TDEXX equation**

The lowest eigenvalues of Eq. (18) for a given frequency \( \omega \) can be efficiently obtained by iteratively solving Eq. (18) by a Davidson algorithm (see, e.g., Ref. 51). However, due to the nonlinearity of Eq. (18), i.e., the frequency dependence of the matrix \( X(\omega) \), this, in general, does not lead to eigenvalues \( \Omega_n \) corresponding to excitation energies. Only if the frequency \( \omega \) in Eq. (18) equals one of the eigenvalues \( \Omega_n \), i.e., if \( \omega = \Omega_n \) then this eigenvalue corresponds to an excitation energy. This means that for each excitation energy, the frequency \( \omega \) needs to be adjusted to the corresponding eigenvalue, which in turn depends on the frequency. This adjustment can be straightforwardly done in an iterative manner, it requires, however, in each iteration step a solution of Eq. (18). Usually, only a few (three to five) iteration steps are necessary. Nevertheless, this means that instead of obtaining all excitation energies of interest by carrying out the Davidson algorithm once, it has to be carried out for each excitation several times. This amounts to a drastic increase in computational effort compared to a conventional TDDFT response approach within the adiabatic approximation. Alternatively, the excitation energies of interest can also be obtained by interpolation from excitation energy data generated, e.g., on a regular frequency grid. This, however, also requires at least four or more (depending on the range of excitation energies to be computed) diagonalization steps in comparison to just one as in standard TDDFT.

If the matrix \( X(\omega) \) in Eq. (18) is decomposed according to Eq. (8) into matrices \( A, B, \) and \( \Delta \) with matrix elements given by Eqs. (9)–(11), then, after rearrangement of terms, Eq. (18) assumes the form

\[
[e^2 + e^{1/2} (A + B + \Delta) e^{1/2}] z_n = \Omega_n^2 [I - e^{-1/2} (A - B + \Delta) e^{-1/2}] z_n.
\]

Indeed, the way the matrix elements \( X(\omega) \) are written in Eq. (8) was chosen because then the TDEXX Eq. (18) assumes the form of Eq. (31). This is crucial because Eq. (31), in contrast to the original Eq. (18), is linear. More precisely, the fact that the TDEXX problem is a linear one is hidden if it is formulated according to Eq. (18) while it becomes obvious in Eq. (31). This means the linear generalized eigenvalue problem (31) directly yields the squares of all excitation energies and no frequency iteration is required. However, it cannot be solved by a standard Davidson algorithm. Instead, special versions of the Davidson algorithm for generalized eigenvalue problems are required. This means the advantage of having at hand a linear formulation the TDEXX response problem is accompanied by having to deal with a generalized instead of a simple eigenvalue problem.

The fact that Eq. (31) is a linear generalized eigenvalue equation means that frequency-dependent TDEXX response methods, like conventional TDDFT response methods, yield as many excitation energies as there are products of occupied times unoccupied orbitals. (Note that we have neglected terms in the function \( h_\ell \) of Eq. (6) for the exchange kernel. We have no indications that these terms could lead to additional excitation energies, indeed we have no indication that these terms have any non-negligible effect at all. However, we did not investigate any further potential implications of these terms on the number of excitations.) Because an exact TDDFT response method has to yield all excitations that are accompanied by a linear response of the electron density including excitations that, within an independent electron picture, are described as two-electron excitations, the unknown frequency-dependent correlation kernel has to introduce a nonlinearity leading to additional excitations, which are neither present in conventional adiabatic TDDFT methods nor in the frequency-dependent TDEXX method considered here.

Formally, we can convert Eq. (31) into a regular eigenvalue equation. To this end, we first introduce the abbreviation

\[
D = e^{-1/2} [A - B + \Delta] e^{-1/2}
\]

12. **Time-dependent density functional theory**
and rewrite Eq. (31) as
\[
[\varepsilon^2 + \varepsilon^{1/2} [A + B + \Delta] \varepsilon^{1/2}] z_n = \Omega^2_{\varepsilon} [1 - D] z_n. \tag{33}
\]
Provided the matrix \(1 - D\) is positive definite, the generalized eigenvalue Eq. (32) is equivalent to the regular Hermitian eigenvalue equation
\[
(1 - D)^{-1/2} \left[ \varepsilon^2 + \varepsilon^{1/2} [A + B + \Delta] \varepsilon^{1/2} \right] (1 - D)^{-1/2} p_n = \Omega^2_{\varepsilon} p_n \tag{34}
\]
with
\[
p_n = (1 - D)^{1/2} z_n. \tag{35}
\]

Construction of the matrix \((1 - D)^{-1/2}\), like the explicit construction of any of the involved matrices, except those that are diagonal, has to be avoided in a computationally efficient algorithm. Therefore, Eq. (34) is of no help directly. We now expand the matrix \((1 - D)^{-1/2}\) into a Taylor expansion, according to
\[
(1 - D)^{-1/2} \approx 1 + \frac{1}{2} D + \frac{3}{4} D^2 + \cdots \tag{36}
\]
and substitute this Taylor expansion into the eigenvalue Eq. (34) to convert it into the form
\[
\left(1 + \frac{1}{2} D + \frac{3}{4} D^2 + \cdots \right) \left[ \varepsilon^2 + \varepsilon^{1/2} [A + B + \Delta] \varepsilon^{1/2} \right] \times \left(1 + \frac{1}{2} D + \frac{3}{4} D^2 + \cdots \right) p_n = \Omega^2_{\varepsilon} p_n, \tag{37}
\]
with
\[
z_n = (1 + \frac{1}{2} D + \frac{3}{4} D^2 + \cdots) p_n. \tag{38}
\]
Equation (37) lends itself for an iterative solution with a regular Davidson algorithm provided the Taylor expansion (37) converges fast enough. If only the leading term of the Taylor expansion is taken into account, then the frequency dependence in the adiabatic TDEXX response equation is neglected, i.e., the adiabatic approximation is made, resulting in an adiabatic TDEXX (termed as ATDEXX in the following) response method with the simplified eigenvalue equation
\[
[\varepsilon^2 + \varepsilon^{1/2} [A + B + \Delta] \varepsilon^{1/2}] p_n = \Omega^2_{\varepsilon} p_n. \tag{39}
\]

Vector matrix multiplications as they are required in a Davidson algorithm now consist of \(2n + 1\) instead of one individual vector matrix multiplication compared to adiabatic TDDFT response methods with \(n\) being the order up to which the Taylor expansion needs to be taken into account. The vector matrix multiplications with the matrix \(D\) like those with the matrix \([A + B + \Delta]\) can be carried out efficiently without explicitly constructing the matrices. For a value of \(n = 2\) that is shown later on to be sufficient to closely approach the full frequency-dependent results the number of individual vector matrix multiplication increases by a factor of five. The resulting computational effort should still be of the same order of magnitude as that for conventional TDDFT methods, in particular as that of conventional TDDFT methods with hybrid functionals like B3LYP that require the solution of a TDDF-like problem, which has twice the dimension of the eigenvalue problem considered here. The scaling with system size of a TDEXX method based on Eq. (37) is identical to that of other TDDFT response methods or the TDHF method. In summary, on the basis of Eq. (37) TDEXX response methods can be implemented that are competitive to TDHF or conventional TDDFT response methods with respect to the computational effort.

C. Relation between TDEXX and TDHF
The basic equation of TDHF,51–54
\[
\begin{pmatrix}
\varepsilon & 0 \\
0 & \varepsilon
\end{pmatrix} + \begin{pmatrix} A & B \\
B & A \end{pmatrix}
\begin{pmatrix} x \varepsilon & y \varepsilon \\
x \varepsilon & y \varepsilon
\end{pmatrix}
= \Omega_{\varepsilon} \begin{pmatrix} 1 & 0 \\
0 & -1 \end{pmatrix}
\begin{pmatrix} x \varepsilon & y \varepsilon \\
x \varepsilon & y \varepsilon
\end{pmatrix},
\tag{40}
\]
has twice the dimension of the eigenvalue equations occurring in TDDFT response methods. The matrices \(\varepsilon, A,\) and \(B\) are defined as above, however, with respect to HF eigenvalues and orbitals instead of EXX eigenvalues and orbitals. This means for matrices that differ only because they refer to different types of orbitals or eigenvalues, i.e., EXX or HF orbitals or eigenvalues, the same symbol is used and the context determines what is exactly meant. Equation (40) can be alternatively written in the form of two coupled matrix equations with half the original dimension, i.e., with the same dimension as the eigenvalue equations occurring in TDDFT response methods,
\[
[\varepsilon + A] x_n + B y_n = \Omega_{\varepsilon} x_n, \tag{41}
\]
\[
B x_n + [\varepsilon + A] y_n = -\Omega_{\varepsilon} y_n. \tag{42}
\]
By inserting the two above equations into each other and by using the definition
\[
z_n = \varepsilon^{-1/2} (x_n + y_n), \tag{43}
\]
the generalized eigenvalue equation
\[
\left[\varepsilon^2 + \varepsilon^{1/2} [A + B] \varepsilon^{1/2}\right] z_n
= \Omega^2_{\varepsilon} \left(1 + \varepsilon^{-1/2} [A - B] \varepsilon^{-1/2}\right)^{-1} z_n \tag{44}
\]
is obtained, which is equivalent to the original TDHF Eq. (40).

In order to relate TDEXX and TDHF methods, we exploit the fact that the exact exchange-only KS determinant, the EXX determinant, and the HF determinant are almost identical.38,39,55 If the small differences between the two determinants are neglected, then the occupied HF and EXX orbitals can be transformed into each other by a unitary transformation and the same holds true for the unoccupied HF and EXX orbitals. The transformation matrices that transform the occupied and unoccupied HF orbitals into EXX orbitals shall be denoted by \(U_{\text{occ}}\) and \(U_{\text{unocc}}\). The direct product \(U = U_{\text{occ}} \otimes U_{\text{unocc}}\) of these matrices is a unitary matrix transforming products of occupied times unoccupied HF orbitals into products of occupied times unoccupied EXX orbitals. If we carry out a similarity transformation of the matrices \(A\) and \(B\) constructed from HF orbitals with the matrix \(U\) and
its transposed, then the matrices $A$ and $B$ turn into the corresponding matrices constructed with EXX orbitals. A diagonal matrix $e$ containing differences of HF eigenvalues turns into the matrix $e + \Delta$, which is a sum of a matrix $e$ containing differences of KS eigenvalues and the matrix $\Delta$ with matrix elements that are given by expectation values of KS orbitals according to Eq. (11).39 If we now carry out a similarity transformation of the TDHF Eq. (40) with a block diagonal matrix containing on the diagonal twice the matrix $U$, then we obtain the equation

$$
\begin{pmatrix}
\epsilon \\
0
\end{pmatrix}
+ \begin{pmatrix}
A + \Delta & B \\
B & A + \Delta
\end{pmatrix}
\begin{pmatrix}
x_n \\
y_n
\end{pmatrix}
= \Omega_n \begin{pmatrix}
1 & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
x_n \\
y_n
\end{pmatrix}.
$$

(45)

If the HF and EXX determinants were exactly identical, then Eq. (45) would be exactly equivalent to the original TDHF Eq. (40). It would be a TDHF equation represented in products of EXX orbitals. Because HF and EXX determinants are very close but not exactly identical, Eq. (45) will yield results not identical but very close to TDHF. The differences will reflect the differences of HF and EXX determinants.

Like the original TDHF Eq. (40), we can transform Eq. (45) into a generalized eigenvalue equation of half the dimension

$$
\begin{pmatrix}
\epsilon^2 + \epsilon \epsilon^{1/2} [A + B + \Delta] \epsilon^{1/2} \\
0
\end{pmatrix} z_n = \Omega_n^2 \begin{pmatrix}1 + D \end{pmatrix}^{-1} z_n.
$$

(46)

It is instructive to compare Eq. (46) with the generalized TDEXX Eq. (33). The two equations only differ by the matrix in front of the eigenvectors $z_n$ on the right-hand side of the equation. The meaning of this difference becomes clearer if we first turn Eq. (46) into the regular eigenvalue equation

$$(1 + D)^{1/2} \begin{pmatrix}
\epsilon^2 + \epsilon \epsilon^{1/2} [A + B + \Delta] \epsilon^{1/2} \\
0
\end{pmatrix} \begin{pmatrix}
p_n \\
p_n
\end{pmatrix} = \Omega_n^2 \begin{pmatrix}1 + D \end{pmatrix}^{-1} p_n
$$

(47)

with

$$
p_n = (1 + D)^{-1/2} z_n.
$$

(48)

and then insert the Taylor expansion

$$(1 + D)^{1/2} \approx 1 + \frac{1}{2} D - \frac{1}{8} D^2 + \cdots
$$

(49)

to obtain

$$(1 + \frac{1}{2} D - \frac{1}{8} D^2 + \cdots) \begin{pmatrix}
\epsilon^2 + \epsilon \epsilon^{1/2} [A + B + \Delta] \epsilon^{1/2} \\
0
\end{pmatrix} \begin{pmatrix}
p_n \\
p_n
\end{pmatrix} = \Omega_n^2 \begin{pmatrix}1 + D \end{pmatrix}^{-1} p_n
$$

(50)

with

$$
z_n = (1 + \frac{1}{2} D - \frac{1}{8} D^2 + \cdots) p_n.
$$

(51)

Comparison of Eq. (50) and Eq. (37) shows that the TDEXX and TDHF equations differ only in terms of second order in the Taylor expansions (36) and (49). In addition, the differences caused by the small differences in EXX and HF determinants have to be taken into account. These differences, however, are also small. In summary, the comparison of Eq. (50) and Eq. (37) together with the similarity of HF and EXX determinants explains why TDEXX response methods yield quite similar results as TDHF methods. A consequence of this similarity is that TDEXX response methods like TDHF can treat charge transfer excitations and excitations into states with Rydberg character and that excitations in long chain-like aromatic molecules should not be a problem for TDEXX response methods. On the other hand, TDEXX response methods exhibit the same low accuracy for valence-valence excitations as TDHF methods.

TDEXX response methods have two important advantages over TDHF methods. First, within the TDDFT framework correlation functionals can be included. This might give the chance to improve the accuracy of TDEXX methods. Second, the EXX method yields meaningful occupied and, in contrast to HF methods, also meaningful unoccupied orbitals. Therefore it is usually easy to determine the nature of an electronic excitation by simply inspecting the corresponding eigenvector $z_n$. In TDHF this is often not possible in such a simple way. For example, the eigenvectors $z_n$ corresponding to excitations into states with Rydberg character, in TDHF, contain a very large number of small entries that do not help in characterizing the excitations, whereas in TDEXX response methods, in these cases the eigenvectors $z_n$ are dominated by one entry that corresponds to an excitation from the involved occupied to the involved unoccupied Rydberg orbital. This happens because the EXX method yields well defined, bound, physical meaningful Rydberg orbitals with negative eigenvalues, whereas HF yields unoccupied orbitals that usually exhibit positive eigenvalues and therefore do not correspond to bound, physically meaningful orbitals.

D. Tamm–Dancoff approximation

The Tamm–Dancoff (TD) approximation to the TDHF Eq. (40) neglects the matrix $B$ that couples the contributions $x_n$ and $y_n$ to the TDHF eigenvectors. By this, the TDHF Eq. (40) is decoupled into two separate eigenvalue equations for $x_n$ and $y_n$ with eigenvalues $\Omega_n$ and $-\Omega_n$. If we apply the TD approximation to Eq. (45), i.e., to the TDHF equation expressed in EXX orbitals (if differences between the HF and EXX determinants are neglected), then we obtain the two equations

$$
(\epsilon + A + \Delta) x_n = \Omega_n x_n
$$

(52)

and

$$
(\epsilon + A + \Delta) y_n = -\Omega_n y_n,
$$

(53)

which imply

$$
x_n = y_n.
$$

(54)

Because Eq. (52) and (53) are equivalent, only one of them needs to actually be solved. Note that the TD approximation yields a qualitatively correct description of charge-transfer excitations like the fully coupled Eq. (45).

As discussed in Sec. II.C., the TDHF Eq. (40) is equivalent to the generalized eigenvalue Eq. (44), which has half the
dimension as the original TDHF Eq. (40). Similarly Eq. (45), the TDHF equation expressed in EXX orbitals, is related to the generalized eigenvalue Eq. (46). If the TD approximation is applied to Eq. (46), then we obtain

\[
\left[ \varepsilon^2 + e^{1/2} [A + \Delta] e^{1/2} \right] z_n = \Omega_n^2 \left[ 1 + e^{-1/2} [A + \Delta] e^{-1/2} \right]^{-1} z_n.
\]

(55)

By multiplying from the left by \((1/2)e^{-1/2}\), by inserting the relation

\[
z_n = e^{-1/2} 2 x_n = e^{-1/2} 2 y_n,
\]  

(56)

which follows from Eq. (43) with Eq. (54), and by rearranging, we obtain the equation

\[
(e + A + \Delta)^2 x_n = \Omega_n^2 x_n,
\]

(57)

which is equivalent to Eqs. (52) and (53).

If we apply a TD approximation, that is the approximation \(B = 0\), to the TDEXX Eq. (31), then the equation

\[
\left[ \varepsilon^2 + e^{1/2} [A + \Delta] e^{1/2} \right] z_n = \Omega_n^2 \left[ 1 - e^{-1/2} [A + \Delta] e^{-1/2} \right] z_n
\]

(58)

results. This equation cannot be turned into the form of a simple eigenvalue problem analogous to Eqs. (52) and (57). This means the TD approximation does not lead to a simple eigenvalue problem in the TDEXX case.

For the systems considered later on (see Sec. IV), the matrix \([1 - e^{-1/2} [A + \Delta] e^{-1/2}]\) turned out to be not positive definite and consequently Eq. (58) did not yield physically reasonable, i.e., real-valued positive, eigenvalues \(\Omega_n^2\). The approximation to set \(B = 0\), therefore, seems not to be a reasonable approximation in the case of TDEXX in contrast to the TDHF case, despite the fact that the full TDEXX and TDHF methods are closely related as discussed in Sec. II.C. This may be explained by considering the Taylor expansions (37) and (50) of the TDEXX and TDHF equations with respect to the matrix \(D = e^{-1/2} [A - B + \Delta] e^{-1/2}\). If differences between the HF and the EXX determinants are negligible, then the similarity of the TDEXX and TDHF method can be explained by the fact that the Taylor series Eqs. (36) and (49) and thus the TDEXX and TDHF Eq. (37) and (50) differ only in terms of second order in \(D\). Because the matrix \(D\) is small compared to the unit matrix these terms have only a small effect. The matrix \(D\) contains small matrix elements because the matrices \(A\) and \(B\) partially cancel each other. If, however, the matrix \(B\) is neglected, then this cancellation no longer exists, the Taylor series no longer converges that rapidly, and terms of quadratic and higher order in \(D\) may be significant.

III. COMPUTATIONAL DETAILS

Excitation energies were calculated for the three organic molecules ethylene, acetaldehyde, and pyridine. The geometries of the molecules were taken from Ref. 56.

The ground-state EXX calculations were performed in two steps. First the exact-exchange potentials were calculated with the OEP (optimized effective potential) method and the balanced orbital and auxiliary triple-zeta basis sets from Ref. 35. The choice of the basis sets in OEP calculations has to be made carefully since OEP calculations with standard contracted orbital basis sets yield wrong exchange-correlation potentials and thus wrong KS orbitals and eigenvalues.35,49,57 In the second step, the thus obtained EXX potentials, represented in the auxiliary basis sets, were used in a subsequent ground-state density-functional theory (DFT) calculation using a smaller orbital basis set. In this second ground-state DFT calculation only the Coulomb potential was optimized self-consistently. All results shown in this work were obtained with the 6-311+(3+d,p)+** orbital basis set from Refs. 56 and 58 that, in addition to the 6-311++G** standard basis set,39 is augmented with the following diffuse functions with exponents: carbon/s+p: 0.0131928,0.00440, oxygen/s+p: 0.0254518,0.00848, nitrogen/s+p: 0.0192470,0.00642, and hydrogen/s: 0.0108434,0.00361.

In order to analyze the impact of the Kohn–Sham orbitals and/or the Kohn–Sham eigenvalue spectrum on the excitation energies, we have also done calculations with various other approximations for the ground-state. By comparison of the EXX single-particle spectrum with more accurate KS eigenvalues obtained with the localized and asymptotically corrected Perdew-Burke-Ernzerhof hybrid (LPEC0AC) exchange-correlation potential,60,64 it was found that the main differences (due to electron correlation) occur close to the highest occupied (HOMO) and the lowest unoccupied (LUMO) KS orbital eigenvalues, while the low lying occupied and higher unoccupied EXX and LPEC0AC KS orbital energies are closer to each other and thus do not seem to be affected as much by electron correlation effects.

The LPEC0AC exchange-correlation potential has been chosen here as a reference since it has been proven to yield accurate electron densities, molecular electric properties, and first- and second-order intermolecular interaction energies.60,62-64 The 25% exact exchange contribution in this xc potential, however, has been replaced by a modified model exact-exchange potential developed by Becke and Johnson.65 In this modified exchange potential the Slater potential contribution was approximated using the Becke–Roussel exchange model66 with an optimized \(\gamma\) value of 1.15 (see Ref. 67). The asymptotic correction for the total xc potential was done using the gradient regulated asymptotic correction scheme by Grünning et al.68 with the derivative discontinuity shifts (ethylene: 0.0820 Hartree, acetaldehyde: 0.0895 Hartree, and pyridine: 0.0727 Hartree) calculated as the difference of the negative LPEC0 HOMO energies and the PBE0 ionization potentials (see below).

Therefore, in one set of calculations, we have used the following correction method for obtaining more accurate KS eigenvalues from the EXX orbital eigenvalue spectrum

\[
e_i = \epsilon_i^{\text{EXX}} + \alpha \frac{\beta}{\beta + (\epsilon_i^{\text{EXX}} - \epsilon_N^{\text{EXX}})^2}.
\]

(59)

where \(\alpha\) and \(\beta\) are parameters and \(\epsilon_N^{\text{EXX}}\) is the EXX HOMO eigenvalue. Since for \(i = N\) Eq. (59) reduces to \(\epsilon_N = \epsilon_N^{\text{EXX}}\)
+ α, the parameter α was set to the difference between the EXX HOMO energy and the negative ionization potential of the molecule in the calculations, i.e.,

\[ \alpha = (-E_{\text{EXX}})^{1/2} - (-E_{\text{HF}})^{1/2}, \tag{60} \]

such that the corrected HOMO orbital energy is identical to the ionization potential as in exact KS theory.\(^{69}\) The ionization potentials for the systems studied in this work have been determined by unrestricted DFT calculations using the PBE0 functional with the aug-cc-pVTZ basis set\(^{70}\) (ethylene: 10.441 eV, acetaldehyde: 10.079 eV, and pyridine 9.555 eV). The corresponding HOMO energies from the EXX method were ethylene: \(-10.216\) eV, acetaldehyde: \(-11.548\) eV, and pyridine \(-9.446\) eV. The parameter β in Eq. (59) has been set to values of 0.02 and 0.03 in the calculations [Eq. (59) was evaluated in atomic units]. TDEXX calculations were then performed by using unmodified EXX orbitals and modified KS eigenvalues as obtained with Eq. (59).

Furthermore, correlated ground-state DFT calculations were performed by adding local and semi-local correlation functionals to EXX, namely VWN (Vosko–Wilk–Nusair)\(^{71}\) and PBEC (Perdew–Burke–Ernzerhof correlation).\(^{72}\) The calculations have been done in the same way as described above for pure EXX calculations except that the employed semi-local correlation potential was optimized, too, and not held fixed as the exact-exchange potential. Note that the matrix elements of the Δ matrix defined in Eq. (11) have been evaluated with the corresponding matrix elements of the exact-exchange potential only and not with the total xc (exchange-correlation) potential matrix elements.

We have also tested a hybrid approach in which the adiabatic or nonadiabatic exact exchange kernel is combined with the adiabatic local density approximation (ALDA) kernel. This was done by modifying Eq. (31) in the following way

\[
\begin{align*}
\left[ e^{2} + e^{1/2} \left[ \alpha(A + B + \Delta) \right] + (1 - \alpha) \left( 4C + K_{\text{ALDA}}^{\text{xc}} \right) e^{1/2} \right] z_{n} \\
= \Omega_{n}^{2} \left[ 1 - e^{-1/2} \left[ \alpha(A - B + \Delta) e^{-1/2} \right] z_{n} \right],
\end{align*}
\]

(61)

where α is a switching parameter that can have values between 0 (full ALDA kernel) and 1 (full TDEXX kernel).\(^{73}\)

The calculations with the hybrid time-dependent EXX-AlDA kernel were done in conjunction with the localized and asymptotically corrected LPBE0AC xc potential\(^{60,61}\) (see above). Since in this model potential, not such a clear separation of exact exchange and correlation is possible, the matrix elements of A given in Eq. (11) were calculated with the matrix elements of the full LPBE0AC xc potential.

All calculations were performed with the developers version of the Molpro quantum chemistry program.\(^{73}\)

### IV. RESULTS AND DISCUSSION

Table I displays the percentage of unphysical contributions of linear combinations of products of occupied times unoccupied orbitals to the eigenvectors \(z_{n}\) according to the measure \(\frac{\langle t_{0}^{\dagger} t_{n} \rangle}{\langle t_{n}^{\dagger} t_{n} \rangle}\), Eq. (26). The linear combinations of products of occupied times unoccupied orbitals with zero norm are determined with respect to the overlap matrix (norm matrix) \(\tilde{S}\) of Eq. (27) and form the Null space of the overlap matrix. As described in Sec. II A, large contributions of \(\frac{\langle t_{0}^{\dagger} t_{n} \rangle}{\langle t_{n}^{\dagger} t_{n} \rangle}\) for a given excitation indicate that this excitation does not correspond to a physically meaningful TDDFT excitation on the basis of the linear response Eq. (13). If a threshold of \(10^{-12}\) is used to define the Null space of \(\tilde{S}\), then Table I shows that all excitations are virtually free of unphysical contributions. For a threshold of \(10^{-10}\) the percentage of unphysical contributions still lies below one percent in all cases. For a threshold of \(10^{-8}\) the percentage of contribution with a norm below this threshold can rise to \(10\%\). However, a norm in the order of \(10^{-8}\) can no longer be considered as zero. In summary, we conclude that all excitations in Table I are proper TDDFT excitations and that the eigenvalue Eq. (16) is valid for these excitations without requiring a projection as described in Ref. 37. Therefore, the following discussion will only refer to the solutions of the unprojected eigenvalue Eq. (16).

Tables II–IV show the lowest singlet excitation energies for ethylene, acetaldehyde, and pyridine calculated using time-dependent Hartree–Fock (TDHF) based on TDHF orbitals and eigenvalues and by methods based on EXX orbitals combined with various approximations for the exchange-correlation kernel as described in Sec. II. (In the tables, the acronym of the method, the orbitals and eigenvalues were calculated with, is given in parenthesis after the acronym of the response method.) Furthermore, EXX eigenvalue differences corresponding to the excitations are displayed. The energetically lowest excitations in ethylene and...
acetaldehyde are mostly of Rydberg character, while in the case of pyridine the four considered excitations are the lowest valence-valence excitations. In case of ethylene, it can be seen that all methods yield almost identical results for the Rydberg excitations, for the experimental values for the excitation energies of ethylene are very close to TDHF based on HF orbitals. Furthermore the Taylor expansion approximations to TDEXX and TDHF(EXX), denoted as TDEXX[n] and TDHF(EXX)[n], respectively [n: order of expansion, see Eqs. (37) and (50)] are close to their infinite order counterparts already at first order. This underlines the usefulness of approaches based on the expansions desribed in Sec. II.B. and II.C. A comparison of the calculated excitation energies with the experimental ones displayed in the last line of Table II shows a good agreement for all Rydberg excitations. In case of the π → π* excitation, however, the TDEXX excitation energy is about 0.3 eV too low. This, interestingly, is corrected if the Tamm–Dancoff approximation to TDHF(EXX), denoted as TDHF(TD)[EXX] [Eq. (52)], is made. Then the experimental π → π* excitation energy is reproduced up to +0.04 eV. All methods considered in Table II except ATDEXX reproduce the experimental values for the excitation energies of ethylene with mean absolute deviations of less than 0.2 eV.

This is clearly different for acetaldehyde where all methods (based on EXX orbitals) overestimate the experimental excitations depicted in Table III in all cases except of

### Table II

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### Table IV

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ALDA(Exx), by about 1−1.3 eV on average and in the case of ALDA(Exx) by about 0.6 eV on average. Table III also shows that in this case, the xc kernel has a significant effect on both the \( n \rightarrow \pi^* \) valence and on the Rydberg excitations. For example, the comparison between ATDEXX and TDEXX shows a difference of \(-0.24 \) eV for the \( n \rightarrow \pi^* \) excitation and up to \(+0.46 \) eV for the Rydberg excitation. This shows that the use of the nonadiabatic terms in the kernel has a nonuniform effect on the excitation energies and does not always lead to improvements of the ATDEXX method if compared with experimental results. In case of acetaldehyde, see Table III, the TDEXX performs notably better than ATDEXX for the \( n \rightarrow \pi^* \) excitation energy, while in case of the five Rydberg excitations considered this is reversed. The Tamm–Dancoff approximation to TDHF(Exx), i.e., TDHF[TD](Exx), yields excitation energies of acetaldehyde that are very close to the TDEXX and TDHF values, which are also close to each other. The excitation energies from the ALDA(Exx) approach, on the other hand, are clearly different to those from TDEXX: for the \( n \rightarrow \pi^* \) transition an excitation energy that is \(+0.64 \) eV higher is found while the Rydberg excitation energies are constantly smaller by as much as \(1.26 \) eV. In fact, the ALDA(Exx) Rydberg excitation energies are fairly close to the experimental values while the corresponding \( n \rightarrow \pi^* \) excitation energy lies \(1.26 \) eV too high (see Table III). Another notable difference to the ethylene results from Table II is that the first order Taylor expansion approximation to TDEXX (TDEXX[1]) deviates more from the infinite order solutions. This is even more so in case of pyridine where one also finds a larger deviation between the TDEXX and the TDHF(Exx) excitation energies (see Table IV). Here it is found that even the second order terms in the expansion of Eq. (37) are not yet sufficient to obtain converged results, deviations of up to \(0.22 \) eV between TDEXX[2] and TDEXX are observed for the four lowest valence excitations as can be seen in Table IV. Table IV also shows relative strong deviations for all approaches with respect to the experimental reference energies with relative errors of up to \(30\% \). Notable exceptions are the first \( \pi \rightarrow \pi^* \) excitation energy which is nicely reproduced by ATDEXX and the second \( \pi \rightarrow \pi^* \) excitation energy which is well described by TDEXX. It is also interesting to see that the Exx eigenvalue differences reproduce the first three experimental excitation energies much better than the TDEXX method while with the adiabatic TDEXX kernel only the \( n \rightarrow \pi^* \) excitations are changed in comparison to Exx. A similar trend is also found for acetaldehyde where all Rydberg type excitations are better described by \(\Delta\varepsilon(Exx)\) than with ATDEXX or TDEXX (see Table III). Among the systems studied in this work, the neglect of the nonadiabatic contributions to the Exx kernel has the largest effect for the excitation energies of pyridine, e.g., a large difference of about \(-1.5 \) eV between ATDEXX and TDEXX is found for the second \( n \rightarrow \pi^* \) excitation energy. Nevertheless, the ATDEXX method still overestimates the experimental \( n \rightarrow \pi^* \) excitation energy of \(5.43 \) eV by almost \(1 \) eV.

These results show that it is important to account for electron correlation effects in order to obtain a better agreement with the experiment. In the TDEXX method correlation is neglected while exchange is treated exactly. Correlation enters at two points: (i) in the calculation of the KS orbitals and eigenvalues via the correlation potential and (ii) in the actual TDDFT response calculation via correlation contributions to the xc kernel. In order to get a certain estimate of the first effect, we have considered the impact of modifications of the orbital eigenvalues on the excitation energies using the correction scheme of Eq. (59) in conjunction with unmodified Exx orbitals. The corresponding results for the excitation energies for the three considered molecules for the approaches ATDEXX, ALDA(Exx), and TDHF[TD](Exx) are listed in Tables V–VII under the labels ATDEXX(\(\beta\)), ALDA(Exx)(\(\beta\)), and TDEXX[TD](Exx)(\(\beta\)) [with \(\beta = 0.02, 0.03\) corresponding to the parameter from Eq. (59)]. A comparison with the standard results for ethylene and pyridine from Tables II and IV shows that the ATDEXX(\(\beta\)) approaches yield only marginal improvements over ATDEXX. In fact, in case of pyridine the ATDEXX(\(\beta\)) excitation energies are even slightly worse than the ATDEXX values on average. This can be explained with the rather small differences between the Exx HOMO energies and the negative ionization energies obtained with the PBE0 method, (see Sec. III), so that the correction of Eq. (59) did not have a large effect on the KS energy levels. This is verified by the small differences of the uncoupled eigenvalue spectra \(\Delta\varepsilon\) in Tables II, V and IV, VII, respectively. This indicates that the larger deviations between the TDEXX excitation energies and the experimental ones for pyridine are not due to errors in the KS eigenvalue spectrum but are mainly due to approximations in the xc kernel. For example, it can be seen in Table VII that with the exception of the \(B_2\) excitation the results for ALDA(Exx)(\(\beta\)) are notably better than the ATDEXX(\(\beta\)) ones. The use of the Tamm–Dancoff approximation to TDHF[TD](Exx)(\(\beta\)) in Table VII) or the full nonadiabatic Exx kernel (not shown) did not lead to an improvement here with exception of the \(A_1\) excitation (see Table VII). For acetaldehyde the effect of a correction of the Exx eigenvalues in contrast to the situation for ethylene and pyridine is dramatically different. As described in Sec. III, a strong difference of \(1.5 \) eV between the Exx HOMO energy and the calculated negative ionization potential is found and therefore the KS eigenvalues are largely affected by the correction scheme of Eq. (59). As can be seen in Table VI, strong improvements are obtained for excitations calculated for acetaldehyde using the ATDEXX(\(\beta\)) approach. For example, with \(\beta = 0.03\) the average absolute deviation to the experimental values amounts to only \(0.06 \) eV compared to ATDEXX where an average deviation of about \(1 \) eV is found. A similar improvement is also found for TDHF[TD](Exx)(\(\beta\)) compared to the uncorrected TDEXX[TD](Exx) approach. The TDEXX[TD](\(\beta\)) and also the ALDA(Exx)(\(\beta\)) results are, however, not as good as the ATDEXX(\(\beta\)) excitation energies.

In order to test whether such improvements can also be obtained if the Exx functional is combined with a standard local or semilocal correlation functional, instead of applying the explicit correction scheme of Eq. (59), we have also performed ground-state calculations with a combination of the Exx potential with VWN (Vosko–Wilk–Nusair local correlation functional) and PBE(P (Perdew–Burke–Ernzerhof GGA

12. Time-dependent density functional theory
### Table V. Experimental and calculated transition energies for ethylene calculated by combining the adiabatic EXX kernel, the HF kernel in the Tamm–Dancoff approximation according to Eq. (52), and the ALDA kernel with a modified EXX eigenvalue spectrum [ATDEXX(0.25)(LPBE0AC), TDEXX(0.25)(LPBE0AC), TDEXX(EXX+PBE), ATDEXX(EXX+PBE)]. Also shown are results obtained by combining EXX/ALDA hybrid kernels defined in Eq. (61) with KS orbitals and eigenvalues from the LPBE0AC potential [TDEXX-ALDA(0.25)(LPBE0AC), ATDEXX-ALDA(0.5)(LPBE0AC), with the corresponding scaling factor $\alpha$ from Eq. (61)]. Furthermore, KS eigenvalue differences $\Delta \varepsilon$ corresponding to the excitations are displayed for EXX, EXX+VWN, and LPBE0AC orbitals. The standard TDPBE and TDPBE0 results and the experimental data are taken from Ref. 56. Energies are in eV.

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<tr>
<td>ATDEXX-ALDA(0.25)</td>
<td>4.37</td>
<td>6.67</td>
<td>7.32</td>
<td>7.73</td>
<td>8.31</td>
<td>8.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDEXX-ALDA(0.25)</td>
<td>4.46</td>
<td>7.03</td>
<td>7.65</td>
<td>8.03</td>
<td>8.73</td>
<td>8.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATDEXX-ALDA(0.5)</td>
<td>4.42</td>
<td>6.93</td>
<td>7.60</td>
<td>7.98</td>
<td>8.73</td>
<td>8.96</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Exp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table VI. Experimental and calculated transition energies for acetaldhyde. See Table V for details. Energies are in eV.

<table>
<thead>
<tr>
<th>$A^*$</th>
<th>$n \rightarrow \pi^*$</th>
<th>$2A^*$</th>
<th>$3A^*$</th>
<th>$4A^*$</th>
<th>$6A^*$</th>
<th>$7A^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta(\text{EXX}(0.02))$</td>
<td>4.30</td>
<td>5.99</td>
<td>6.84</td>
<td>7.26</td>
<td>7.61</td>
<td>7.85</td>
</tr>
<tr>
<td>$\Delta(\text{EXX}(0.03))$</td>
<td>4.45</td>
<td>6.11</td>
<td>6.94</td>
<td>7.35</td>
<td>7.70</td>
<td>7.94</td>
</tr>
<tr>
<td>$\Delta(\text{EXX}+\text{VWN})$</td>
<td>5.35</td>
<td>7.80</td>
<td>7.91</td>
<td>8.80</td>
<td>9.47</td>
<td>10.01</td>
</tr>
<tr>
<td>$\Delta(\text{EXX}+\text{PBE})$</td>
<td>5.23</td>
<td>7.78</td>
<td>7.89</td>
<td>8.73</td>
<td>9.39</td>
<td>9.84</td>
</tr>
<tr>
<td>$\Delta(\text{LPBE0AC})$</td>
<td>4.00</td>
<td>6.29</td>
<td>6.99</td>
<td>7.64</td>
<td>8.28</td>
<td>8.49</td>
</tr>
<tr>
<td>ATDEXX(0.02)</td>
<td>4.15</td>
<td>6.73</td>
<td>7.42</td>
<td>8.62</td>
<td>9.88</td>
<td>9.80</td>
</tr>
<tr>
<td>ATDEXX(0.03)</td>
<td>4.29</td>
<td>6.85</td>
<td>7.52</td>
<td>8.70</td>
<td>9.41</td>
<td>8.51</td>
</tr>
<tr>
<td>ALDA(0.02)</td>
<td>4.58</td>
<td>6.06</td>
<td>6.68</td>
<td>7.25</td>
<td>7.63</td>
<td>7.85</td>
</tr>
<tr>
<td>Exp</td>
<td>4.38</td>
<td>8.34</td>
<td>9.06</td>
<td>9.11</td>
<td>9.92</td>
<td>10.05</td>
</tr>
<tr>
<td>TDPB0(PBE)</td>
<td>4.38</td>
<td>7.53</td>
<td>8.00</td>
<td>8.77</td>
<td>8.88</td>
<td>8.65</td>
</tr>
<tr>
<td>TDPB0(PBE)</td>
<td>4.75</td>
<td>8.45</td>
<td>9.10</td>
<td>9.19</td>
<td>10.04</td>
<td>10.12</td>
</tr>
<tr>
<td>TDEXX(0.02)</td>
<td>4.61</td>
<td>7.60</td>
<td>8.25</td>
<td>8.45</td>
<td>9.22</td>
<td>9.38</td>
</tr>
<tr>
<td>TDEXX(0.05)</td>
<td>4.46</td>
<td>7.03</td>
<td>7.65</td>
<td>8.03</td>
<td>8.73</td>
<td>8.96</td>
</tr>
<tr>
<td>ATDEXX(0.05)</td>
<td>4.42</td>
<td>6.93</td>
<td>7.60</td>
<td>7.98</td>
<td>8.60</td>
<td>8.84</td>
</tr>
<tr>
<td>ATDEXX(0.25)</td>
<td>4.37</td>
<td>6.67</td>
<td>7.32</td>
<td>7.73</td>
<td>8.31</td>
<td>8.71</td>
</tr>
<tr>
<td>TDPB0(PBE)</td>
<td>4.11</td>
<td>5.43</td>
<td>5.88</td>
<td>6.05</td>
<td>6.12</td>
<td>6.22</td>
</tr>
<tr>
<td>TDPB0(PBE)</td>
<td>4.24</td>
<td>6.45</td>
<td>6.95</td>
<td>7.17</td>
<td>7.45</td>
<td>7.49</td>
</tr>
<tr>
<td>Exp</td>
<td>4.28</td>
<td>6.82</td>
<td>7.46</td>
<td>7.75</td>
<td>8.43</td>
<td>8.69</td>
</tr>
</tbody>
</table>
**TABLE VII.** Experimental and calculated transition energies for pyridine. See Table V for details. Energies are in eV.

<table>
<thead>
<tr>
<th></th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$A_2$</th>
<th>$A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \epsilon$(EXX(0.02))</td>
<td>5.12</td>
<td>4.99</td>
<td>5.54</td>
<td>5.40</td>
</tr>
<tr>
<td>$\Delta \epsilon$(EXX(0.03))</td>
<td>5.11</td>
<td>4.98</td>
<td>5.53</td>
<td>5.39</td>
</tr>
<tr>
<td>$\Delta \epsilon$(EXX+VWN)</td>
<td>5.15</td>
<td>4.94</td>
<td>5.57</td>
<td>5.36</td>
</tr>
<tr>
<td>$\Delta \epsilon$(EXX+PBE)</td>
<td>5.03</td>
<td>4.97</td>
<td>5.45</td>
<td>5.39</td>
</tr>
<tr>
<td>$\Delta \epsilon$(PBE0)</td>
<td>4.15</td>
<td>4.80</td>
<td>4.52</td>
<td>5.17</td>
</tr>
<tr>
<td>ATDEXX(0.02)</td>
<td>5.73</td>
<td>5.07</td>
<td>6.41</td>
<td>5.43</td>
</tr>
<tr>
<td>ATDEXX(0.03)</td>
<td>5.72</td>
<td>5.06</td>
<td>6.40</td>
<td>5.42</td>
</tr>
<tr>
<td>ALDA(EXX(0.02))</td>
<td>5.41</td>
<td>5.58</td>
<td>5.58</td>
<td>6.38</td>
</tr>
<tr>
<td>TDEXX(TD)(EXX)</td>
<td>5.99</td>
<td>6.07</td>
<td>7.29</td>
<td>6.41</td>
</tr>
<tr>
<td>TDHF(TD)(EXX)(0.02)</td>
<td>6.06</td>
<td>6.13</td>
<td>7.36</td>
<td>6.47</td>
</tr>
<tr>
<td>ATDEXX(EXX+VWN)</td>
<td>5.76</td>
<td>5.02</td>
<td>6.47</td>
<td>5.40</td>
</tr>
<tr>
<td>TDEXX(EXX+VWN)</td>
<td>6.29</td>
<td>6.33</td>
<td>8.01</td>
<td>6.49</td>
</tr>
<tr>
<td>ATDEXX(EXX+PBE)</td>
<td>5.63</td>
<td>5.06</td>
<td>6.31</td>
<td>5.44</td>
</tr>
<tr>
<td>TDEXX(EXX+PBE)</td>
<td>6.15</td>
<td>6.36</td>
<td>7.81</td>
<td>6.54</td>
</tr>
<tr>
<td>TDEXX-ALDA(0.5)(LPBE0)</td>
<td>5.51</td>
<td>5.79</td>
<td>6.42</td>
<td>6.49</td>
</tr>
<tr>
<td>TDEXX-ALDA(0.25)(LPBE0)</td>
<td>5.02</td>
<td>5.57</td>
<td>5.42</td>
<td>6.41</td>
</tr>
<tr>
<td>ATDEXX-ALDA(0.5)(LPBE0)</td>
<td>4.87</td>
<td>5.15</td>
<td>5.25</td>
<td>5.88</td>
</tr>
<tr>
<td>ATDEXX-ALDA(0.25)(LPBE0)</td>
<td>4.70</td>
<td>5.26</td>
<td>4.94</td>
<td>6.10</td>
</tr>
<tr>
<td>TDPBE(PBE)</td>
<td>4.34</td>
<td>5.31</td>
<td>4.44</td>
<td>6.17</td>
</tr>
<tr>
<td>TDPBE0(PBE0)</td>
<td>4.85</td>
<td>5.53</td>
<td>5.21</td>
<td>6.33</td>
</tr>
<tr>
<td>Exp.</td>
<td>4.59</td>
<td>4.99</td>
<td>5.43</td>
<td>6.38</td>
</tr>
</tbody>
</table>

The correlation functional (or correlation potential) for the excitation energies using EXX+VWN and EXX+PBE orbitals and eigenvalues with ATDEXX and TDEXX kernels are displayed in the Tables V–VII and labeled ATDEXX(EXX+VWN), ATDEXX(EXX+PBE), TDEXX(EXX+VWN), TDEXX(EXX+PBE). It can be clearly seen in case of ethylene (Table V) and acetaldehyde (Table VI) that the use of the standard correlation potentials do not lead to improvements over ATDEXX or TDEXX results, while for pyridine only slight improvements are obtained by ATDEXX(EXX+VWN), ATDEXX(EXX+PBE). For acetaldehyde the scheme of Eq. (59) leads to a smaller HOMO–LUMO gap compared to the uncorrected EXX eigenvalue differences, while the additional LDA or GGA correlation potential increases the HOMO–LUMO gap and therefore cannot improve the exchange-only results for acetaldehyde. This finding shows that standard (semi)local correlation potentials are not good candidates to be used in conjunction with the EXX functional.

Often good results are obtained by hybrid approaches that mix a certain amount of exact (HF or EXX) exchange (conventionally 20–25%) with a standard GGA exchange functional. We have tested such a hybrid functional termed Ernzerhof hybrid (PBE0) but is asymptotically corrected (see Sec. III). The resulting orbitals have been combined with the TDEXX-ALDA and ATDEXX-ALDA hybrid method of Eq. (61) where a scaling parameter of $\alpha = 0.25$ and 0.5 has been used. The results for this approach are shown in Tables V–VII (labeled TDEXX-ALDA($\alpha$)(LPBE0) and ATDEXX-ALDA($\alpha$)(LPBE0) with $\alpha = 0.25$ and 0.5) together with the standard time-dependent PBE and PBE0 excitation energies (labeled TDPBE and TDPBE0). In case of ethylene (Table V), it can be observed that the TDEXX-ALDA($\alpha$)(LPBE0) and ATDEXX-ALDA($\alpha$)(LPBE0) hybrid methods perform rather well for the lower excitation but deviate stronger from experiment for some of the higher lying excitation energies. Altogether it can be seen in Table V that the hybrid approach yields excitations that are worse than the excitation energies from ATDEXX($\beta$), but that are clearly better than both the TDPBE and TDPBE0 results. This finding is certainly due to the incorrect asymptotic behavior of the xc potentials of the PBE and the PBE0 functional and the subsequently wrong description of Rydberg states. The same holds true for the Rydberg excitations of acetaldehyde shown in Table VI, where deviations of up to 30% are found for TDPBE and 14% for TDPBE0 with respect the experiment. In contrast to this, the TDEXX-ALDA($\alpha$)(LPBE0) and ATDEXX-ALDA($\alpha$)(LPBE0) hybrid methods yield Rydberg excitation energies for acetaldehyde that are rather close to the experiment if a scaling factor of $\alpha = 0.25$ is used. Furthermore the $n \rightarrow \pi^*$ excitation in acetaldehyde is relatively well described by the hybrid method, the experimental value of 4.28 eV is overestimated by only 0.1–0.2 eV. The average absolute deviation from the experimental transition energies of acetaldehyde for the ATDEXX-ALDA($\alpha$)(LPBE0) approach of 0.09 eV is almost as small as for ATDEXX($\alpha$), where a deviation of 0.06 eV is found. A clear improvement, over both standard TDEXX and the TDEXX results with modified KS eigenvalue spectra is observed for pyridine (see Table VII). Here, all hybrid methods shown in the Table, with exception of TDEXX-ALDA(0.5)(LPBE0), deviate on average only by 0.3 eV from the experimental values for the four excitations. This is also clearly better than standard TDDFT based on the PBE functional, i.e., TDPBE, but of a similar accuracy as it is found for TDPBE0 (see Table VII). In summary, the TDEXX-ALDA($\alpha$)(LPBE0) and ATDEXX-ALDA($\alpha$)(LPBE0) hybrid methods give a rather balanced description of both Rydberg-type and valence excitations, while the ATDEXX($\beta$) approach and related methods perform better for Rydberg excitations whereas standard TDDFT better describes valence excitations.

V. CONCLUDING REMARKS

The recently introduced frequency-dependent time-dependent density-functional response method based on the exact-exchange kernel, TDEXX, has been transformed into a practical and efficient computational scheme. The new generalized eigenvalue equation for the TDEXX method, Eq. (33), is not much more difficult to solve than the standard TDDFT response eigenvalue equation due to Casida, see also Refs. 45 and 76, and can be used in conjunction with iterative Davidson solvers for generalized eigenvalue equations or, if the Taylor expansion approximation of Eq. (37) is employed, in conjunction with standard Davidson solvers for eigenvalue problems. When deriving the new eigenvalue Eq. (33) underlying the present TDEXX implementation, the basic TDDFT response Eq. (14) is replaced by a
matrix response equation, Eq. (16), by making the assumption that linear dependencies of products of occupied times unoccupied KS orbitals have no significant effect. To check whether this assumption is justified, a diagnosis scheme for eigenvectors of the TDEXX eigenvalue equation was developed and applied. In all cases it was found that unphysical contributions from linear combinations of products of occupied times unoccupied orbitals with zero norm are very small. Therefore, the above assumption seems to be justified and a projection of the second order in Eq. (33) on the linearly independent occupied-virtual orbital product space was not necessary.

The excitation energies obtained with the new TDEXX method were found to be very similar to those obtained with TDHF. This finding can be explained by an analytical comparison of the underlying eigenvalue equations of the TDHF and TDEXX method. If differences between HF and EXX determinants, which are known to be small, are disregarded, and TDEXX method. If differences between HF and EXX determinants, which are known to be small, are disregarded, then with the help of unitary transformations between occupied HF and EXX orbitals as well as unoccupied HF and EXX orbitals it was shown that the TDHF and TDEXX method differ only in terms of second order in Eq. (33) on the linearly independent occupied-virtual orbital product space was not necessary.

A comparison between TDEXX excitation energies and experimental excitation energies for ethylene, acetaldehyde, and pyridine has shown a good agreement only in case of acetaldehyde, but for ethylene and pyridine this approach was less successful. Also the combination of the ALDA xc potential for the ground-state kernels. Orbital-dependent correlation functionals that are derived from perturbation theory, e.g., according to Refs. 77 and 78, however, would lead to significantly higher computational costs while it seems unclear whether this would lead to a clearly better agreement with the experiment considering the results of Ref. 78. More economical solutions to the electron correlation problem in our orbital-dependent time-dependent density-functional method will be investigated in a future study.

APPENDIX A: FUNCTION DETERMINING THE EXCHANGE KERNEL

In contrast to the main text, in Appendix A we consider the somewhat more general case that the molecular orbitals may be complex. The function \( h_k(r, r', \omega) \) defining the exchange kernel of Eq. (6) can be decomposed into four terms \( h_k^{[p]}(r, r', \omega) \) with \( p = 1, 2, 3, 4 \):

\[
h_k(r, r', \omega) = \sum_{p=1}^{4} h_k^{[p]}(r, r', \omega). \tag{A1}
\]

The four terms are given by

\[
h_k^{[1]}(r, r', \omega) = -2 \sum_{ij} \sum_{ab} \left[ \frac{\phi_i^*(r)\psi_a(r)(ab|ji)\phi_j^*(r')\psi_b(r')}{(\epsilon_j - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_b + \omega + i\eta)} + \frac{\phi_i^*(r)\psi_i(r)(i|bj)\phi_j^*(r')\psi_b(r')}{(\epsilon_j - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_b - \omega - i\eta)} \right]. \tag{A2}
\]

\[
h_k^{[2]}(r, r', \omega) = -2 \sum_{ij} \sum_{ab} \left[ \frac{\phi_i^*(r)\psi_a(r)(ab|ji)\phi_j^*(r')\psi_b(r')}{(\epsilon_j - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_b - \omega - i\eta)} + \frac{\phi_i^*(r)\psi_i(r)(i|bj)\phi_j^*(r')\psi_b(r')}{(\epsilon_j - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_b - \omega + i\eta)} \right]. \tag{A3}
\]

\[
h_k^{[3]}(r, r', \omega) = -2 \sum_{ij} \sum_{a} \left[ \frac{\phi_i^*(r)\psi_a(r)(i|\phi^N_{\sigma}(r) - \hat{v}_x|i)\phi_j^*(r')\psi_j(r')}{(\epsilon_j - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_b + \omega + i\eta)} + \frac{\phi_i^*(r)\psi_i(r)(i|\phi^N_{\sigma}(r) - \hat{v}_x|i)\phi_j^*(r')\psi_j(r')}{(\epsilon_j - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_b - \omega - i\eta)} \right] + 2 \sum_{i} \sum_{ab} \left[ \frac{\phi_i^*(r)\psi_a(r)(i|\phi^N_{\sigma}(r) + \hat{v}_x|i)\phi_j^*(r')\psi_j(r')}{(\epsilon_j - \epsilon_a + \omega + i\eta)(\epsilon_j - \epsilon_b + \omega + i\eta)} + \frac{\phi_i^*(r)\psi_i(r)(i|\phi^N_{\sigma}(r) + \hat{v}_x|i)\phi_j^*(r')\psi_j(r')}{(\epsilon_j - \epsilon_a - \omega - i\eta)(\epsilon_j - \epsilon_b - \omega - i\eta)} \right]. \tag{A4}
\]
and

\[
\hat{h}^{[1]}_{\alpha}(\mathbf{r}, \mathbf{r}', \omega) = -2 \sum_{\alpha} \sum_{\alpha}^{\text{occ}} \left[ \frac{\varepsilon_{\alpha}(\mathbf{r})\varepsilon_{\alpha}(\mathbf{r}') (\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}') + \eta)}{(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}) + \eta)(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}'))} + \frac{\varepsilon_{\alpha}(\mathbf{r})\varepsilon_{\alpha}(\mathbf{r}') (\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}') - \eta)}{(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}) - \eta)(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}'))} \right] + 2 \sum_{\alpha} \sum_{\alpha}^{\text{unocc}} \left[ \frac{\varepsilon_{\alpha}(\mathbf{r})\varepsilon_{\alpha}(\mathbf{r}') (\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}') + \eta)}{(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}) + \eta)(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}'))} + \frac{\varepsilon_{\alpha}(\mathbf{r})\varepsilon_{\alpha}(\mathbf{r}') (\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}') - \eta)}{(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}) - \eta)(\varepsilon_{\alpha} - \varepsilon_{\alpha}(\mathbf{r}'))} \right].
\]

(A5)

Matrix elements of the type \(\langle aj | bi \rangle\) are defined by

\[
\langle aj | bi \rangle = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \phi^b_{a}(\mathbf{r}) \phi^a_{j}(\mathbf{r}) \phi^b_{i}(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|.
\]

(A6)

The parameter \(\eta\) in the denominators guarantees that perturbations are switched on adiabatically. In applications the limit \(\eta \to 0\) is considered.

The contributions due to \(h^{[1]}\) in earlier work\(^37\) had only negligible effect and therefore are neglected in this work.

**APPENDIX B: RESPONSE FUNCTION IN TERMS OF EXX EIGENVALUES AND EIGENVECTORS**

In Appendix B we derive a sum over states expression for the response function of an electronic system in terms of the excitation energies \(\varepsilon_{\alpha}\) and the corresponding eigenvectors \(\mathbf{z}_{\alpha}\) resulting from solving the TDEXX Eq. (31). From this expression for the response function follows expression (19) for the oscillator strengths in terms of eigenvectors \(\mathbf{z}_{\alpha}\).

Starting point is Eq. (14) for the response of the electron density due to an external perturbation. A sufficient condition for Eq. (14) to be obeyed is that Eq. (16) holds true, which can be reformulated as

\[
\left[ \omega^2 - \varepsilon_{\alpha}(\mathbf{r}) - \varepsilon_{\alpha}(\mathbf{r}') \right] \mathbf{z}(\omega) = 4 \varepsilon_{\alpha} \mathbf{v}^{(1)}(\omega)
\]

(B1)

if the matrices \(\mathbf{C}\) and \(\mathbf{X}(\omega)\) are expressed by the matrices \(\mathbf{A}\), \(\mathbf{B}\), and \(\mathbf{\Delta}\) according to Eqs. (8) to (12).

Next we introduce a matrix \(\mathbf{Z}\) that shall contain in its columns the eigenvectors \(\mathbf{z}_{\alpha}\) of the TDEXX Eq. (31) and a diagonal matrix \(\mathbf{\Omega}\) that shall contain the eigenvalues \(\varepsilon_{\alpha}\) of the TDEXX Eq. (31). With the matrices \(\mathbf{Z}\) and \(\mathbf{\Omega}\) the TDEXX Eq. (31) can be rewritten according to

\[
\left[ \varepsilon^2 + \omega^2 - \varepsilon_{\alpha}(\mathbf{r}) - \varepsilon_{\alpha}(\mathbf{r}') \right] \mathbf{Z}
\]

\[
= \left[ 1 - \varepsilon^{-1/2} [\mathbf{A} - \mathbf{B} + \mathbf{\Delta}] \varepsilon^{-1/2} \right] \mathbf{Z} \mathbf{\Omega}^{-1}.
\]

(B2)

Because the TDEXX Eq. (B2) is a generalized eigenvalue equation, its eigenvalues can and shall be chosen orthonormal with respect to the norm of the overlap matrix

\[
\mathbf{S} = \left[ 1 - \varepsilon^{-1/2} [\mathbf{A} - \mathbf{B} + \mathbf{\Delta}] \varepsilon^{-1/2} \right]
\]

(B3)

occurring on its right-hand side, i.e.,

\[
\mathbf{Z}^T \mathbf{S} \mathbf{Z} = \mathbf{1},
\]

(B4)

which implies

\[
\mathbf{Z} \mathbf{Z}^T = \mathbf{S}^{-1}
\]

(B5)

and

\[
\mathbf{S} \mathbf{Z} \mathbf{Z}^T \mathbf{S} = \mathbf{S}.
\]

(B6)

Next, we multiply the TDEXX Eq. (B2) from the right by \(\mathbf{Z}^T \mathbf{S}\), insert Eqs. (B3) and (B5), and obtain

\[
\omega^2 + \omega \varepsilon^1/2 [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \omega \varepsilon^1/2 = \mathbf{S} \mathbf{Z} \mathbf{\Omega}^2 \mathbf{Z}^T \mathbf{S}.
\]

(B7)

If we insert this equation together with Eq. (B6) into Eq. (B1), then we obtain

\[
\left[ \omega^2 \mathbf{S} \mathbf{Z} \mathbf{Z}^T \mathbf{S} - \mathbf{S} \mathbf{Z} \mathbf{\Omega}^2 \mathbf{Z}^T \mathbf{S} \right] \mathbf{z}(\omega) = 4 \varepsilon \mathbf{v}^{(1)}(\omega)
\]

(B8)

or

\[
\left[ \mathbf{S} \mathbf{Z} (\omega^2 \mathbf{1} - \mathbf{\Omega}^2) \mathbf{Z}^T \mathbf{S} \right] \mathbf{z}(\omega) = 4 \varepsilon \mathbf{v}^{(1)}(\omega).
\]

(B9)

With Eqs. (B4) and (B5), it follows that the inverse of the matrix \([\mathbf{S} \mathbf{Z} (\omega^2 \mathbf{1} - \mathbf{\Omega}^2) \mathbf{Z}^T \mathbf{S}]\) on the left-hand side of Eq. (B9) is the matrix \([\mathbf{Z} (\omega^2 \mathbf{1} - \mathbf{\Omega}^{-2})^{-1} \mathbf{Z}^T]\). Multiplication
of Eq. (B9) from the left with this inverse yields the vector \( \mathbf{z}(\omega) \) as

\[
\mathbf{z}(\omega) = 4 \left[ \mathbf{Z} \left( \omega_1^2 - \Omega_2^2 \right)^{-1} \mathbf{Z}^T \right] \mathbf{e}^{1/2} \mathbf{v}^{(1)}(\omega) \\
= 4 \sum_n \mathbf{z}_n (\omega_1^2 - \Omega_2^2)^{-1} \mathbf{z}_n^T \mathbf{e}^{1/2} \mathbf{v}^{(1)}(\omega).
\]

(B10)

Insertion of expression (B10) for \( \mathbf{z}(\omega) \) into Eq. (17) for the linear response \( \rho^{(1)}(\omega, \mathbf{r}, \mathbf{r}') \) of the electron density to a frequency-dependent perturbation \( \mathbf{v}^{(1)}(\omega, \mathbf{r}) \) yields

\[
\rho^{(1)}(\omega, \mathbf{r}, \mathbf{r}') = 4 \sum_{ia} \sum_{jb} \phi_{ia}(\mathbf{r}) \left[ \mathbf{e}^{1/2} \mathbf{z}_n (\omega_1^2 - \Omega_2^2)^{-1} \mathbf{z}_n^T \mathbf{e}^{1/2} \right]_{ia, jb} \prod_{\omega} \left( \mathbf{e}^{1/2} \mathbf{v}^{(1)}(\omega, \mathbf{r}) \right) \\
= \int d\mathbf{r} \prod_{\omega} \chi(\omega, \mathbf{r}, \mathbf{r}') \mathbf{v}^{(1)}(\omega, \mathbf{r}),
\]

(B11)

Equation (B11) implies that the response function \( \chi(\omega, \mathbf{r}, \mathbf{r}') \) of an electronic system within the TDEXXX approach is given by

\[
\chi(\omega, \mathbf{r}, \mathbf{r}') = \prod_{\omega} \left[ \mathbf{e}^{1/2} \mathbf{z}_n (\omega_1^2 - \Omega_2^2)^{-1} \mathbf{z}_n^T \mathbf{e}^{1/2} \right]_{ia, jb} \prod_{\omega} \phi_{ia}(\mathbf{r}) \prod_{\omega} \phi_{jb}(\mathbf{r}') \\
= \int d\mathbf{r} \prod_{\omega} \chi(\omega, \mathbf{r}, \mathbf{r}') \mathbf{v}^{(1)}(\omega, \mathbf{r}),
\]

with \( \mathbf{U}_n \) defined as \( \mathbf{U}_n = \mathbf{z}_n \mathbf{e}^{1/2} \Omega_2^{-1/2} \), see Ref. 79. From this expression of the response function, the frequency-dependent polarizability tensor can be obtained by integrating over components of the dipole operator with respect to both \( \mathbf{r} \) and \( \mathbf{r}' \) and expression (19) for the oscillator strengths follows.
12. Time-dependent density functional theory

13. Orbital-dependent correlation functionals

13.1. Local correlation potentials from Brueckner coupled-cluster theory

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Local correlation potentials from Brueckner coupled-cluster theory

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Local correlation potentials have been obtained from the nonlocal Brueckner coupled-cluster correlation potentials for the rare-gas atoms He, Ne, and Ar and the CO molecule. It is shown that the local correlation potential can mainly be expressed as a sum of two components: a “pure” correlation part and a relaxation contribution. While the total correlation potentials show an oscillating behavior near the nuclei, indicating the atomic shell structure, their components decrease rather monotonously, with a step structure in case of Ne and Ar. By looking at the determinantal overlap and one-electron properties it has been found that the orbitals obtained from these local potentials form a determinant which very well corresponds with the Brueckner determinant. Thus the previously found closeness between the Hartree–Fock determinant and the exchange-only Kohn–Sham determinant [Della Sala and Görling, J. Chem. Phys. 115, 5718 (2001)] is confirmed also for the correlated case. © 2005 American Institute of Physics. [DOI: 10.1063/1.1947167]

I. INTRODUCTION

Kohn–Sham density-functional theory (DFT) has become a widely used method in chemistry for studying molecules and solids. The reason for this is that DFT reduces the need to determine a complex wave function, as in wave-function theories such as configuration interaction or coupled cluster, to the search for an energy functional of the electron density. Apart from computational advantages, it can also be argued that the density is a more comprehensible quantity than a wave function. As Kohn and Sham have shown, the real many-particle system can be mapped to a system of noninteracting electrons which move in a local multiplicative potential.¹ The great advantage of this approach is that only a part of the total energy functional, namely, the exchange-correlation (xc) functional, remains unknown. However, despite the certainty that an exact xc functional exists from which the exact ground-state energy of the many-particle system can be determined, up to now only approximate forms of it have been obtained. Most of the commonly used xc functionals are generalized gradient extensions [generalized gradient approximations (GGA’s)] of the local-density approximation (LDA) functional. In order to approach the exact functional, both empirically parametrized GGA’s as well as functionals adjusted to reproduce known bounds of the exact xc functional have been used with some success in recent years.²⁻⁷

However, among other deficiencies which can be ascribed to the self-interaction error due to the use of approximate forms of the exchange functional, all of the GGA functionals lack the capability to describe long-range correlation effects. Accounting for these effects is crucial, e.g., in order to describe intermolecular interactions. This lack of commonly used DFT methods may simply be understood from the view that GGA functionals are locally dependent on the density, meaning that dispersion interactions between well-separated molecular fragments are not contained in the xc energy in this case. As the description of intermolecular interactions is of crucial importance in chemistry in order to understand, for example, protein docking or liquids, many attempts have been made in recent years to develop DFT methods which incorporate these interactions.⁸⁻¹¹ However, despite the success of some of these methods, most of them do not account for the locality problem of the xc functional but treat the dispersion interaction as a separate term which has to be added to the total energy of a molecular system.

The proper description of electron correlation effects therefore turns out to be an important task in order to make DFT methods more reliable for the study of weak molecular interactions. This becomes dramatically apparent if one compares approximate GGA correlation potentials with exact potentials derived from high-level ab initio densities as has been done for the helium atom:¹²,¹³ none of the six GGA correlation potentials used in Ref. 12 is able to reflect the structure of the exact correlation potential. In fact, all of them are mostly attractive in the region of \( r = [0.5 \rightarrow \infty] \) \( a_0 \), while the exact potential is repulsive in this region.

Formally, exact DFT theories which account for long-range correlation effects have been developed by several groups, among others by Görling and Levy¹⁴ and Bartlett and co-workers.¹⁵,¹⁶ Both the Görling–Levy perturbation theory and the ab initio DFT method by Bartlett and co-workers are based on the idea that all higher-order correlation corrections to the electron density coming from the perturbation expansion of the density-functional energy, and hence the Kohn–Sham potential, should vanish if the local zeroth-order potential is the exact Kohn–Sham potential. If the latter is true then it already should give the exact electron density of the real many-particle system. From this starting point nth-order approximations for the exact xc potential can be obtained by expanding the density matrix up to nth order and setting its first- and higher-order contributions to zero. This scheme has recently been developed and implemented up to second order.
13. Orbital-dependent correlation functionals

by Bartlett and co-workers. The process leads to optimized effective potential (OEP) equations which have to be solved recursively; i.e., the \( n \)th-order potential which has to be determined depends on the \((n - 1)\)th-order potential. Such second-order correlation potentials for the helium, neon, and beryllium atom have been shown to reproduce the local characteristics of the “exact” correlation potentials.16 Furthermore, the corresponding total energies are comparable or even superior to second-order Möller–Plesset (MP2) energies when compared with coupled-cluster singles, doubles, and triples (CCSDT), depending on the choice of the diagonal blocks of the Kohn–Sham Hamiltonian. These numerical results indicate that the Kohn–Sham perturbation theory provides a theory which approaches the exact Kohn–Sham limit through extension to higher order.

In this work an alternative approach will be investigated in which the local Kohn–Sham potential is directly obtained from the nonlocal Brueckner potential via the solution of the optimized effective potential (OEP) equation. The nonlocal Brueckner potentials are obtained from a corresponding Brueckner coupled-cluster doubles calculation, and thereby the approach provides a way of how certain terms in a corresponding Kohn–Sham perturbation theory can be summed up to infinity. In this way this method may also be understood as the simplest form of a coupled-cluster DFT method which only incorporates single excitations through the localization of the Brueckner correlation potential. The determinant formed from the coupled-cluster Brueckner orbitals has been shown to yield first- and second-order molecular properties which very well agree with those from a corresponding Brueckner coupled-cluster doubles (BCCD) finite-field calculation (the scheme has been termed as Brueckner orbital expectation value (BOX) method in Ref. 17). Indeed, it has been found that BOX gives electric properties which are closer to coupled-cluster singles and doubles with perturbative triples [CCSD(T)] results than to MP2 ones if the correlation effect is large.18 It is therefore believed that in this case the here presented Brueckner orbital Kohn–Sham (BOKS) scheme performs better for the prediction of molecular properties than the Kohn–Sham perturbation theory at second order.

Initiated by the findings that both the determinant formed out of the Brueckner orbitals and the determinant formed from the Kohn–Sham orbitals obtained from approximate xc potentials perform equally well for the description of first-order intermolecular interaction energies,18 there has recently been some interest about the closeness between Brueckner and (exact or approximate) Kohn–Sham orbitals.19–21 Indeed, the fact that not only the electrostatic interaction energies, which merely depend on the monomer densities, but also the first-order exchange energies from Brueckner and (approximate) Kohn–Sham orbitals are in good agreement18 shows that also the orbitals should be close to each other. This can be constituted because the first-order exchange interaction energies depend on the density matrices of both monomers. Recently, Lindgren and Salomonson have investigated the relation between Brueckner (perturbation) theory and Kohn–Sham theory on a sophisticated theoretical level. They devised a generalized Kohn–Sham scheme [Brueckner Kohn–Sham (BKS) method] in which the local multiplicative xc potential of the standard Kohn–Sham scheme is replaced by a nonlocal exchange potential and correlation potential where the latter is obtained from making the \( n \)th order many-body perturbation energy expressions stationary with respect to orbital variations. Lindgren and Salomonson have shown that, if performed to infinite order of perturbation theory, leads to a nonlocal correlation potential which defines Brueckner orbitals, i.e., those orbitals which yield a determinant which has maximum overlap with the exact wave function. Since the Brueckner determinant only incorporates all single excitations of the true wave function, it is clear that it cannot give the exact electronic ground-state density. Therefore Lindgren et al. had to introduce an additional local correction potential into the BKS Euler–Langrange equations in order to fulfill the basic requirement of Kohn–Sham theory that the orbitals of the pseudoparticle system should give the exact electronic density. They conclude with the remark that this local correction potential should be rather small, basing on the previous numerical findings that Brueckner orbitals already yield a density which is close to the exact one.

Some previous investigations19 and the results in this work show that this is indeed the case. It would therefore be interesting to find approximations to this remaining unknown local correction potential, either in a BKS scheme with a nonlocal xc potential counterpart or, as presented in this work, in a BOKS scheme with a local xc counterpart.

The organization of the paper is as follows: The next section describes the theoretical foundations of Brueckner coupled-cluster theory and the optimized effective potential method utilized in order to obtain the local correlation potentials. Section III presents the technical details of the computations. In Sec. IV the structure of the BOKS correlation potential is investigated by dividing it into a (pure) correlation part and a relaxation potential. This might be valuable for future approximations of the correlation potential in DFT methods. This is followed by an investigation of the similarity between the Brueckner determinant and the Kohn–Sham determinant obtained from the local xc potentials. Finally, Sec. V summarizes the results and discusses possible extensions of the method.

II. THEORY

A. The nonlocal correlation potential in Brueckner coupled-cluster theory

In coupled-cluster (CC) theory size-consistent expressions for the energy are achieved through setting the wave operator \( \Omega \), which acts on a reference state \( \Phi_0 \), to the exponential form

\[
|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle,
\]

where \( \Psi \) is the CC wave function and \( \hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots \) is the cluster operator. The choice of the reference state \( \Phi_0 \) may formally be any state which is not orthogonal to \( \Psi \). In general, one chooses a determinant which minimizes a given functional; e.g., if this functional is the energy functional then the reference state is the Hartree–Fock determinant. In
Brueckner coupled-cluster (BCC) theory one chooses the reference state which has a maximum overlap with the exact wave function. It can be shown that this condition leads to the (weaker) condition that the singly excited state does not mix with the exact wave function

$$\langle \Phi|^\Psi \rangle = 0.$$  \hspace{1cm} (2)

In coupled-cluster theory this means that the single-excitation amplitudes vanish; i.e., $T^1 = 0$, leading to an “absorption” of the single excitations into the reference state. If this condition is met, then the orbitals forming the reference state are Brueckner orbitals. Since in practice one has to truncate the cluster operator $T$ at a distinct order, the $T^1 = 0$ condition accordingly defines approximate Brueckner orbitals which are then fulfilling the maximum-overlap criterion in the restricted space. With $T = T_v + T_s$ the singles amplitude equation can be used to formulate a generalized Fock (or Brueckner effective Hamiltonian) matrix which defines the Brueckner orbitals.\(^{22,23}\) The occupied–virtual block of this matrix can be written as

$$F_{ia} = f_{ia} + \sum_{jb} t_{ij}^b \langle a|b\rangle + \frac{1}{2} \sum_{jbc} \langle aj|bc\rangle_j - \frac{1}{2} \sum_{jkb} \langle ib|jk\rangle_j,$$  \hspace{1cm} (3)

where indices $i, j, k, \ldots$ denote occupied (spin) orbitals and $a, b, c, \ldots$ denote virtual orbitals. In Eq. (3) $F_{pq}$ is the conventional Hartree–Fock Fock matrix, $t_{ij}^b$ is a double-excitation amplitude defined through the CC doubles amplitude equation\(^{24}\) and $\langle ij|ab\rangle$ is an antisymmetrized two-electron integral in Dirac’s notation. Through setting $F_{ia} = 0$, which is the Brillouin–Brueckner condition,\(^{25}\) one achieves that the single excitations vanish. As in case of the Brillouin theorem in Hartree–Fock theory this condition, together with the orthonormality constraint, is completely sufficient to define the orbitals, so that the choice of the occupied–occupied and virtual–virtual blocks is more or less arbitrary. If one chooses\(^{23}\)

$$F_{ik} = f_{ik} + \frac{1}{2} \sum_{j} \langle kj|ab\rangle t_{ij}^b$$  \hspace{1cm} (4)

for the occupied–occupied part, then the total energy can be written as

$$E = \frac{1}{2} \sum_j (h_{ij} + F_{ij}),$$  \hspace{1cm} (5)

where $h$ is the one-electron Hamiltonian. Note that with this choice the Brueckner Fock matrix has to be symmetrized in each coupled-cluster cycle.

We now relate the Brueckner correlation potential, which is implicitly defined in Eq. (3), to the second-order Brueckner correlation potential in Ref. 19. The diagrammatical representation of the last three terms in Eq. (3) is given in Fig. 1 where the thick bottom line represents a double amplitude, the dashed lines in the second and third diagram represents an antisymmetrized two-electron operator, and the cross angle in the first diagram comprises the one-electron contributions of the total Hamiltonian. Comparing these diagrams with those from Fig. 4 in Ref. 19 it can be seen that diagram 1 corresponds with diagram 3 with diagram 4, and diagram 3 with diagram 6 in Ref. 19. As the correlation potential of Fig. 4 in Ref. 19 is restricted to the second order, here the doubles amplitudes are given as $t_{ij}^b = \langle ij|ab\rangle/(\epsilon_j - \epsilon_i - \epsilon)$, as indicated by the dashed bottom lines in Fig. 4 of Ref. 19. Note that, as Brueckner orbitals and natural orbitals differ at first in the third order of perturbation theory,\(^{22}\) the second-order correlation potential of Ref. 19 also defines approximate natural orbitals (see also Ref. 25). Thus it is clear that the diagrams defining the second-order correlation potential also appear in the second-order expansion of the density matrix as given in Ref. 16. In fact, a direct relation between this work and the \textit{ab initio} DFT method as presented in Ref. 16 can be made by omitting all those contributions of the density-matrix expansion which come from doubles and higher-order amplitudes, namely, diagrams 3, 4, 6, 7, and 8 of Ref. 16.

As in Ref. 19 the contributions to the Brueckner correlation potential can be interpreted as follows: The second diagram in Fig. 1 is a (pure) correlation contribution which means that the corresponding operator, when acting on an occupied orbital, excites it directly into an unoccupied orbital, leaving the other occupied orbitals frozen. The third diagram of Fig. 1 is a relaxation contribution because the other occupied orbitals are affected when orbital $i$ is excited to an unoccupied orbital $a$. If, as proposed in Ref. 19, one uses these two terms also for the diagonal part of the Brueckner Fock matrix, a second-order extension to Koopman’s theorem is obtained where (in case of the occupied part) the correlation contribution always lowers the occupied orbital energies and the relaxation part gives always a positive contribution to the orbital energies.\(^{26}\) Finally, the first diagram in Fig. 1 appears because the Brillouin theorem no longer holds in the BCC theory. It can be stated, however, that its contribution to the total correlation potential is rather small.

13. Orbital-dependent correlation functionals

![Diagram 1](image)

**FIG. 1.** Diagrammatical representation of the Brueckner correlation potential in the Brueckner coupled-cluster doubles (BCCD) method.

B. Optimized effective potential (OEP) method

The fundamental equation of the optimized effective potential (OEP) method is given by\(^{14,27,28}\)

$$\int \chi(r, r') \psi(r') dr' = \sum_{ia} \phi_i^a(r) \phi_n(r) \frac{\langle i|j|a\rangle}{\epsilon_i - \epsilon_a} + \text{c.c.},$$  \hspace{1cm} (6)

which relates a nonlocal potential $\hat{U}_{NL}$ to a local multiplicative potential $\chi(r)$. In Eq. (6) $\phi_i^a$ and $\phi_n$ denote an occupied and virtual orbital, $\epsilon_i$ and $\epsilon_a$ are the corresponding eigenvalues, and $\chi(r, r')$ is the static Kohn–Sham (KS) response function.
\[ \chi(r, r') = \sum_{ia} \frac{d_i^a(r) \phi_a(r) \bar{d}^{*}_{ia}(r') \phi_{ia}(r')}{\epsilon_{ia} - \epsilon_a} + \text{c.c.} \]  

(7)

If one sets the nonlocal potential \( \hat{\nu}^{\text{NL}} \) to the Hartree–Fock exchange potential, then Eq. (6) is the exact exchange (EXX) equation of DFT.\(^{29–31}\) It has to be noted that Eq. (6) should be understood as a pointwise identity which has to be fulfilled in a least-squares sense. Finding the solution \( \nu(r) \) to this integral equation is not trivial since the KS response function defined in Eq. (7) has singularities. One way to circumvent this problem, which has been introduced by Görling,\(^{29}\) is to express the local potential as the electrostatic potential of a corresponding charge density \( \rho(r) \),

[\text{motivated by the Poisson equation. By substituting Eq. (8) into Eq. (6), expanding the charge density in an auxiliary basis set of Gaussian-type functions}]

\[ \nu(r) = \int \frac{\rho(r')}{|r - r'|} dr'. \]  

(8)

[\text{expanding both sides with the Coulomb norm in the same auxiliary basis set, Eq. (6) can be recasted into the matrix equation}]

\[ \mathbf{Xc} = \mathbf{t}, \]  

(9)

where

\[ X_{aq} = \sum_{ia} \frac{\langle P|ia\rangle\langle Q|ia\rangle}{\epsilon_{ia} - \epsilon_a}, \]  

(10)

[\text{and} \langle P|ia\rangle \text{is a three-index Coulomb integral over one auxiliary function} f_p \text{ and an occupied–virtual orbital pair. If the solution vector} \mathbf{c} \text{ to this equation has been found, then the local potential is given as}]

\[ \nu(r) = \sum_{p} c_p \int \frac{f_p(r')}{|r' - r|} dr'. \]  

(12)

The advantage of this approach in solving Eq. (6) is that Eq. (9) always has a unique solution since the charge density \( \rho(r) \) in Eq. (8) is always unique.

While the described approach to solve the OEP equation has previously been used to calculate the local exact exchange potential of DFT,\(^{29}\) where the charge density of Eq. (8) is reduced to the exchange charge density \( \rho_e(r) \), it can also be used to calculate a local exchange-correlation potential when one replaces \( \rho_e(r) \) by \( \rho_s(r) \). The latter then represents a charge density which also includes correlation effects, as pointed out in Ref. 29. In this work the local Brueckner correlation potential is obtained by setting the nonlocal potential matrix elements \( \langle i|\hat{\nu}^{\text{NL}}|a\rangle \) to the terms given in Eq. (3) or Fig. 1. The orbitaleigenvalues in Eqs. (10) and (11) are obtained from canonicalizing the Brueckner orbitals in the occupied–occupied and virtual–virtual space through the diagonalization of the Hartree–Fock Fock matrix. Note that the energy denominators in Eq. (6) are merely weight factors, so that the choice of the diagonal blocks of the effective Fock matrix will not have a substantial effect on the solution of Eq. (9).

The total local Brueckner xc potentials are obtained by setting \( \langle i|\hat{\nu}^{\text{NL}}|a\rangle = -h_{ia} - J_{ia} \) in Eq. (11) where \( h_{ia} \) and \( J_{ia} \) are occupied–virtual matrix elements of the one-electron Hamiltonian and the Coulomb potential in the Brueckner basis. As the integral over the exact xc charge density\(^{32}\) is equal to the integral over the exchange-only charge density, which is \(-1\), the same procedure as used in Ref. 29 has been applied in order to ensure a proper asymptotic decay of \(-1/r\) of the xc potential.

### III. COMPUTATIONAL DETAILS

The local Brueckner xc potentials and its components have been obtained for the three rare-gas atoms He, Ne, and Ar and the CO molecule. For CO a bond length of 2.132\(a_0\) has been used. The matrix elements defining the Brueckner Fock matrix of Eq. (3) were obtained from a Brueckner coupled-cluster doubles calculation as parts of the singles residual by using the efficient coupled-cluster code of MOLPRO.\(^{33–34}\) All electrons have been correlated in the calculations. The uncontracted augmented correlation-consistent polarized valence sextuple zeta (aug-cc-pV6Z) basis set of Wilson et al.\(^{35}\) has been used in each case, where the \( g \) and higher angular momentum functions have been omitted.

The OEP method as described in Sec. II B has been implemented in the developers' version of the MOLPRO program.\(^{34}\) For the auxiliary basis set needed to construct the matrix \( \mathbf{X} \) and the vector \( \mathbf{t} \) of Eq. (9), the product basis set of the corresponding aug-cc-pV6Z basis set has been used in case of the rare-gas atoms, as proposed in Ref. 36. Because of the spherical symmetry of the xc potentials only \( s \) functions were used in this case. In order to reduce numerical problems near the nuclei, all functions with an exponent greater than 3000, in case of He and Ne, and all functions with an exponent greater than 500, in case of Ar, have been omitted. For the CO molecule the correlation-consistent polarized valence quintuple zeta (cc-pV5Z) JK-fit basis set of Weigend\(^{37}\) has been used.

In order to obtain the individual components of the total Brueckner correlation potential, namely, the (pure) correlation potential (second diagram in Fig. 1) and the relaxation potential (third diagram in Fig. 1), the OEP equations have been solved with the corresponding matrix elements defined in Eq. (3) only. The total local Brueckner xc potential has been used in a subsequent Kohn–Sham DFT calculation utilizing a modified version of the DFT part of the MOLPRO program.\(^{34}\) Here the same basis sets used for the BCCD calculations have been employed.

### IV. RESULTS AND DISCUSSION

The Brueckner correlation potential for He, Ne, and Ar and the CO molecule is shown as the sum of its components in Figs. 2–5. It has been found that the contribution given by the first diagram in Fig. 1 to the total correlation potential is rather small in each case. Therefore the total correlation po-
potentials are expressed as the sum of $V_{\text{corr}}$ and $V_{\text{rel}}$.

In the case of the helium atom, Fig. 2 shows that the correlation contribution $V_{\text{corr}}$ monotonously increases to zero from $r=0$ to larger distances from the nucleus. Contrary to this, the relaxation potential $V_{\text{rel}}$ is a monotonously decreasing function but with a smaller negative slope near the nucleus than $V_{\text{corr}}$. Therefore the total correlation potential, given as the sum of $V_{\text{corr}}$ and $V_{\text{rel}}$, possesses a characteristic peak structure in the region of 0.8 $a_0$. Essentially the same behavior of the components of the correlation potential is also observed for the neon and argon atoms. However, both for neon and argon $V_{\text{corr}}$ and $V_{\text{rel}}$ display in a sense the atomic shell structure: in the case of $V_{\text{rel}}$, this can be seen by the changing slope in the region of 0–1 $a_0$, while $V_{\text{corr}}$ possesses small peaks near the nucleus, and in the case of argon a broader shallow peak at about 0.4 $a_0$ is also observed. As a consequence, the total correlation potentials for neon and argon possess an oscillating behavior near the nucleus, while their long-range behavior is mainly determined by the relaxation part. For the neon atom the structure of the correlation potential is consistent with previous investigations.\(^{15}\) In the case of the argon atom the total correlation potential has a small dip in the peak at 0.4$a_0$. Since the same structure has also been found in correlation potentials of argon\(^{18}\) determined by the method of Zhao et al.,\(^{38}\) this dip is not a result of numerical problems of the OEP method but is supposed to come from an incomplete basis set.

The correlation potential for the CO molecule along the molecular axis is shown in Fig. 5. As for the neon and argon atoms one can observe small peaks near the nuclei. In the region between the nuclei and in the outer regions broader peaks occur, which again come from the slower decreasing $V_{\text{rel}}$ compared to $V_{\text{corr}}$. The relaxation potential $V_{\text{rel}}$ also contains small dips at a distance of about 0.5$a_0$ from the nuclei. It is a well-known deficiency of the Hartree–Fock method that it predicts a wrong sign corresponding to C$^+$O$^−$ of the CO molecule along the molecular axis. The solid vertical lines denote the positions of the carbon atom (at $r=−1.2178a_0$) and the oxygen atom (at $r=0.9142a_0$).
dipole moment of the CO molecule. The overall shape of the total correlation potential can be used in order to explain why correlation methods are able to amend this deficiency: the broader peak of the potential on the oxygen site due to the stronger contribution of \( n_{\text{el}} \) leads to a lowering of the electronic density in this region, while the peak at the carbon atom site is much smaller. Since the total dipole moment of CO is rather small, this effect is sufficient to change the sign electronic density in this region, while the peak at the carbon site is much smaller. The observation that the deviations from one for the overlaps tend to increase with the size of the system can be assigned to the fact that in the limit of an infinite system two determinants which differ by a phase factor can describe the same physical situation, as pointed out in Ref. 30.

### Table I. Deviations from one of the overlap between the Hartree–Fock (HF), the Brueckner (BO), and the Brueckner Kohn–Sham (KS) determinants.

<table>
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<th>System</th>
<th>Overlap</th>
<th>1 overlap ((10^{-4}))</th>
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<tr>
<td>He</td>
<td>(BOHF)</td>
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<tr>
<td></td>
<td>(KSHF)</td>
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<td></td>
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<tr>
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<td>(KSHF)</td>
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<td>(KSHF)</td>
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</tbody>
</table>

In Table II first-order electric properties and highest occupied molecular orbital (HOMO) eigenvalues are given for the Brueckner and the Brueckner Kohn–Sham determinants, respectively. It can be seen that the Brueckner Kohn–Sham determinant nearly reproduces the radial expectation values and (in the case of the CO molecule) the dipole moment calculated with the Brueckner determinant. Thus these values confirm the conclusion, which has been drawn from the comparison of the determinantal overlaps, that the Brueckner and the Brueckner Kohn–Sham determinants are very close to each other. A comparison of the one-electron properties with those from higher level full configuration interaction (FCI) and CCSD(T) values respectively shows that the Brueckner and the Brueckner Kohn–Sham determinants describe the respective property on an accurate correlated level (see also Refs. 17 and 18).

A well-known property of the Kohn–Sham method is that the negative eigenvalue of the highest occupied Kohn–Sham orbital is equal to the exact ionization potential of the respective molecular system. Since, as described in Sec. II B, the total local xc potentials have been obtained by fixing the constraint that they decay as \(-1/r\) in the asymptotic region as the exact xc potential, the HOMO eigenvalues of the Brueckner Kohn–Sham orbitals are compared with the negative experimental ionization potentials in Table II. Though the Brueckner Kohn–Sham orbitals are not the “exact” Kohn–Sham orbitals, the HOMO eigenvalues for the rare-gas atoms are astonishingly close to the respective negative ionization potentials. For the CO molecule, however, a somewhat larger deviation of 0.015 a.u. between the HOMO eigenvalue and the negative experimental ionization energy is found. Note, though, that for the Hartree–Fock method one obtains a HOMO energy of \(-0.5550\) a.u., so that the HOMO energy obtained from the Brueckner Kohn–Sham scheme is clearly closer to the experimental negative ionization energy than is predicted by Koopman’s theorem.

The very good agreement of the HOMO energy of the Brueckner Kohn–Sham orbital with the exact negative ionization potential of the helium atom indicates that the Brueckner Kohn–Sham 1s orbital should be very close to the exact Kohn–Sham 1s orbital. Therefore in Fig. 6 a comparison is made between the local Brueckner orbital Kohn–Sham

### Table II. First-order expectation values \((\langle r^2 \rangle, \langle \mu_z \rangle)\) and HOMO orbital energies \((\epsilon_{\text{HOMO}})\) for the Brueckner (BO) and the Brueckner Kohn–Sham (KS) determinants. All values are in a.u.

<table>
<thead>
<tr>
<th>System</th>
<th>BO</th>
<th>KS</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.376</td>
<td>2.376</td>
<td>2.389(^a)</td>
</tr>
<tr>
<td>Ne</td>
<td>9.538</td>
<td>9.537</td>
<td>9.583(^c)</td>
</tr>
<tr>
<td>Ar</td>
<td>25.937</td>
<td>25.929</td>
<td>26.033(^c)</td>
</tr>
<tr>
<td>CO</td>
<td>24.181</td>
<td>24.189</td>
<td>24.340(^c)</td>
</tr>
</tbody>
</table>

\(^a\)Fci finite-field result (aug-cc-pV5Z basis set) from Ref. 18. 
\(^b\)Negative experimental ionization potential from Ref. 40. 
\(^c\)CCSD(T) finite-field result (aug-cc-pV5Z basis set) from Ref. 18.
(BOKS) correlation potential and the essentially exact correlation potential derived from a 204-term Hylleraas wave function. The diagram shows that the BOKS correlation potential reproduces the shape of the exact correlation potential. The exact potential steeply increases in the region of $0-0.75a_0$ and then falls off to zero relatively rapidly. In contrast to this, the slope of the BOKS correlation potential is smaller in the region near the nucleus and it falls off much slower than the exact potential. Note that similar findings have also been made for neon and argon. From Fig. 2 it could be seen that the long-range behavior of the BOKS correlation potential is dominated by its relaxation contribution. One may therefore conclude that this term is mainly responsible for the difference between the BOKS and the exact KS $1s$ orbital for helium.

V. SUMMARY AND OUTLOOK

In this work the local structure of the correlation potential obtained from the nonlocal Brueckner correlation potential has been investigated by dividing it into a “pure” correlation and a relaxation part. It has been found that the rather complex structure of the local correlation potentials can easily be comprehended from its components which show a characteristic behavior due to the atomic shell structure. Therefore these findings might be valuable for modeling the correlation potential by using approximate density- or orbital-functional forms to it. Such a procedure has already been successfully used in the past in order to approximate the response and the Slater potential of the local exchange potential of DFT. The development of accurate correlation functionals and potentials is a crucial task in current DFT methods since it has been found that correlation potentials from common correlation functionals show severe differences when compared with their exact counterparts.

The total local Brueckner xc potentials have been used to generate the Kohn–Sham orbitals and orbital eigenvalues in a self-consistent Kohn–Sham calculation. It has been found that the occupied orbitals form a determinant which is in very good agreement with the Brueckner determinant obtained from the corresponding nonlocal xc potential. Therefore the previous finding that the Hartree–Fock determinant and the exact-exchange Kohn–Sham determinant are close to each other is also demonstrated for the Brueckner and the Brueckner Kohn–Sham determinant. The here presented method can be related to the transformation local Hartree–Fock (TLHF) method of Ref. 30 because the local xc potential is calculated only once from the nonlocal xc matrix elements and is then held fixed in the subsequent Kohn–Sham calculation. In order to devise an approach in which the local potential is also optimized the following “Brueckner DFT” scheme could be used:

- In the $n$th coupled-cluster cycle the Brueckner Fock matrix $F^\text{BO}$ according to Eq. (3) is calculated from the orbitals and amplitudes of the preceding cycle.
- The exchange-correlation part of $F^\text{BO}$ is then used to calculate its local xc counterpart via the OEP Eq. (6).
- The Fock matrix $F^\text{BOKS}$ in which the nonlocal xc part of $F^\text{BO}$ is replaced by the local xc potential matrix elements is diagonalized in order to obtain new Brueckner Kohn–Sham orbitals.

With these orbitals new transformed integrals and doubles amplitudes needed for the next cycle and the calculation of the BCC energy are obtained via Eq. (5). A second-order approximation to this approach can be adapted by using the second-order perturbation theory expressions for the doubles amplitudes. In this case the resulting orbitals are believed to be similar to those from second-order ab initio DFT described in Ref. 16.

Note that in order to obtain the xc matrix elements no numerical integration is needed, since with the approach described in Sec. II B the xc matrix can simply be obtained from the sum over the products of the coefficients $c_F$ of Eq. (9) with the three-index Coulomb integrals given in Eqs. (10) and (11). The latter ones can easily be calculated analytically. This approach would be a correlated counterpart to the local Hartree–Fock approach from Ref. 30. As it has been found that the determinants from the TLHF and the LHF scheme equally well compare with the Hartree–Fock determinant, the same is also presumed for the two schemes described in this work.

A comparison between the Brueckner correlation potential and the exact correlation potential for the helium atom shows that the Brueckner correlation potential already reflects the essential behavior of the exact one. The main differences between both potentials were mainly in the short-range and the far long-range part where the Brueckner correlation potential decreases too slowly compared with the exact potential. Since these differences are rather small compared with the total xc potential, this investigation numerically supports the assumption of Lindgren and Salomonson that a local correction potential in their BKS scheme should only give a minor contribution to the total potential.

A great advantage of the Brueckner Kohn–Sham orbitals over the conventional Brueckner orbitals is that due to the $-1/r$ behavior of the local xc potential the virtual orbitals are
also “self-interaction free,” leading to virtually infinite bound orbitals in the limit of a complete basis set. This and the observation that the orbitals which have been obtained from the local Brueckner xc potentials give reasonably good first-order electric properties make the use of Brueckner Kohn–Sham orbitals and orbital eigenvalues in subsequent time-dependent DFT calculations highly promising.

ACKNOWLEDGMENTS

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13.2. Investigation of a localised second-order Brueckner correlation method

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Investigation of a localised second-order Brueckner correlation method

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Local second-order Brueckner correlation potentials have been derived from their non-local counterparts by starting from the assumption that the orbitals generated by these potentials are the same. The structure of the local correlation potentials and its components have been analysed for the neon atom and a range of small molecules, namely HF, HCl, H2O, CO and ethyne. The orbitals from the local Brueckner correlation potentials yield first-order electric molecular properties which are close to those inferred from second-order Möller–Plesset theory and Brueckner coupled cluster doubles with perturbative triples.

1. Introduction

Density functional theory (DFT) is founded on the Hohenberg–Kohn theorems1 (HKT) which state that for a many-particle system in its nondegenerate ground state there is a one to one mapping between the external potential, the particle density and the ground state wave function (HKT1) and that the Hohenberg–Kohn functional $F_{\text{HK}}[\rho] = T[\rho] + V_{\text{xc}}[\rho]$ (where $T$ is the kinetic energy, $V_{\text{xc}}$ the electron–electron interaction and $\rho$ the particle density) is minimised by, and only by, the ground state density $\rho_0$ (HKT2). While the first HKT is a general statement saying that knowledge of the density is sufficient to be able to obtain all ground state properties of the many-particle system, the second HKT gives a recipe for finding this density via the variational principle. Unfortunately, this requires knowledge of the Hohenberg–Kohn functional $F_{\text{HK}}[\rho]$ which up to now remains unknown.

In order to circumvent the difficulty in deriving the exact kinetic energy functional $T[\rho]$, Kohn and Sham2 (KS) have mapped the many-particle system to a non-interacting pseudo-particle system which moves in an external local potential. This ansatz corresponds to a splitting of the HK functional into a known part, namely the kinetic energy functional of the pseudo system, and an unknown part, the Kohn–Sham potential. In fact, as the electron–nucleus and Coulomb interactions for the KS system are also given, the only remaining unknown quantity is the so-called exchange–correlation (xc) functional which will also comprise kinetic energy contributions for the interacting system. Until today many approximations for the xc functional have been developed, usually based on the local density approximation (LDA) functional. In quantum chemistry, the generalised gradient approximation (GGA) extensions to LDA and their hybrid variants, which use some amount of exact exchange from Hartree–Fock theory,3 have successfully been used in a broad range of fields. However, it is known that GGAs fail to reproduce certain properties of the exact functional. For example, GGAs do not correct the self-interaction contributions of the Coulomb term, and this can only be partially remedied by some mix of Hartree–Fock exchange or asymptotic correction approaches for the xc potential.4,5 Furthermore, the exact functional is in some way non-locally dependent on the density while GGA functionals are strictly local. This leads, as one of the main consequences, to the fact that GGAs are not able to describe weak interactions between non-bonded complexes.6 This makes their use questionable for e.g. the description of liquids or the determination of protein structures.

A strategy to remedy these known problems of GGA functionals is to use density functionals which only implicitly depend on the density. One group of such functionals are the so-called meta-GGAs which depend on the kinetic energy density.7,8 Another group is the orbital functionals where the xc functional and its derivatives are given in terms of the molecular orbitals.9–12 The advantage of the latter approach is that a large contribution of the xc functional, namely the exchange term, is already known as an exact orbital functional and thus can be described without any further approximations. The use of the exchange orbital functional in DFT methods is denoted as the EXX (exact exchange)13,14 or OEP (optimised effective potential)15–17 method in the literature. This approach may be seen as the DFT counterpart to Hartree–Fock theory in wave function methods and it naturally solves the self-interaction problem of GGA functionals. In contrast to Hartree–Fock, in EXX an excited electron always feels the correct asymptotic $-1/r$ potential, so that the virtual orbitals in EXX are much improved compared to Hartree–Fock theory. Consequently, the EXX approach has advantages over the Hartree–Fock method for the description of excited states and response properties.18

Unfortunately, other than approximate GGA exchange functionals, the EXX methods, as Hartree–Fock, yield an exchange hole which is too diffuse compared to the exact total xc hole. This is e.g. manifested in the well known failure to describe dissociating molecules both with EXX and Hartree–Fock (note that conventional GGA KS methods also can not properly describe dissociation processes and one has to use extensions to it, e.g. spin-polarised KS procedures). Therefore, the EXX functionals have to be accompanied by a non-local correlation functional in order to properly reproduce these

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13. Orbital-dependent correlation functionals

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non-dynamic correlation effects. An obvious possibility is to use the correlation energy expression derived from many-body perturbation theory, which is also a functional of the molecular orbitals. Several groups have developed Kohn–Sham schemes based on perturbation theory, most notably the Göring–Levy perturbation theory\(^{19}\) and the OEP-MBPT(2) or \textit{ab initio} DFT approaches by Bartlett and co-workers.\(^{20,21}\) Both in the Göring–Levy perturbation theory and \textit{ab initio} DFT method the xc energy and potential are expanded in different orders of perturbation theory where the \(n\)th order terms recursively depend on the \(n–1\)th order terms. Using functional differentiations of the xc energy expressions one can then derive explicit expressions of the xc potential which depend on the Kohn–Sham orbitals and eigenvalues and on the inverse of the static Kohn–Sham Green’s function. A different approach has been developed by Mori-Sánchez \textit{et al.}\(^{11}\) which starts from an expansion of the local Kohn–Sham potential in Gaussian functions, the coefficients of which are determined such that the many-body energy expression is minimised.

Recently local correlation potentials have been derived from the non-local potentials from a Brueckner coupled cluster double (BCCD) wave function by using the optimised effective potential approach.\(^{22}\) This approach differs from those of ref. 19 and 21 because it is not based on a perturbation expansion in the Kohn–Sham basis but uses a direct transformation from a non-local to a local potential. It has been found that the orbitals, termed Brueckner Kohn–Sham orbitals (BKSOs) in ref. 22, obtained from these local correlation (and exchange) potentials yield a determinant which is close to the corresponding Brueckner determinant.

In this work, the equality of Brueckner orbitals (BOs) and BKSOs will be used as a starting assumption in order to derive a local second-order Brueckner correlation potential. For this, the methodology previously used for the exchange-only case by Della-Sala and Göring will be applied\(^{23}\) (note that a similar approach has been developed by Baerends \textit{et al.} which is based on an energy denominator approximation to the Kohn–Sham Green’s function\(^{24}\)). The exchange only variant, termed the localised Hartree–Fock (LHF) method in ref. 23, has been shown to yield Kohn–Sham orbitals which are indeed close to their Hartree–Fock counterparts. Here it will be shown that the orbitals from the correspondingly termed localised second-order Brueckner orbital method (LBO2) give first-order electric molecular properties which are in good agreement with those of corresponding wave function correlation methods for a range of small systems, namely Ne, HF, HCl, H\(_2\)O, CO and ethylene. Furthermore, the orbital energy from the highest occupied molecular orbital (HOMO) of the LBO2 orbitals strongly corrects the corresponding HOMO energies from LHF if compared to the negative vertical ionisation potentials from the restricted open-shell closed loop cluster singles and doubles with perturbative triples (RCCSD(T))\(^{25}\) results. As in ref. 22, the structure of the local correlation potentials will be investigated by splitting it up into distinct parts: a ‘pure’ correlation potential and a relaxation term. In addition, unlike in ref. 22, these are supplemented by a respective response term which arises due to the response to density variations as the corresponding Slater potential in the LHF method (we note here that in ref. 23 this term has been termed the ‘correction potential’ since it is not identical to the density response term of EXX due to the approximations of the LHF method described above; as the differences between these two terms can be presumed to be small,\(^{23}\) we drop this distinction in this work). It therefore has to be emphasised that in this work the terms ‘pure correlation’ and ‘relaxation’ have a different meaning than in ref. 22. The partitioning of the correlation potential will be described in the following section.

2. Methods

Without loss of generality the formulae presented in this section are given for the closed shell case and for real valued orbitals. Occupied orbitals are indexed with \(i, j, k, \ldots\) and virtual orbitals with \(a, b, c, \ldots\).

2.1. The non-local second-order Brueckner correlation potential

Considering a system of \(N\) electrons in an external potential \(\mathbf{V}_{\text{ext}}\) and using the conventional Møller–Plesset type partitioning of the Hamiltonian

\[
\hat{H} = \hat{H}_0 + \mathbf{V} = \sum_{i} \left[ \hat{h}(i) + \hat{u}(i) \right] + \sum_{i,j} \frac{1}{\varepsilon_{ij} - \varepsilon_{i}} - \sum_{i} \hat{u}(i) \tag{2.1}
\]

where \(\hat{h}\) is the conventional one-electron Hamiltonian and \(\hat{u}\) is an arbitrary one-electron potential, for an arbitrary determinant reference state \(\Phi\) the total energy up to second-order is given as

\[
E = E^{(0)} + E^{(1)} + E^{(2)} \tag{2.2}
\]

where

\[
E^{(0)} + E^{(1)} = \langle \Phi | \hat{H} | \Phi \rangle \tag{2.3}
\]

\[
E^{(2)} = \sum_{i} \sum_{a} \left| \langle \Phi | \mathbf{V} | \phi^a_i \rangle \right|^2 + \sum_{i} \sum_{ab} \left| \langle \phi^a_i | \mathbf{V} | \phi^b_j \rangle \right|^2 \tag{2.4}
\]

where \(\varepsilon\) are the eigenvalues of the zeroth-order Hamiltonian. It can be seen that the sum of the zeroth- and first-order energy is just the energy expectation value of the Hamiltonian and thus contains no correlation energy. If \(\Phi\) was the Hartree–Fock determinant it would be equal to the Hartree–Fock energy. By applying the Slater–Condon rules the second-order correlation energy can be written as

\[
E^{(2)} = \sum_{i} \sum_{a} \left| \langle \phi^a_i | \mathbf{f}_a \rangle \right|^2 - (a|j) \langle j|a \rangle + \sum_{i} \sum_{ab} \left| 2 \langle a|b \rangle - (a|j) \langle j|b \rangle \right|^2 \tag{2.5}
\]

\[
= \sum_{i} \sum_{a} \left| \mathbf{f}_a \right|^2 + \sum_{i} \sum_{ab} \left| 2 \langle a|b \rangle - (a|j) \langle j|b \rangle \right|^2 \tag{2.6}
\]

where \(\hat{f} = \hat{h} + \hat{u}\) and \((a|b)\) is a two-electron repulsion integral over spatial orbitals in chemist’s notation.

Lindgren \textit{et al.}\(^{26}\) have shown that minimising the total second-order energy expression with respect to orbital variations leads to a non-local correlation potential which defines a
13. Orbital-dependent correlation functionals

set of orbitals which remove all singles from the second-order wave function. These orbitals can thus be termed approximate Brueckner orbitals. The explicit orbital form for the occupied–virtual block of the non-local second-order Brueckner correlation potential is given as (compare with Fig. 4 of ref. 26)

\[ (i|v^{BO}_{c,v}(a) = (i|v^{BO}_{c,v}(a) + (i|v^{AO}_{c,v}(a) \tag{2.7} \]

with

\[ (i|v^{BO}_{c,v}(a) = \frac{f_{ii}}{\epsilon_i - \epsilon_a} + \sum_{\mu \neq i} \frac{f_{ii}f_{\mu i}}{(\epsilon_i - \epsilon_{\mu})(\epsilon_i - \epsilon_a)} \]

\[ - \sum_{\mu \neq i} \frac{f_{ii}f_{\mu i}}{(\epsilon_i - \epsilon_{\mu})(\epsilon_i - \epsilon_a)} + \sum_{\mu} \frac{2(\epsilon_i \epsilon_{\mu} - \epsilon_i \epsilon_a) - \epsilon_{\mu}^2}{(\epsilon_i - \epsilon_a)^2} \]

\[ (2.8) \]

and

\[ (i|v^{BO}_{c,v}(a) = \sum_{\mu} f_{\mu i}[2\epsilon_{\mu} \phi_{\mu}^{e} - \phi_{\mu}^{e}e] + (i|v^{BO}_{c,v}(a) + (i|v^{BO}_{c,v}(a) \tag{2.9} \]

where

\[ (i|v^{BO}_{c,v}(a) = \sum_{\mu \neq i} [2(ab\phi_{\mu}^{e} - (ac)\phi_{\mu}^{e}] \phi_{\mu}^{e} \tag{2.10} \]

\[ (i|v^{BO}_{c,v}(a) = - \sum_{\mu \neq i} [2(ik\phi_{\mu}^{e} - (ik)\phi_{\mu}^{e}] \phi_{\mu}^{e} \tag{2.11} \]

where \( v^{BO}_{c,v} \) has been partitioned into a single \( v^{BO}_{c,v} \) and double \( v^{BO}_{c,v} \) excitation part. Furthermore, as in Brueckner coupled cluster doubles theory,\(^{30,31}\) the double excitation part is split into three terms in eqn (2.9), namely a term involving the non-diagonal contributions to the Fock matrix, a ‘pure’ correlation term \( v^{BO}_{c,v} \) and a relaxation potential \( v^{BO}_{c,v} \). As described in ref. 26 the meaning of these terms is as follows: the ‘pure’ correlation potential, if acting on an occupied orbital, excites it directly into an unoccupied orbital leaving the other occupied orbitals frozen. Contrary to this, the relaxation potential affects the other occupied orbitals when it excites an occupied orbital. As a consequence the lowest \( N \) particles will relax through the action of \( v^{BO}_{c,v} \). In section 4 it will be shown that the localised ‘pure’ correlation and relaxation potentials possess a very characteristic and clearly different form.

The question now remains how the occupied–occupied and virtual–virtual blocks of the correlation potential should be chosen. As in Hartree–Fock theory this choice is arbitrary, since for the stationary condition it is only required that

\[ (i|f + v^{BO}_{c,v}(a) = 0 \tag{2.12} \]

coupled cluster method,\(^{32}\) this only approximately holds if the outer diagonal elements of the occupied–occupied block are also corrected. Obviously, the total effective Fock matrix is then no longer Hermitian and has to be symmetrised during the SCF iterations. In cases where the anti-Hermitian contributions are larger, Stolarczyk et al. suggest that a diagonalisation of non-Hermitian matrices should be carried out.\(^{32}\)

It has to be noted that there is no guarantee that a minimisation of the energy functional defined in eqn (2.2)–(2.5) converges in general. Mori-Sánchez et al.\(^{1,31}\) have recently applied a direct minimisation procedure for the generalised second-order energy functional under the additional constraint that the orbitals stem from a local potential, i.e. in an OEP approach. They have reported convergence problems for all but two-electron systems and ascribe these to small occupied–unoccupied eigenvalue gaps which produce problems especially for the minimisation of the negative definite single excitation term (first term on the right-hand side of eqn (2.5)). On the other hand, Beste et al.\(^{33}\) have numerically investigated an iterative optimisation procedure to obtain Brueckner orbitals through the projection approach using eqn (2.7)–(2.11) and have stated no convergence problems. Note that the projective and variational Brueckner orbitals differ from each other in general,\(^{34}\) even in the full CI limit.\(^{35}\) Thus a different behaviour with regard to the convergence properties of variational and projective Brueckner methods, which are based on the Brillouin–Brueckner condition (eqn (2.12)), can be expected.

Eqn (2.1)–(2.5) correspond to partitioning Scheme 1 of ref. 33, which does not provide an invariance with respect to orbital rotations within the occupied or virtual space. This can be remedied if the non-diagonal occ–occ or virt–virt elements of the effective Hamiltonian are also included in the unperturbed Hamiltonian, leading to iterative equations for the first-order single- and double-excitation amplitudes (partitioning Scheme 2 of ref. 33). While this work follows the scheme described in ref. 26 (which corresponds with the partitioning of Scheme 1 of ref. 33), the way that different partitionings of the Hamiltonian affect the Brueckner orbitals will have to be investigated in future. A comparison of the dipole moments calculated for six small molecules from Brueckner determinants obtained from the two partitioning schemes described above indicates that the orbitals from both schemes are rather close to each other.\(^{33}\)

2.2. The localised second-order Brueckner correlation potential

The many-particle equations for the Brueckner determinant \( \phi^{BO} \) and a corresponding Brueckner Kohn–Sham determinant \( \phi^{BOKS} \) may be written as

\[ [\hat{T} + \hat{V}_{xc} + \hat{J} + \hat{V}^{BO}_{xc}] \phi^{BO} = E^{BO}\phi^{BO} \tag{2.13} \]

\[ [\hat{T} + \hat{V}_{xc} + \hat{J} + \hat{V}^{BOKS}_{xc}] \phi^{BOKS} = E^{BOKS}\phi^{BOKS} \tag{2.14} \]

where \( \hat{T} \) is the kinetic energy operator, \( \hat{V}_{xc} \) is the nuclear attraction term, \( \hat{J} \) is the Coulomb operator and \( E \) are the sums of the one-particle energies in both cases. The terms \( \hat{V}^{BO}_{xc} \) and \( \hat{V}^{BOKS}_{xc} \) denote the sums of the one-particle non-local and local exchange–correlation potentials, respectively. In the case
of the non-local Brueckner approach the total xc potential is just the sum of the non-local exchange potential \( v^x(\mathbf{r}, \mathbf{r}') = \sum_{\phi_i} \phi_i(\mathbf{r}) \phi_i(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| \) and the non-local correlation potential defined in eqn (2.7)–(2.11).

In order to derive an expression for the local xc potential \( v^{\text{BOKS}}_{\text{xc}}(\mathbf{r}) \) which corresponds to its non-local counterpart \( v^{\text{BO}}_{\text{xc}} \), we follow the same strategy as Della Sala and Görling\(^{23}\) and assume that the determinants from the non-local and local potentials are identical, i.e. \( \rho^{\text{BO}} = \rho^{\text{BOKS}} = \rho \). This ansatz is justified by the recently found closeness between the Brueckner determinant of a Brueckner coupled cluster doubles wave function and the Kohn–Sham determinant derived from the corresponding local xc potential acquired through the OEP approach.\(^{22}\) By applying the same transformations as Della Sala and Görling\(^{23}\) one then arrives at formally the same expression for the xc potential as in the exchange-only case

\[
v^{\text{BOKS}}_{\text{xc}}(\mathbf{r}) = v^x_{\text{Sl}}(\mathbf{r}) + v^{\text{BOKS}}_{\text{xc}}(\mathbf{r}) \quad (2.15)
\]

where \( \rho \) is the electronic density and \( \phi_i \) are the molecular orbitals. In eqn (2.15) \( v^x_{\text{Sl}}(\mathbf{r}) \) is the Slater potential\(^{35}\) which governs the long-range behaviour of the xc potential and can be defined as the electrostatic integral over the xc hole density.\(^{37,38}\) The second term \( v^{\text{BOKS}}_{\text{xc}}(\mathbf{r}) \) is the response potential and it corrects the Slater potential in the short-range part. As described above, we keep the terminology of ref. 38, though there will be slight differences between the ‘exact’ response potential defined e.g. in ref. 38 and in the current approximation. As in the exchange-only case,\(^{23}\) the Krieger–Li–Iafrate approximation\(^{39}\) can be obtained by neglecting all terms with \( i \neq j \) in the second sum of eqn (2.16). A similar approach has been developed by Engeler et al. in the framework of the OEP approach.\(^{40}\)

From eqn (2.16) it can be seen that the calculation of the response potential requires the knowledge of the local potential in advance and thus an iterative solution has to be adapted by starting from some initial guess for \( v^{\text{BOKS}}_{\text{xc}}(\mathbf{r}) \). Another variant, termed the transformation local Hartree–Fock (TLHF) in the exchange-only case, defines the local potential in one step by determining the coefficients \( c_{ij} = (\langle i | v^{\text{BO}}_{\text{xc}} - v^{\text{BOKS}}_{\text{xc}} | j \rangle)/\rho(\mathbf{r}) \) through the solution of a linear equation system which only needs the orbitals from the non-local potential as input (defined in eqn (19) and (20) of ref. 23).

In order to arrive at a practical computational scheme, we now make a rough approximation by representing the non-local second-order Brueckner correlation potential in the Hartree–Fock basis. From eqn (2.7)–(2.11) it can then be seen that all terms will drop with the exception of \( v^{\text{corr}}_{\text{BO}} \) and \( v^{\text{relx}}_{\text{cor}} \) (eqn (2.10)). Then, the linear equation system needed to determine the coefficients \( c_{ij} = \langle i | v^{\text{BO}}_{\text{xc}} - v^{\text{BOKS}}_{\text{xc}} | j \rangle /\rho(\mathbf{r}) \) is solved with the Hartree–Fock orbitals as input. We note that this approach is similar to the OEP-MBPT(2)D variant used in ref. 20 and may be justified by the fact that due to the similarity between Hartree–Fock and Brueckner orbitals the corresponding terms in eqn (2.8) and (2.9) are rather small. The local xc potential is then calculated only once and held fixed in a subsequent Kohn–Sham calculation, thus relaxing the other contributions of the Kohn–Sham potential. The numerical results presented in section 4 and those for the exchange-only case\(^{41}\) justify this procedure.

The calculation of the Slater potential \( v^x_{\text{Sl}}(\mathbf{r}) \) needs special attention. For this, the action of the non-local potential on an occupied orbital is needed: \( v^{\text{BO}}_{\text{xc}} \phi(\mathbf{r}) \). Following the notation of Stolarczyk and Monkkos,\(^{28}\) the kernels for the correlation and relaxation contributions may be written as

\[
(c | v^{\text{corr}}_{\text{BO}} | \bullet) = \sum_{\beta \neq \alpha} \langle \alpha | \beta \rangle (c | \alpha \rangle /\delta_{\alpha \beta} - (\langle \alpha | \beta \rangle /\delta_{\alpha \beta})^2 \delta(\mathbf{r} - \mathbf{r}) \quad (2.17)
\]

\[
(c | v^{\text{relx}}_{\text{cor}} | \bullet) = \sum_{\beta \neq \alpha} \langle \alpha | \beta \rangle (c | \alpha \rangle /\delta_{\alpha \beta} - (\langle \alpha | \beta \rangle /\delta_{\alpha \beta})^2 \delta(\mathbf{r} - \mathbf{r}) \quad (2.18)
\]

where \( \langle \alpha | \beta \rangle \) denotes an overlap integral over orbitals \( \phi_\alpha \) and \( \phi_\beta \). With these definitions the contributions from \( v^{\text{corr}}_{\text{BO}} \) and \( v^{\text{relx}}_{\text{cor}} \) to the Slater potential are given as

\[
v^{\text{corr}}_{\text{cor}}(\mathbf{r}) = \frac{2}{\rho(\mathbf{r})} \sum_{\beta \neq \alpha} \sum_{\alpha} \phi_\alpha(\mathbf{r}) \phi_\alpha(\mathbf{r}) (c | \alpha \rangle /\delta_{\alpha \beta} - (\langle \alpha | \beta \rangle /\delta_{\alpha \beta})^2 \delta(\mathbf{r} - \mathbf{r}) \quad (2.19)
\]

\[
v^{\text{relx}}_{\text{cor}}(\mathbf{r}) = -\frac{2}{\rho(\mathbf{r})} \sum_{\beta \neq \alpha} \sum_{\beta \neq \alpha} \phi_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r}) (c | \alpha \rangle /\delta_{\alpha \beta} - (\langle \alpha | \beta \rangle /\delta_{\alpha \beta})^2 \delta(\mathbf{r} - \mathbf{r}) \quad (2.20)
\]

where the following definition has been used

\[
v^{\text{corr}}_{\text{cor}}(\mathbf{r}) = \int \frac{\phi^*_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.21)
\]

For the relaxation potential it can now be observed that the equality

\[
E^S = \sum_{\alpha} \langle \alpha | v^{\text{corr}}_{\text{cor}} | \alpha \rangle /\delta_{\alpha \alpha} = \frac{1}{2} \int \rho(\mathbf{r}) \phi^*(\mathbf{r}) d\mathbf{r} \quad (2.22)
\]

does not hold, while it is naturally fulfilled in the exchange-only case and for the correlation term for which the above integral yields the exchange and correlation energy, respectively. As a consequence the relaxation potential, as defined in eqn (2.20), is shifted compared to the correct local potential. In order to remedy this behaviour we extend the second summation in eqn (2.20) over all orbitals so that one gets

\[
v^{\text{relx}}_{\text{cor}}(\mathbf{r}) = \frac{2}{\rho(\mathbf{r})} \sum_{\beta \neq \alpha} \sum_{\alpha} \phi_\alpha(\mathbf{r}) \phi_\alpha(\mathbf{r}) (c | \alpha \rangle /\delta_{\alpha \beta} \phi_\beta(\mathbf{r}) |\mathbf{r} - \mathbf{r}'| \quad (2.23)
\]

which makes use of the resolution of the identity (RI) in the MO basis:

\[
\sum_{\alpha} \phi_\alpha(\mathbf{r}) \phi_\alpha(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') \quad (2.24)
\]

If the total number of orbitals is spanned by the same number of atomic basis functions, as usually is the case, then this RI is identical to that used in ref. 23 to approximate the exchange-
only Slater potential. Since in praxis the number of orbitals is finite, eqn (2.24) will only approximately hold. In ref. 23 it has been pointed out that the use of truncated basis sets leads to errors in the asymptotic region because standard basis sets usually only contain a few diffuse functions. Since compared to the exchange-only Slater potential, which decreases as \(1/r\) in the asymptotic region, the relaxation potential is rather short-ranged, in this work its RI representation in eqn (2.23) has been multiplied by the damping factor \(\rho(r)(\rho(r) + \gamma)\) which (for \(1 \gg \gamma > 0\)) is one in the valence regions and goes smoothly to zero in the asymptotic region. The constant \(\gamma\) has been adjusted to a value of \(10^{-5}\) which (for \(1\)) only Slater potential. Since in praxis the number of orbitals is finite, eqn (2.24) will only approximately hold. In ref. 23 it has been pointed out that the use of truncated basis sets leads to errors in the asymptotic region because standard basis sets usually only contain a few diffuse functions. Since compared to the exchange-only Slater potential, which decreases as \(1/r\) in the asymptotic region, the relaxation potential is rather short-ranged, in this work its RI representation in eqn (2.23) has been multiplied by the damping factor \(\rho(r)(\rho(r) + \gamma)\) which (for \(1 \gg \gamma > 0\)) is one in the valence regions and goes smoothly to zero in the asymptotic region. The constant \(\gamma\) has been adjusted to a value of \(10^{-5}\) which (for \(1\))

While the exact local correlation potential decreases as \(\sim -\text{const.}\, r^4\), the components of the local second-order Brueckner correlation potential possess the following asymptotic behaviour:

- the response potential (second term in eqn (2.16)) goes to zero for \(r \to \infty\), as in the exchange-only case because the summation excludes the HOMO for which

\[
2|\phi_{\text{HOMO}}(r)|^2 \approx \rho(r) \quad (2.25)
\]

holds

- the ‘pure’ correlation potential (eqn (2.19)) consists of two terms for which one finds

\[
\phi_{\text{core}}(r) \to \text{const.} \frac{\phi_{\text{HOMO}}(r)\phi_{\text{unocc}}(r)}{|\phi_{\text{HOMO}}(r)|^2} \quad (2.26)
\]

where \(\phi_{\text{core}}(r)\) denotes the unoccupied state with the slowest decrease and \(n \geq 2\). Since all unoccupied orbitals decay more slowly than \(\phi_{\text{HOMO}}\), the term \(\phi_{\text{HOMO}}(r)\phi_{\text{unocc}}(r)/|\phi_{\text{HOMO}}(r)|^2\) diverges exponentially and thus the two terms of \(v_{\text{core}}\) will diverge for \(r \to \infty\). It is unlikely that the two terms will cancel each other in the asymptotic region and as a consequence the total ‘pure’ correlation potential will diverge in the asymptotic region.

- for the relaxation potential (eqn (2.20) and (2.23)) the asymptotic behaviour is given by

\[
v_{\text{relx}}(r) \to \text{const.} \frac{\phi_{\text{HOMO}}(r)\phi_{\text{unocc}}(r)}{|\phi_{\text{HOMO}}(r)|^2} \quad (2.27)
\]

and thus, as with \(v_{\text{core}}(r)\), an exponential divergency is found for \(r \to \infty\). As there is no damping of the \(\phi_{\text{HOMO}}(r)\phi_{\text{unocc}}(r)\)/ \(\rho(r)\) contribution by \(1/r^4\) as in case of \(v_{\text{core}}(r)\), the relaxation potential grows even more rapidly in the asymptotic region than the ‘pure’ correlation potential.

As a consequence, the total second-order Brueckner correlation potential diverges in the asymptotic region and does not recover the proper \(\sim -\text{const.}\, r^4\) behaviour. This finding is in agreement with the analysis of the second-order OEP correlation potential of Bonetti et al.\(^{41-45}\) Therefore a numerical correction in the asymptotic area, as described above, is needed in general.

### 3. Computational details

The local second-order Brueckner correlation potential has been calculated for the systems Ne, HF, HCl, H$_2$O, CO and ethyne as described in section 2.2. For HF, HCl and CO bond lengths of 1.7327, 2.4000 and 2.1320 $\alpha_0$ were used, respectively. For H$_2$O a bond length of 1.8094 $\alpha_0$ and an angle of 104.51° has been used. In case of ethyne the C–C bond has been set to 2.2730 $\alpha_0$ and the C–H bond to 2.0065 $\alpha_0$. The molecules have always been oriented such that the origin is the centre of mass and the main symmetry axis lies in the $z$ direction.

In all cases the augmented quadruple $\zeta$ basis sets of Dun-ning et al.\(^{46}\) have been used. The non-local Brueckner correlation potential as described in section 2.1 has been calculated by using density fitting of the two-electron integrals\(^{47,48}\) in order to reduce computational efforts. For this the MP2-fitting basis of Weigend et al.\(^{49}\) was employed.

The non-local Brueckner potential has been calculated by using Hartree–Fock orbitals and orbital eigenvalues as input. Since the occupied–occupied blocks of the non-local potential are non-Hermitian, they have been symmetrised before they were used to determine the local xc potentials. The non-Hermitian contributions were always found to be rather small.

Sufficiently fine integration grids have been used throughout. The xc potentials derived in one step were then used in a subsequent self-consistent Kohn–Sham calculation to determine Kohn–Sham orbitals and eigenvalues.

The first-order molecular electric properties determined from the Kohn–Sham determinant obtained in this way were compared to the corresponding expectation values from the Brueckner determinant of a Brueckner coupled cluster doubles calculation,\(^{31}\) termed the BOX method in ref. 50. In addition, molecular properties have been calculated from analytical MP2 response calculations and from Brueckner coupled cluster double with perturbative triples (BCCD(T)) finite field calculations.

All calculations have been performed using the Molpro quantum chemistry package.\(^{31}\) Unless otherwise noted, core electrons have not been correlated.

### 4. Results

#### 4.1. Correlation potentials

The ‘pure’ correlation and relaxation potentials as given in eqn (2.19) and (2.23) and their sums are displayed in Figs. 1–8 for the several systems studied in this work (we may skip the declaration ‘pure’ in the following and emphasise that we do not refer to the total correlation potential unless this is explicitly stated). In all cases it can be seen that the correlation potentials are strictly attractive in the core and valence regions while their relaxation counterparts are repulsive over the whole range of space. This can be physically understood, since correlation effects attract the electrons while relaxation effects move the electrons apart from each other. Though having used...
a slightly different definition for the contributions to the total correlation potential, this finding agrees with the observations in ref. 22. In that work the correlation and relaxation potentials also included the response terms of eqn (2.15). Moreover it can be seen that the relaxation contributions clearly dominate the correlation potentials, which quickly tend to zero in the asymptotic range. In contrast to this, the relaxation potentials go to zero in the asymptotic area rather slowly. As a consequence the sum of the two contributions is mostly positive. Note that the total magnitude of the sum $v_{corr} + v_{relx}$ in the outer regions is by far smaller than that of the exchange potential which generally decreases as $1/r^{3}$.

Figs. 1–8 show that the correlation potentials possess sharp peaks near to the nucleus while one can observe a broader peak for the relaxation potentials at nearly the same position. In Fig. 7 one can see that for both the correlation and the relaxation potential these peaks are more pronounced on the oxygen site while on the carbon site they are smaller by a factor of about two for the correlation contribution and three for the relaxation contribution. Thus, though one would intuitively expect a different behaviour due to the larger electronegativity of oxygen compared to the carbon atom, the sum of the correlation and relaxation terms is much more repulsive near to the oxygen atom than to the carbon atom. Below it will be seen that the response contribution partially corrects this property. An interesting difference between the correlation and relaxation potentials, which can be observed for HF, HCl and ethyne in Figs. 3, 4 and 8, is that the correlation potentials have slight peaks at the hydrogen positions while the relaxation potentials are smooth and do not show any structure at all in this region. However, the presence of the hydrogen atom is indicated by the slight asymmetry of the relaxation potentials. The structure of the correlation potential is clearly conserved in the sum of both potentials.

In the bonding region of the C–O and C–C bond of CO and ethyne it can be seen that the potentials approximately display
a superposition of the peaks on the far-bond regions. This has the effect that for the sum of correlation and relaxation a relatively sharp peak occurs in the bonding region for these two systems.

It has to be noted that the structure of the potentials in the core region clearly changes if core correlation is included. This is exemplarily shown for the Ne atom (Figs. 1 and 2) and the HCl molecule (Figs. 4 and 5). In case of neon, Fig. 2 shows that $v_{\text{corr}}$ and $v_{\text{relx}}$ now do not vanish near the nucleus but stay finite. While for the correlation potential a small and sharp peak now occurs close to the nucleus, the relaxation potential has become a step structure with a large offset compared to the magnitude of its correlation counterpart. The same behaviour is also found for the HCl molecule (see Fig. 5) where the step structure of the relaxation part reflects the two core shells of chloride. The effect of core correlation for the total correlation potential is shown for the neon atom in Fig. 9. With exception of the small peak near the nucleus which occurs in the all-electron potential, the two curves look nearly the same. Since this difference of the two potentials can be ascribed to the change of the ‘pure’ correlation potentials in Fig. 1 and 2, it can be concluded that the step structure of the relaxation potential is largely quenched by its response contribution.

The total correlation potential $v_c$ and its components, namely the ‘pure’ correlation ($v_{\text{corr}}$), relaxation ($v_{\text{relx}}$) and response ($v_{\text{respc}}$) contribution, is shown for the HF and CO molecule in Figs. 10 and 11 (we note here that $v_{\text{respc}}$ only refers to the response to the correlation part of the Slater potential). In case of HF the response potential has a low broad peak at the fluoride site and goes to some small value in the asymptotic region. Therefore the structure of the total correlation potential does not change very much compared to the sum $v_{\text{corr}} + v_{\text{relx}}$ displayed in Fig. 3. The only remarkable difference between $v_c$ and $v_{\text{corr}} + v_{\text{relx}}$ is that the total correlation potential...
potential vanishes slower in the asymptotic region. For the CO molecule a different behaviour of the response potential is observed (see Fig. 11). In the region of the carbon atom and in the bonding region its contribution is nearly zero while it has a broad negative peak on the oxygen site. Thus it strongly quenches the large relaxation contribution in this region. The overall shape of the total correlation potential is very similar to that obtained from the non-local Brueckner coupled cluster doubles potential.22 Note that the response contributions to the correlation potential is clearly different from the response potentials in the exchange-only case where it possesses a characteristic step structure which displays the atomic shells.23,38

4.2. Molecular properties and HOMO eigenvalues

The local xc-potentials have been used to determine Kohn–Sham orbitals and eigenvalues in a self-consistent Kohn–Sham calculation for the various systems. According to the exchange-only variant (termed as local Hartree–Fock method in ref. 23) we will term the method localised second-order Brueckner orbital method (LBO2) in the following (the distinction between the one-step transformation procedure and the full transformation is omitted here and, based on the findings for the exchange-only case,41 it is assumed that the differences will be small). Some first-order electric molecular properties for LBO2, Hartree–Fock and three other correlation methods, namely MP2 (second order Möller–Plesset), BCCD(T) (Brueckner coupled cluster singles doubles with perturbative triples) and BOX (Brueckner Orbital Expectation value approach)50 are compiled in Table 1. It can be seen that in nearly all cases LBO2 is able to reproduce the correlation effects predicted by MP2 and BCCD(T) for the various properties. While for HF, HCl and H2O the dipole moments from LBO2 are close to those of MP2, for CO one finds a small improvement over MP2 if BCCD(T) is taken as reference. In case of strong correlation effects the BOX method is known to perform well50,54 (see also Table 1) and so it appears that this also holds to some extent for expectation values from second-order Brueckner orbitals. With only few exceptions the BOX values and those from LBO2 are rather close to each other. The BOX method sometimes does not fully reproduce radial density moments from higher level correlation methods.

Table 1  Dipole ($\mu$), quadrupole ($Q$) and radial density ($r^2$) moments. All values are in a.u.

<table>
<thead>
<tr>
<th>System</th>
<th>Property</th>
<th>HF</th>
<th>MP2</th>
<th>BCCD(T)</th>
<th>BOX</th>
<th>LBO2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>1.735</td>
<td>1.735</td>
<td>1.713</td>
<td>1.729</td>
<td>1.737</td>
</tr>
<tr>
<td>HF</td>
<td>$r^2$</td>
<td>10.956</td>
<td>11.387</td>
<td>11.312</td>
<td>11.230</td>
<td>11.297</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>2.794</td>
<td>2.734</td>
<td>2.722</td>
<td>2.679</td>
<td>2.734</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>1.797</td>
<td>1.841</td>
<td>1.808</td>
<td>1.823</td>
<td>1.827</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>0.779</td>
<td>0.731</td>
<td>0.727</td>
<td>0.741</td>
<td>0.729</td>
</tr>
<tr>
<td></td>
<td>$Q_{zz}$</td>
<td>5.450</td>
<td>4.848</td>
<td>4.861</td>
<td>5.013</td>
<td>5.013</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>25.817</td>
<td>25.676</td>
<td>25.659</td>
<td>25.306</td>
<td>25.533</td>
</tr>
</tbody>
</table>
as can be seen for CO or ethyne in Table 1. Here the radial
density moments from LBO2 are clearly better than those of
BOX if compared to BCCD(T). In case of HCl, MP2 and
BOX even predict a wrong sign for the correlation effect of the
radial moment, while LBO2 at least describes the correlation
effect qualitatively correctly. In summary, it can be stated that
the LBO2 approach yields electric molecular properties on a
reasonable correlated level.

Table 2 shows the orbital energies of the highest occupied
molecular orbital (HOMO) for Hartree–Fock (HF) and LBO2
for the six studied systems. It is a well known fact that
Koopman’s theorem predicts ionisation energies which are
too large on magnitude compared to the exact ionisation
potentials due to the neglect of important relaxation contribu-
tions. In Table 2 nearly exact vertical ionisation energies from
the restricted open-shell coupled cluster (RCCSD(T)) meth-
od25 are shown, and one can see that, with the exception of
ethyne, the negative HOMO energies from HF are indeed too
high. This has important consequences for the calculation of
response properties with the HF method, e.g. dipole polar-
abilities are usually 10% too low compared to the exact ones.
Against this, the HOMO energies of LBO2 given in Table 2
are in most cases clearly closer to the negative ionisation
energies from RCCSD(T) than the HF HOMO energies. This
naturally follows from the fact that the important relaxation
contributions are included in the LBO2 occupied orbital
energies. It has to be noted that relaxation effects always give
a positive contribution to Koopman’s theorem while correla-
tion effects always lead to a lowering of the eigenvalues.55
Thus the relaxation effects in the LBO2 method are obviously
larger than the correlation contributions and this nicely agrees
with the investigations of the local potentials (see section 4.1).
Indeed the values in Table 2 show that the HOMO energies
from LBO2 are generally slightly too high compared to the
negative RCCSD(T) ionisation energies. Interestingly, in the
case of ethyne, the correlation and relaxation contributions
seem to cancel each other, since here the LBO2 HOMO energy
is identical to the HF HOMO energy. The matrix elements
($\phi_{\text{HOMO}}^{\text{core}}|\phi_{\text{HOMO}}^{\text{virt}}$) and ($\phi_{\text{HOMO}}^{\text{rel}}|\phi_{\text{HOMO}}^{\text{core}}$) of the non-local potentials are found to be $-0.0847$ and $0.0764$ a.u. in this
case and thus confirm this conclusion.

5. Conclusions
The non-local second-order Brueckner correlation potential
has been localised by using the assumption that the orbitals
from the non-local and local potentials are identical. It has
been shown that the total correlation potential splits up into
quantum chemically interpretable contributions which possess
characteristic structures in different regions of the molecular
system. These findings might help to model new correlation
potentials and functionals. This is an important challenge in
density functional theory as the commonly used generalised
gradient functionals are not able to account for long-range
correlation effects which are crucial, e.g., to study intermole-
cular interactions. Furthermore, there is a need to develop new
correlation functionals which can accompany exact exchange
due to the failure to reproduce left–right correlation effects of
standard correlation functionals.6,56

The method presented in this work, termed as LBO2
(localised second-order Brueckner orbital method), represents
a generalisation of the local Hartree–Fock approach by Della
Sala and Görling3 and offers significant advantages over the
optimised effective potential (OEP) method as it does not
require the numerically difficult inversion of the Kohn–Sham
response function. Furthermore, it does, in principle, not rely
on the use of additional auxiliary basis sets as commonly used
variants of the OEP approach. The correlation potentials
obtained for a range of small systems were of good quality
and the orbitals which have been obtained from these gave
molecular properties which well agreed with those of other
wave function based correlation methods.

The nominal scaling behaviour of the method is $N^6$ ($N$ being
a measure of the molecular size) and therefore the same as that
of the MP2 method. For the construction of the non-local
potential matrix elements, density fitting of the two-electron
repulsion integrals has been exploited in order to reduce the
dependency on the atomic basis set size. The most time-
consuming step of an LBO2 calculation is the generation of the
‘pure’ correlation potential (eqn (2.19)) which scales as
$n_{\text{grid}} \times n_{\text{occ}} (n_{\text{occ}} + 1)/2 \times n_{\text{occ}}^2$, where $n_{\text{grid}}$ is the number
of points of the numerical quadrature grid. However, this scaling
can be drastically reduced by using the same resolution of the
identity (RI) technique as for the relaxation potential (eqn (2.23)).
The results in this work have shown that the relaxation
potentials could fairly well be represented over a broad
molecular range through this approximation. In the asympto-
tic range the RI approximations to the correlation potential
can properly be damped, since here the exchange potential
gives the dominant contribution (which decreases as $-1/r$
compared to a decay of $-\text{const.}/r^6$ for the exact correlation
potential52).

The local second-order Brueckner potentials have been
calculated by using Hartree–Fock orbitals and orbital eigen-
values as input. While the findings for the correlation poten-
tials and molecular properties for the various systems justified
this simple approximation, it has to be analysed how the
potentials and properties of the Kohn–Sham orbitals change
if the potentials are fully optimised as in the related local
Hartree–Fock method. Work along this line is in progress.

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13.3. Random phase approximation correlation energies with exact Kohn-Sham exchange

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- exchange kernel
- fluctuation dissipation theorem
RESEARCH ARTICLE

Random phase approximation correlation energies with exact Kohn–Sham exchange

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The random phase approximation (RPA) correlation energy is expressed in terms of the exact local Kohn–Sham (KS) exchange potential and corresponding adiabatic and nonadiabatic exchange kernels for density-functional reference determinants. The approach naturally extends the RPA method in which, conventionally, only the Coulomb kernel is included. By comparison with the coupled cluster singles doubles with perturbative triples method it is shown for a set of small molecules that the new RPA method based on KS exchange yields correlation energies more accurate than RPA on the basis of Hartree–Fock exchange.

Keywords: random phase approximation; exact exchange; Kohn–Sham; orbital-dependent functional; exact exchange kernel

1. Introduction

The description of electron correlation effects has been shown to be essential for an accurate description of molecular energetics, structures and properties. Because of this, in recent years, there has been much effort to improve the methods that are in use to determine correlated wave functions and energies and also the underlying algorithms that are used for their computer implementation. Concerning the latter point the most significant developments probably were density-fitting methods [1–5] that reduce the computational cost with respect to the basis set size and secondly methods that treat electron correlation using localised orbitals [5–9].

The nowadays most widely used approaches to describe electron correlation effects are Møller–Plesset (MP) perturbation theory [10–14], coupled-cluster (CC) methods [11,14,15] and density-functional theory (DFT) [14,16–18]. Principally all three approaches aim at describing electron correlation exactly, i.e. they offer the possibility to obtain the exact ground-state energy of the nonrelativistic Schrödinger equation. In practice, however, approximations have to be introduced: in MP and CC theory the wave function is usually restricted to include at most triple excitations from the given reference determinant while in the case of DFT the yet unknown exchange-correlation (xc) functional has to be approximated.

The most prominent approximations of the xc functional are the local density approximation (LDA) [16–18] and generalised gradient approximation (GGA) functionals [16–20] that describe the xc energy in terms of the electron density and its gradient. More recently these methods were further improved by introducing functionals depending on the laplacian of the density or the kinetic energy density (meta GGAs) [21–24] or functionals that include fractions of non-local exchange (hyper GGAs) [25–28]. Unfortunately it was found that GGAs and many of their extensions suffer from a number of shortcomings, most importantly they are unable to describe long-range correlation effects or dispersion interactions [18,29].

An important step forward in the development of density functionals was therefore to introduce functionals that are dependent on occupied or even on both occupied and unoccupied molecular orbitals and thus only implicitly dependent on the electron density [30–49]. While such orbital-dependent functionals on the one hand have the advantage that exchange interactions in molecules can be treated exactly [35–37,41,49–51] and thus the self-interaction error of the Coulomb interaction term is cancelled exactly, on the other hand, within the framework of orbital-dependent functionals, accurate expressions for the correlation functional can be obtained from many-body perturbation theory [31,33,34,45,48,52–57] or coupled-cluster theory [42]. Indeed it has been

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demonstrated that orbital-dependent functionals derived from second-order perturbation theory are capable to describe dispersion interactions \([34,58]\) and yield improved total energies and molecular properties compared with standard GGA functionals \([39,40]\). There are, however, a number of points that limit the use of correlation functionals derived from perturbation theory: first the standard second-order correlation energy expression is variationally unstable \([54,59]\) and so has to be modified in the energy denominators \([40,45]\), second the use of perturbation theory methods is problematic for extended and periodic systems which have a small or vanishing band gap. Finally it was shown in the case of Møller–Plesset perturbation theory that the perturbation expansion of the correlation energy or of molecular properties often diverges \([60–63]\).

Because of this there is the need to derive new orbital-dependent functionals that sum certain types of perturbation diagrams up to infinity as it is for example done in coupled-cluster theory. One such method is the random phase approximation (RPA) \([12,13,64–72]\) which can be seen as an approximate coupled-cluster doubles (CCD) approach in which the doubles amplitudes are restricted to those portions that lead to ring diagrams \([12,73]\).

The name random phase approximation stems from a classical mechanical treatment of the collective properties of the electron gas by Bohm and Pines \([74,75]\). Later on Nozieres and Pines demonstrated that in a quantum-mechanical framework RPA is equivalent to the addition of singly excited determinants to an independent particle determinant \([76]\) and Ehrenreich et al. have then shown the equivalence with the perturbed self-consistent field method \([77]\). Historically, however, the earliest RPA calculations were not based on antisymmetrised wave functions and RPA was originally associated with ring sums for the electron gas in which the interactions were not antisymmetrised. This term of the RPA is still used and usually referred to in solid state physics (see e.g. \([78]\)) while in quantum chemistry the term RPA is often used as another term for time-dependent Hartree–Fock (TDHF) because RPA here is used mainly for the determination of excitation energies and response properties \([13,79–81]\). In order to avoid the confusion that arises due to these different definitions it has become common to term RPA methods including exchange interactions either ‘RPA with exchange’ or ‘full RPA’ while RPA methods excluding exchange terms are termed just RPA or ‘direct RPA’.

The RPA method without exchange has been shown to yield the exact correlation energy of the electron gas in the high density limit \([12,65]\) and thus may be very useful for larger and particularly extended electronic systems. However, from a diagrammatical point of view ‘direct RPA’ has the disadvantage that it contains many exclusion principle violating (EPV) diagrams whose cancelling counterparts are absent. This deficiency is most severe for small systems with small basis sets, and this might explain that it did not play a significant role in quantum chemical treatments.

This is different for the ‘RPA with exchange’ which apart from its use for the calculation of response properties and excitation energies has also been used to directly determine non-multipole expanded dispersion energies \([13,82–84]\) and total correlation energies \([85–88]\). In 1977 Szabo and Ostlund analysed the full RPA correlation contribution to the interaction energy of two remote molecules and showed that the dispersive part of the interaction is described on the coupled Hartree–Fock level (identical with TDHF) \([86]\). The ‘full RPA’ method should therefore be more suited to describe intermolecular interactions than second-order Møller–Plesset theory which describes the dispersion energy contribution only on an uncoupled Hartree–Fock level \([86,89]\). However, the full RPA method nevertheless has not been widely used for the determination of correlation energies and this may stem from the fact that coupled-cluster methods turned out to be more accurate while not much more expensive.

Very recently a revival of RPA methods in quantum chemistry has occurred as RPA was found to be an attractive starting point for the development of new orbital-dependent density functionals \([44,46,73,90–96]\). Compared with the second-order perturbation theory functionals described above, RPA based functionals do not possess a variational instability, can be applied also to extended systems with small band gaps and they describe dispersion interactions on a coupled TDFT level which has been found to give very accurate dispersion energies in the framework of the DFT-SAPT (symmetry-adapted intermolecular perturbation theory) method \([97]\). Moreover, Furche has shown \([92]\) that the correlation energy of the direct RPA method can be computed with an efficient algorithm that scales only as \(N^5\) with the molecular size and therefore the computational cost does not exceed the cost from perturbation theory based functionals. However, while for bulk properties of solids the direct RPA method has been shown to give a good agreement with experimental results \([78]\), for molecular systems its performance for, e.g. the prediction of atomisation energies was found to be not much better than with standard GGA functionals \([91]\). Because of this the exchange-(correlation) interactions omitted in direct RPA have to be accounted for and...
a straightforward approach to do so is the inclusion of local exchange-correlation kernels derived from the functional derivatives of GGA functionals [44]. It has been shown that in conjunction with hybrid functionals this extension to the RPA, termed fluctuation-dissipation theorem DFT (FDT-DFT), yields atomisation energies and intermolecular interactions that outperform direct RPA results [44]. However, it has been shown that the use of local xc kernels in the framework of FDT-DFT leads to unphysical pair density functions that diverge for small interelectronic distances and this apparently leads to a slow basis set convergence of correlation energies [44].

One solution to this problem consists of a separation of the electron interaction into a short-range and a long-range part and to treat the RPA correlation for the long-range part only while the short-range interactions are described using GGA functionals. Such short-range–long-range functionals have very recently been developed by Scuseria and co-workers [94,95] and Toulouse et al. [96]. Both types of functionals were especially tested for the description of van der Waals interactions and it was found that they perform exceedingly better than direct RPA [95,96]. It should be noted here that the long-range RPA part is different in both functionals: the functional from Scuseria and co-workers uses direct RPA only while the functional from Toulouse et al. in addition contains the exchange kernel according to the TDHF formalism. Another extension to the RPA correlation functional was proposed by Jiang and Engel that was based on adding the second-order exchange energy perturbation expression to the direct RPA energy [46]. This approach, however, leads to the same problematic properties of the functional as described above for the pure second-order perturbation theory functionals.

A natural extension to direct RPA functionals are full RPA functionals that account for exchange interactions by using directly the exact exchange kernel of DFT [98–100]. The exact exchange kernel, that is the functional derivative of the exact KS-exchange potential with respect to the electron density, in contrast to standard GGA kernels is both nonlocal and frequency-dependent and therefore does not lead to an unphysical behaviour of the pair density for small interelectronic distances. The exact KS exchange potential is determined and used in EXX (exact-exchange) methods [35,36,41] within the framework of the optimised effective potential method [31,48,101] that yields derivatives of orbital-dependent functionals with respect to the electron density. First implementations of the adiabatic and nonadiabatic KS exchange kernel [102,103], however, relying on expansions of the Kohn–Sham response function in auxiliary basis sets suffered from numerical instabilities and are therefore impractical for the accurate determination of response properties and energies. We have recently implemented the exact-exchange kernel using a modified TDDFT method ([104], see also Section 2.3) and this new approach has been used to calculate excitation energies of weakly bound dimers, demonstrating that the time-dependent EXX method is capable to describe charge-transfer excitations. Independently a time-dependent EXX method for atomic systems using cubic splines radial basis functions has been implemented by Hellgren and von Barth and it was shown that this approach yields excitation energies and dispersion coefficients that are close to the corresponding TDHF results [93,105]. Furthermore Hellgren and von Barth have also calculated correlation energies using RPA with the exact-exchange kernel for a few closed-shell atomic systems and report a significantly good agreement with accurate configuration interaction (CI) correlation energies [93].

In this work a RPA method with exact KS exchange (RPA(ExX)) is presented that is applicable to general molecular systems. For this the TDDFT formalism for orbital-dependent xc kernels from [104] will be used that avoids the numerically problematic inversion of the Kohn–Sham response matrices. It will be shown in Section 2.3 that from the full RPA(ExX) method two further approximations can be devised, namely an RPA method including only the adiabatic exact-exchange kernel (RPA(AExX)) and an RPA method with an exchange kernel obtained by scaling the nonadiabatic part of the full exact-exchange kernel with one half (RPA(ExXh)). Section 4 shows and discusses the results for total energies, correlation energies and reaction energies for a set of small organic molecules. Finally Section 5 summarises and concludes.

2. Theory

2.1. Electron correlation energies from the fluctuation-dissipation theorem

The electronic energy of a many-body interacting system is usually split into the reference energy of a single-determinant wave function and a remainder termed the correlation energy. The reference energy is given by:

$$ E_0 = \langle \Phi_0 | H | \Phi_0 \rangle = \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 + v_{\text{xc}}(\phi) \rangle_i + \sum_{ij} \left[ 2 \langle i | j \rangle \langle j | i \rangle - \langle i | j \rangle \langle j | i \rangle \right]. \quad (1) $$

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where \( \Phi_0 \) is the reference determinant, \( \hat{H} \) is the electronic hamilton operator, \( \phi_i \) denotes an occupied orbital, \( \tilde{v}_{\text{ext}} \) is the external potential (usually containing electron–nucleus interactions) and \( (ij|kl) \) is a two-electron repulsion integral in chemists notation. Note that, in the following, for convenience a closed-shell formalism will be considered and spin will be taken into account by appropriate prefactors. Occupied orbitals shall be labelled by \( i, j, k, \ldots \) and unoccupied orbitals by \( a, b, c, \ldots \). The definition of the correlation energy:

\[
E_c = \langle \psi | \hat{H}_c | \psi \rangle - \langle \Phi_0 | \hat{H}_c | \Phi_0 \rangle \tag{2}
\]
depends on the reference determinant \( \Phi_0 \) which \textit{a priori} is not specified (\( \Psi \) may be the exact or an approximation to the exact wave function). If \( \Phi_0 \) is chosen as the HF determinant then the definition of the correlation energy results, which is usually referred to in wave-function-based quantum chemistry methods. In density-functional theory \( \Phi_0 \) is the KS determinant. This leads to another definition of the correlation energy. In this work the reference determinant will be the EXX determinant with orbitals obtained from an exact-exchange method [41] which does not yield Hartree–Fock but EXX orbitals.

Using the fluctuation-dissipation theorem [106,107] the correlation energy of the interacting many-body system can be obtained from a coupling strength integration over the Coulomb-type integral of the correlated part of the pair correlation function \( P^a_c \) [44,106,107]:

\[
E_c = \frac{1}{2} \int_0^1 da \int dr_1 dr_2 \frac{P^a_c(r_1, r_2)}{r_1} \int_0^\infty d\omega \times \left( \chi_a(r_1, r_2, i\omega) - \chi_0(r_1, r_2, i\omega) \right), \tag{3}
\]

where \( \alpha \) is the coupling strength. \( \chi_0 \) is the uncoupled response function and \( \chi_a \) is the coupled response function at coupling strength \( \alpha \). The response functions in Equation (3) are evaluated for complex-valued arguments. The uncoupled response function is given in terms of the orbitals and eigenvalues of the noninteracting KS system:

\[
\chi_0(r_1, r_2, i\omega) = -\sum_{ia} \frac{4\epsilon_{ia}}{\epsilon_{ia} + \alpha^2} \phi_{ia}(r_1)\phi_{ia}(r_2) \tag{4}
\]

where \( \phi_{ia}(r) = \phi_i(r)\phi_a(r) \) denotes an occupied-virtual orbital product and the convention \( \epsilon_{ia} = \epsilon_i - \epsilon_a \) is used. The coupled response function \( \chi_a \) can be obtained from the Dyson-type equation:

\[
\chi_a(r_1, r_2, \omega) = \chi_0(r_1, r_2, \omega) + \int dr_3 dr_4 \chi_0(r_1, r_3, \omega) \times \left[ \frac{\alpha}{P^a_c} + f_{\text{cou}}^{\alpha}(r_3, r_4, \omega) \right] \chi_a(r_4, r_2, \omega), \tag{5}
\]

which is rewritten symbolically by

\[
\chi_a = \chi_0 + \chi_0 W_a \chi_a, \tag{6}
\]

where \( W_a = \alpha/r_{12} + f_{\text{cou}}^{\alpha} \) is the interaction operator comprising Coulomb-, exchange- and correlation-effects. It can be seen that Equation (6) can be solved iteratively obtaining an \( n \)-order expansion of the coupled response function:

\[
\chi_a^{(n)} = \chi_0 + \chi_0 W_a \chi_0 + \chi_0 W_a \chi_0 W_a \chi_0 + \cdots \tag{7}
\]

and in infinite order the interacting response function is given by:

\[
\chi_a = (1 - \chi_0 W_a)^{-1} \chi_0 = (\chi_0^{-1} - W_a)^{-1}. \tag{8}
\]

The response function can also be written as (we assume in the following an implicit dependency on the coupling strength \( \alpha \))

\[
\chi_a(r_1, r_2, i\omega) = -\sum_p \sum_{ia} \frac{4\epsilon_{ia}}{\epsilon_{ia} + \alpha^2} U_{p,ia} U_{p,ib} \phi_{ia}(r_1)\phi_{ib}(r_2), \tag{9}
\]

where \( \epsilon_{ia} \) are the excitation energies and \( U_{p,ia} = (\omega_p)^{-1/2} e^{i \int \epsilon_p^a(x)} \) are obtained from the corresponding eigenvectors \( \mathbf{V}_p \) of the TDHF eigenvalue equation:

\[
\left[ \epsilon^2 + 4\epsilon^3/\hbar \epsilon^{1/2} \right] \mathbf{V}_p = \omega_p^2 \mathbf{V}_p \tag{10}
\]

with

\[
K_{ia,ib}(\omega) = \int dr_1 dr_2 \phi_{ia}(r_1) W(r_1, r_2, \omega) \phi_{ib}(r_2) \tag{11}
\]

and \( \epsilon \) is a diagonal matrix with the elements \( \epsilon_{ia} = \delta_{ia} \epsilon_a - \epsilon_i \).

It is now assumed that the coupling matrix \( K \) and thus the eigenvectors \( \mathbf{U} \) are frequency independent. Then the \( \omega \)-integration in Equation (3) can be done analytically. If in addition also the Coulomb-type integrals over \( r_1 \) and \( r_2 \) are performed the correlation energy can be rewritten as:

\[
E_c = \int_0^1 da \left[ \sum_p \sum_{ia,ib} U_{p,ia} U_{p,ib} (\epsilon_p^a)_{ia} (\epsilon_p^b)_{ib} \right] - \sum_{ia} \epsilon_{ia} \tag{12}
\]
If however the xc-kernel is frequency dependent the correlation energy would have to be obtained from:

\[
E_c = \frac{1}{2\pi} \int_0^1 \mathrm{d}\omega \int_0^\infty \mathrm{d}t \sum_{\mu,\nu} \frac{4x_{\mu\nu}}{x_{\mu\nu} + \omega^2} U_{p,\omega}(i\omega) U_{p,\nu}(i\omega) \langle i\omega | j\omega \rangle
\]

Alternatively the computation of the correlation energy can also be done without solving the eigenvalue Equation (10). For this we define:

\[
\lambda_{i\omega, j\omega}(i\omega) = \frac{4\delta_{i\omega, j\omega}}{x_{i\omega} + \omega^2},
\]

\[
K_{i\omega, j\omega}(i\omega) = \left( i\omega \frac{1}{1 + f_{xc}(i\omega)} | j\omega \right),
\]

\[
\chi_\omega = -(1 + \alpha \Lambda K)^{-1} \lambda
\]

(compare with Equation (8)) so that \( E_c \) can be written as:

\[
E_c = -\frac{1}{2\pi} \int_0^1 \mathrm{d}\omega \int_0^\infty \mathrm{d}t \sum_{i\omega, j\omega} \left( \chi_\omega \right)_{i\omega, j\omega} \left( \lambda_{i\omega, j\omega}(i\omega) \right)_{i\omega | j\omega}.
\]

Note that of course again the uncoupled part involving an \( \alpha \) and \( \omega \) integration of the \( \lambda \) term can be separated as in Equation (12) and again yields the term \( \sum_{i\omega}(i\omega | i\omega) \).

### 2.2. Coupling strength integration

If the exchange-correlation kernel \( f_{xc}^1 \) is approximated by the exchange kernel \( f_{xc}^1 = af_{xc}^1 \) with \( f_{xc} = f_{xc}^{\alpha=1} \) then the electron interaction operator \( W_{\alpha} = (\alpha/r_{12}) + f_{xc}^1 \) turns into \( W_{\alpha} = \alpha W_1 = \alpha W = \alpha[(1/r_{12}) + f_{xc}] \) with \( W = W_{\alpha=1} \) and depends linearly on the coupling strength. The response function at coupling strength \( \alpha \) then is given by:

\[
\chi_\alpha = \chi_0 + \alpha \chi_0 W_\alpha \chi_0 + \alpha^2 \chi_0 W_\alpha W_\alpha \chi_0 + \cdots
\]

and in the occupied-virtual orbital product space (Equation (14)):

\[
\chi_\alpha = -\lambda + \alpha \lambda K \lambda - \alpha^2 \lambda K \lambda K \lambda + \cdots,
\]

so that the coupling strength integration gives:

\[
\int_0^1 \mathrm{d}\alpha \chi_\alpha = -\lambda + \frac{1}{2} \lambda K \lambda - \frac{1}{3} \lambda K \lambda K \lambda + \frac{1}{4} \lambda K \lambda K \lambda K \lambda - \cdots.
\]

It is now convenient to exploit the fact that \( \lambda \) is diagonal and its square root can easily be taken. Using \( K = \lambda^{1/2} K \lambda^{1/2} \) the coupling strength integrated response matrix can be rewritten:

\[
\int_0^1 \mathrm{d}\alpha \chi_\alpha = \lambda^{1/2} \left[ -1 + \frac{1}{2} \tilde{K} - \frac{1}{3} \tilde{K} \tilde{K} + \frac{1}{4} \tilde{K} \tilde{K} \tilde{K} - \cdots \right] \lambda^{1/2}.
\]

Compared with the power series:

\[
-\ln(1 + x) = -x + \frac{1}{2} x^2 - \frac{1}{3} x^3 + \frac{1}{4} x^4 - \cdots
\]

the coupling strength integrated response function can be expressed by

\[
\int_0^1 \mathrm{d}\alpha \chi_\alpha = \lambda^{1/2} \left[ -\ln(1 + \tilde{K}) \tilde{K}^{-1} \right] \lambda^{1/2}.
\]

The logarithm of the symmetric matrix \( (1 + \tilde{K}) \) can be evaluated analytically as:

\[
\ln(1 + \tilde{K}) = U^T \ln(\Lambda) U,
\]

where the matrix \( U \) contains the eigenvectors and \( \Lambda \) is a diagonal matrix containing the eigenvalues of the symmetric matrix \( (1 + \tilde{K}) \). Note that the precondition for applying Equation (22) is of course that the matrix \( (1 + \tilde{K}) \) is positive definite. This was the case for all systems that were studied in this work and so the logarithm according to Equation (22) could always be taken. Finally note also that apart from an eigenvalue decomposition of \( (1 + \tilde{K}) \) other numerical techniques exist to compute logarithms of matrices that might be more efficient for larger matrices [108–110].

Using Equation (22) the correlation energy can now be computed as:

\[
E_c = -\frac{1}{2\pi} \int_0^\infty \mathrm{d}t \sum_{i\omega, j\omega} \left( \chi_\omega \right)_{i\omega, j\omega} \left( \lambda_{i\omega, j\omega}(i\omega) \right)_{i\omega | j\omega},
\]

\[
\lambda^{1/2} \left[ -U^T \ln(\Lambda) U \tilde{K}^{-1} \right] \lambda^{1/2} \left| (i\omega | j\omega) \right.
\]

### 2.3. FD-DFT using the exact-exchange kernel

The frequency dependent exact-exchange kernel can generally be written as [98–100]:

\[
f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 \chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_3, \omega) \times \Lambda_{\mathbf{r}_3, \mathbf{r}_4, \omega}(\mathbf{r}_1, \mathbf{r}_2, \omega)
\]

with \( h_{xc} = h_{xc}^{(1)} + h_{xc}^{(2)} \) given by (note that \( \omega \) is replaced by the complex-valued argument \( i\omega \), so for real
frequencies the signs in front contributions containing \( \omega^2 \) are changed):

\[
\begin{align*}
\hat{h}^{(1)}_{\chi}(\mathbf{r}_1, \mathbf{r}_2, i\omega) &= \sum_{i,j,ab} \left[ -\frac{4\epsilon_{ia}\epsilon_{jb}}{(\epsilon_{ia}^2 + \omega^2)(\epsilon_{jb}^2 + \omega^2)} \right] (i|ab\rangle + \delta_{ab}(\hat{\nu}^{NL}_{\chi} - \hat{\nu}_{\chi}|j\rangle) - \frac{4\epsilon_{ia}\epsilon_{jb}}{(\epsilon_{ia}^2 + \omega^2)(\epsilon_{jb}^2 + \omega^2)} (ib|jd) \right] \phi_{ia}(\mathbf{r}_1)\phi_{jb}(\mathbf{r}_2), \\
\hat{h}^{(2)}_{\chi}(\mathbf{r}_1, \mathbf{r}_2, i\omega) &= \sum_{i,j,ab} \frac{4\epsilon_{ia}}{\epsilon_{ia}^2 + \omega^2} (i|\hat{\nu}^{NL}_{\chi} - \hat{\nu}_{\chi}|a\rangle \left[ \phi_{ia}(\mathbf{r}_1)\phi_{ia}(\mathbf{r}_2) + \phi_{ia}(\mathbf{r}_1)\phi_{ia}(\mathbf{r}_2) \right] \\
&+ \sum_{i,ab} \frac{4\epsilon_{ia}}{\epsilon_{ia}^2 + \omega^2} (i|\hat{\nu}^{NL}_{\chi} - \hat{\nu}_{\chi}|a\rangle \left[ \phi_{ia}(\mathbf{r}_1)\phi_{ia}(\mathbf{r}_2) + \phi_{ia}(\mathbf{r}_1)\phi_{ia}(\mathbf{r}_2) \right]
\end{align*}
\]

with \( (\hat{\nu}^{NL}_{\chi} - \hat{\nu}_{\chi}|j\rangle \) giving the differences of the matrix elements of the nonlocal \( (\hat{\nu}^{NL}_{\chi}) \) and local \( (\hat{\nu}_{\chi}) \) exchange potentials. Unfortunately the computation of the exact-exchange kernel via Equation (24) using finite basis sets is problematic due to the occurrence of the exact-exchange kernel via Equation (24) using finite potentials. Unfortunately the computation of the exact-exchange kernel is obtained that does not involve the inverses of the KS response functions anymore and that would be the exact functional derivative of the exact local KS exchange potential if the occupied-virtual orbital products were linearly independent. As in case of the exact-exchange kernel defined in Equations (24)–(26) it can be split into two parts and the first part can be written as [104]:

\[
[K^{(1)}(i\omega)]_{ia,jb} = \frac{1}{4} \left[ 1 - \frac{\alpha^2}{\epsilon_{ia}\epsilon_{jb}} \right] (-i|\hat{\nu}_{\chi}|a\rangle - \frac{\alpha^2}{\epsilon_{ia}\epsilon_{jb}} (db|ja\rangle,
\]

while the second part, corresponding to Equation (26), contains the occupied–unoccupied matrix elements \( (i|\hat{\nu}^{NL}_{\chi} - \hat{\nu}_{\chi}|a\rangle \). While its computation is more demanding than the computation of \( K^{(1)}(i\omega) \) (see [104] for details) it has been found that its inclusion has a negligible effect for excitation energies or correlation energies of small molecules. This is concordant with the fact that the EXX orbitals can approximately be obtained from an occupied–occupied virtual–virtual unitary transformation of the Hartree–Fock orbitals which is explicitly exploited in approximate exact-exchange density functional theories [37,51]. Therefore the \( K^{(1)} \) contribution has not been included in the calculations of this work.

Since the exchange-kernel of Equation (27) is frequency-dependent we can define two additional approximations that will be used in the calculations:  

\begin{itemize}
  \item adiabatic \( \omega \)-dependent terms in Equation (27) are omitted
  \item (AEXX):
  \item EXX: \( \omega \)-dependent terms in Equation (27) are scaled with one half
\end{itemize}

It will now be shown that the correlation energy defined in terms of the exchange-kernel of Equation (27) is related to the leading, i.e. second order, term in perturbation theory along the adiabatic connection which is the analogue of Møller–Plesset perturbation theory within the KS formalism [31,48]. In order to show this the power series of Equation (17) is truncated after the second term and inserted in Equation (15) yielding:

\[
E_{\chi}^{(2)} = -\frac{1}{2\kappa} \int_0^1 \mathrm{d} \alpha \int_0^\infty \mathrm{d} \omega \sum_{ia,jb} (\alpha(\Lambda K\Lambda)_{ia,jb})(ia|jb) \\
= -\frac{1}{4\kappa} \int_0^\infty \mathrm{d} \omega \sum_{ia,jb} (\Lambda K\Lambda)_{ia,jb}(ia|jb),
\]

The coupling matrix \( K \) can be split into a Coulomb contribution and an exchange contribution:

\[
K = K_{C} + K_{\chi}
\]

with \( K_{\chi} \) given by Equation (27) and \( [K_{\chi}]_{ia,jb} = (ia|jb) \). Accordingly the second-order correlation energy is split into a Coulomb and an exchange part. For the Coulomb part the frequency integration yields (see also [91]):

\[
E_{\chi}^{(2)} = \sum_{ia,jb} \frac{-2(ia|jb)(ia|jb)}{-\epsilon_{ia} + \epsilon_{jb}},
\]

which is the direct part of the second-order correlation energy. For the exchange part one can make use of
the integrals
\[ \int_0^\infty \int_0^\infty \frac{xy - \omega^2}{(x^2 + \omega^2)(y^2 + \omega^2)} \, dx \, dy = 0, \quad x^2, y^2, xy > 0, \]
\[ \int_0^\infty \int_0^\infty \frac{xy + \omega^2}{(x^2 + \omega^2)(y^2 + \omega^2)} \, dx \, dy = \frac{\pi}{x+y} \forall \ x^2, y^2, xy > 0 \]
and obtains:
\[ E^{(2)}_{\text{EXX}} = \sum_{ia, jb} \frac{(ia|j\beta)(j\beta|ia)}{\epsilon_{ia} + \epsilon_{jb}}, \]
which shows that the first part of the exchange-kernel of Equation (27) vanishes upon \( \omega \)-integration and does not contribute to the second-order correlation energy. The sum of \( E^{(2)}_{\text{EXX}} \) and \( E^{(2)}_{\text{C}} \) defined in Equations (30) and (31) yields the correlation energy through second order in the interelectronic interaction as given in [31,48], except for terms proportional to \( [\langle j|\hat{v}_{\text{NL}} - \hat{v}_{\text{XC}}|a\rangle]^2 \) that are small in magnitude and are neglected here. The neglected terms have their origin in the fact that products of occupied and unoccupied orbitals are linear dependent, which is also the reason why HF and exact exchange-only KS determinants are different [111,112].

Finally it is noted that while the full RPA approach with exact KS exchange described in this section scales as \( N^6 \) with the molecular size we have recently implemented the method exploiting density-fitting of occupied-virtual orbital products using a similar approach as the one used in [113] to obtain the response functions for the TDHF or hybrid-DFT methods. The density-fitting RPA(EXX) method only scales as \( N^3 \) with the molecular size and is therefore applicable to relatively large molecular systems. This will be demonstrated for weakly bound van der Waals complexes in a subsequent publication [114].

3. Computational details
Total energies and correlation energies were calculated with the approach described in Section 2 for a set of 21 small organic molecules. The geometries used in this work were optimised at the MP2 (second-order Møller–Plesset perturbation theory) level with the aug-cc-pVTZ basis set [115] and are the same as those used in [116].

The exact-exchange Kohn–Sham (EXX) orbitals and eigenvalues were obtained by first performing numerically stable EXX calculations with the method from [41] for all 21 molecules in two steps. In the first step the exact local KS exchange potential was obtained with the balanced uncontracted triple-zeta orbital and auxiliary basis sets of [41]. In the second step EXX orbitals and eigenvalues were calculated by using the exact local exchange-potential represented in the auxiliary basis set obtained in the first step in a subsequent EXX calculation with the smaller contracted aug-cc-pVTZ orbital basis set [115]. In the EXX calculation of the second step only the Coulomb potential was optimised self-consistently. Correlation energies using the approach described in Section 2 were then calculated using the EXX orbitals and eigenvalues as input, i.e. the calculations were performed in a post Kohn–Sham (post self-consistent field) way.

While the coupling-strength integration required for the computation of the correlation energies (see e.g. Equation (3)) could be done analytically using the approach described in Section 2.2, the \( \omega \) integration over imaginary frequencies can not be done analytically for frequency-dependent exchange-correlation kernels. In this work we have used a 12-point Gauss–Legendre quadrature [117] for the frequency integration which was found to be accurate to approximately \( 10^{-5} \) hartree.

For comparison the molecular energies were also calculated using Hartree–Fock (HF), MP2, coupled cluster with singles and doubles (CCSD) and additionally also perturbative triples (CCSD(T)), the Becke–Lee–Yang–Parr three-parameter hybrid density functional (B3LYP) [25,26], and the random-phase approximation with exact Hartree–Fock exchange (RPA(HF)). The correlation energy for the latter approach can be obtained from Equation (12) if the response eigenvectors \( U \) are given by the solutions of the time-dependent Hartree–Fock equations [13,81].

All calculations were done using the aug-cc-pVTZ basis set [115] and all electrons were correlated. The method described in Section 2 has been implemented in the development version of the Molpro quantum chemistry package [118].

4. Results
The total molecular energies calculated for the set of 21 molecules are displayed in Table 1. The last three lines of the table show the root-mean square errors, the mean absolute errors and the relative percentual deviations from the CCSD(T) reference values of the fifth column. It can be observed that while the MP2 method generally captures over 90% of the correlation effect, with only a few exceptions the CCSD energies are closer to the CCSD(T) reference results than the MP2 ones, as expected. In contrast to this the B3LYP method almost always yields total energies that are about 0.1–0.2 hartree larger in magnitude than...
Table 1. Total energies in hartree, aug-cc-pVTZ basis set. The last four lines display the root mean squared error (RMS), the mean absolute error (MAE), the mean error (ME) and the total relative deviation ($|\Delta|$) to the CCSD(T) reference values for each method.

<table>
<thead>
<tr>
<th>System</th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>B3LYP</th>
<th>RPA(HF)</th>
<th>RPA(AEXX)</th>
<th>RPA(EXX)</th>
<th>RPA(EXXh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>-1.133</td>
<td>-1.165</td>
<td>-1.173</td>
<td>-1.173</td>
<td>-1.173</td>
<td>-1.170</td>
<td>-1.175</td>
<td>-1.175</td>
<td>-1.175</td>
</tr>
<tr>
<td>H2O</td>
<td>-76.060</td>
<td>-76.344</td>
<td>-76.349</td>
<td>-76.358</td>
<td>-76.429</td>
<td>-76.322</td>
<td>-76.375</td>
<td>-76.346</td>
<td>-76.361</td>
</tr>
<tr>
<td>CO2</td>
<td>-187.707</td>
<td>-188.369</td>
<td>-188.358</td>
<td>-188.389</td>
<td>-188.580</td>
<td>-188.294</td>
<td>-188.421</td>
<td>-188.347</td>
<td>-188.385</td>
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<tr>
<td>NH3</td>
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<td>-56.478</td>
<td>-56.489</td>
<td>-56.498</td>
<td>-56.552</td>
<td>-56.465</td>
<td>-56.516</td>
<td>-56.490</td>
<td>-56.503</td>
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<tr>
<td>C2H2</td>
<td>-76.849</td>
<td>-77.198</td>
<td>-77.210</td>
<td>-77.228</td>
<td>-77.313</td>
<td>-77.173</td>
<td>-77.249</td>
<td>-77.210</td>
<td>-77.229</td>
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<td>C2H4</td>
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<td>-78.440</td>
<td>-78.465</td>
<td>-78.481</td>
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<td>-78.429</td>
<td>-78.509</td>
<td>-78.468</td>
<td>-78.489</td>
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<tr>
<td>H2CCO</td>
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<td>-152.385</td>
<td>-152.393</td>
<td>-152.421</td>
<td>-152.584</td>
<td>-152.336</td>
<td>-152.458</td>
<td>-152.390</td>
<td>-152.424</td>
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<tr>
<td>HCOOCH3</td>
<td>-227.879</td>
<td>-228.762</td>
<td>-228.777</td>
<td>-228.814</td>
<td>-229.042</td>
<td>-228.694</td>
<td>-228.868</td>
<td>-228.769</td>
<td>-228.820</td>
</tr>
</tbody>
</table>

RMS $3.4 \times 10^{-1}$ $1.2 \times 10^{-3}$ $5.3 \times 10^{-4}$ $2.0 \times 10^{-2}$ $5.7 \times 10^{-3}$ $1.2 \times 10^{-3}$ $7.5 \times 10^{-4}$ $4.1 \times 10^{-5}$

MAE $5.4 \times 10^{-1}$ $3.2 \times 10^{-2}$ $2.1 \times 10^{-2}$ $1.3 \times 10^{-1}$ $7.0 \times 10^{-2}$ $3.2 \times 10^{-2}$ $2.4 \times 10^{-2}$ $5.3 \times 10^{-3}$

ME $5.4 \times 10^{-1}$ $3.2 \times 10^{-2}$ $2.1 \times 10^{-2}$ $1.3 \times 10^{-1}$ $7.0 \times 10^{-2}$ $3.2 \times 10^{-2}$ $2.4 \times 10^{-2}$ $4.6 \times 10^{-3}$

| $|\Delta|$ [%] | 0.58 | 0.06 | 0.02 | 0.10 | 0.07 | 0.03 | 0.03 | 0.01 |
the respective CCSD(T) values. On the other hand the
RPA method with Hartree–Fock exchange (RPA(HF))
tends to underestimate the CCSD(T) energies slightly.
It is interesting to note here that while RPA(HF) is
superior to MP2 from the theoretical point of view
(it sums up certain types of diagrams to infinity
including all second-order diagrams), on average it
does not give more accurate total energies than the
MP2 method as can be observed from Table 1. For example the mean absolute errors from RPA(HF) are
about twice as large as the MAEs of the MP2 method
for the given set of molecules. In contrast to this
the RPA method with HS exchange (RPA(EXX))
gives total energies that are almost always closer to
CCSD(T) than the MP2 energies and actually the
RPA(EXX) energies are very close to the CCSD
energies, exhibiting similar RMS errors and MAE.
It can also be seen that the RPA(EXX) energies are
always larger in magnitude than their RPA(HF)
counterparts. This is likely due to the different
eigenvalue spectrum of the HF and EXX method,
more precisely the EXX method yields bound unoccu-
pied orbitals and thus smaller energy gaps between
the occupied and lowest unoccupied molecular orbitals.
In contrast to the RPA(EXX) energies the
RPA energies from the adiabatic exchange kernel
(RPA(AEXX)) always overestimate the CCSD(T)
ergies and this led us to devise the RPA(EXXh)
approach in which the frequency
dependent part is scaled by one half. The total energies
of this method are shown in the last column of Table 1.
It can be observed that the correspondence with the
CCSD(T) reference values is excellent, the mean
absolute deviations being only about 5 millihartree
for the studied systems.

The diagram in Figure 1 shows the deviations of the correlation energies of the respective methods
from the CCSD(T) reference correlation energies. Note
that the correlation energy displayed in Figure 1 in all
cases is defined as the difference of the total energies
and the Hartree–Fock energies of the second column
of Table 1 in order to consider comparable values.
Figure 1 also shows that RPA(EXX) correlation
energies are close to CCSD ones while being always
larger than their RPA(HF) counterparts, again likely
due to the different eigenvalue spectrum of HF and
EXX. The diagram in Figure 1 also shows clearly that
the correlation energies of the RPA(EXXh) method
interpolate between the RPA(AEXX) and RPA(EXX)
ergies and as a consequence are very close to the
CCSD(T) reference correlation energies. This is also
summarised in the diagram in Figure 2 which displays
the absolute deviations from the CCSD(T) correlation
energies for all methods averaged over the 21 molecules
studied in this work. Figure 2 shows that the
RPA(AEXX) and RPA(EXX) method clearly improve the accuracy of the correlation energy if compared
with the corresponding RPA(HF) method, but they
have about the same average deviation of 25 milli-
hartree as obtained with the MP2 and CCSD methods.
On the other hand the RPA(EXXh) correlation
ergies deviate from the CCSD(T) reference energies only by 5 millihartree on average.
In order to assess the presented RPA approach with KS exchange for the prediction of reaction energies, we have considered the 14 chemical reactions listed in Table 2. Note that compared to the prediction of total energies this is an even more difficult test for electron correlation methods as the energy differences are typically an order of magnitude smaller than total (correlation) energies and for the reactions studied here they lie in the range of 8 to 80 millihartree. The input energies used for the calculation of the reaction energies all were taken from Table 1. Figure 3 shows the statistical error estimates for all methods averaged over the 14 reactions with CCSD(T) as reference. Interestingly the B3LYP method that yields large deviations from CCSD(T) total energies gives a comparable accuracy for the chemical reactions of Table 2 as MP2. The RPA(EXXh) method on the other hand yields mean absolute errors for the reaction energies of about 1.7 kcal mol$^{-1}$ which is about 0.7 kcal mol$^{-1}$ larger than the deviations obtained with the CCSD method, despite the rather accurate total energies obtained with the RPA(EXXh) method. It can however be observed from Figure 3 that both, the RPA(EXX) and RPA(EXXh) methods improve upon the accuracy of RPA(HF) for the chemical reactions while RPA(AEXX) and RPA(HF) themselves give reaction enthalpies comparable to MP2.

While the comparison with CCSD(T) reaction energies is certainly the ultimate test for any lower level electron correlation method, it may be more equitable to use the CCSD method as the reference approach since both, MP2 and the RPA methods account only for double excitations and thus are rather approximations to the CCSD method. Therefore deviations to CCSD for the chemical reactions are displayed in Figure 4. Here it can now be seen that the RPA(EXX) and RPA(EXXh) methods perform clearly better than MP2 and even than the related

---

**Table 2. Reactions.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_2$ + H$_2$ $\rightarrow$ C$_2$H$_4$</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$ + H$_2$ $\rightarrow$ C$_2$H$_6$</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$ + H$_2$ $\rightarrow$ 2CH$_4$</td>
<td></td>
</tr>
<tr>
<td>CO + H$_2$ $\rightarrow$ H$_2$CO</td>
<td></td>
</tr>
<tr>
<td>H$_2$CO + H$_2$ $\rightarrow$ CH$_3$OH</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$ + H$_2$ $\rightarrow$ 2H$_2$O</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$ + H$_2$O $\rightarrow$ CH$_3$CHO</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$ + H$_2$O $\rightarrow$ C$_2$H$_5$OH</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHO + H$_2$ $\rightarrow$ C$_2$H$_5$OH</td>
<td></td>
</tr>
<tr>
<td>CO + NH$_3$ $\rightarrow$ HCONH$_2$</td>
<td></td>
</tr>
<tr>
<td>CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$</td>
<td></td>
</tr>
<tr>
<td>HNCO + NH$_3$ $\rightarrow$ NH$_2$CONH$_2$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH + CO $\rightarrow$ HCOOCH$_3$</td>
<td></td>
</tr>
<tr>
<td>CO + H$_2$O$_2$ $\rightarrow$ CO$_2$ + H$_2$O</td>
<td></td>
</tr>
</tbody>
</table>

---

**Figure 3.** Root-mean squared errors (RMS), mean absolute errors (MAE) and total relative deviations ($|\Delta|$/%) from CCSD(T) reference values for the 14 reactions of Table 2.

RPA(HF) method. For example the root-mean square errors are only 0.9 and 1.7 kcal mol$^{-1}$ while the MP2 method has a root-mean square error of nearly 12 kcal mol$^{-1}$ for the chemical reactions. As expected
5. Summary

Random phase approximation methods for the correlation energy including exchange interactions have been developed for exact-exchange Kohn–Sham reference determinants using the recently developed TDDFT formalism for orbital-dependent xc functionals that avoids the numerically difficult inversion of the Kohn–Sham response matrix. The exchange kernel derived from this approach, in contrast to standard GGA kernels, is both nonlocal and frequency dependent and therefore improves upon the unphysical behaviour of the pair density at small interelectronic distances occurring in the case of local GGA kernels. Besides RPA with the full exact-exchange kernel (RPA(EXX)) two approximate methods were derived, one in which the frequency dependent part is completely neglected (adiabatic approximation, RPA(AEXX)) and one in which the frequency dependent part is scaled with one half (RPA(EXXh)).

It has been shown for a set of 21 small organic molecules that the RPA(EXX) method underestimates the correlation energy compared to coupled cluster singles doubles with perturbative triples (CCSD(T)) correlation energies while the RPA(AEXX) overestimates the CCSD(T) correlation energies by about the same amount. Accordingly the RPA(EXXh) method yields correlation energies that are close to the CCSD(T) reference energies with an average deviation of only 0.005 hartree for the systems that were studied. All three RPA approaches with exact KS exchange give correlation energies that are on average in a much better agreement with CCSD(T) correlation energies than the corresponding RPA method including Hartree–Fock exact-exchange (RPA(HF)) and the RPA(EXXh) method clearly outperforms second-order Møller–Plesset (MP2) and CCSD in this respect.

However, it was found that the reaction energies for 14 organic reactions obtained by all three introduced RPA methods are only slightly better than corresponding MP2 and RPA(HF) reaction energies if compared to CCSD(T) reference energies and gave worse results than CCSD. However, if compared to CCSD as the reference method for the reaction energies the RPA(EXX) and RPA(EXXh) method performed clearly better than the MP2 and RPA(HF) method for the reactions that were studied. This finding is significant from the point of view that the computational cost of full RPA(EXX) calculations should be not much higher than that of MP2 if density-fitting methods are exploited, as is shown in [114], since both methods then scale as \(N^3\) with respect to the molecular size. The presented RPA(EXX) method is therefore an orbital-dependent functional that can

![Figure 4. Root-mean squared errors (RMS), mean absolute errors (MAE) and total relative deviations (|D|) from CCSD reference values for the 14 reactions of Table 2.](image-url)
be applied to large molecules and may become an attractive method for quantum chemistry applications in the future.

Acknowledgements
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References
13. Orbital-dependent correlation functionals

Molecular Physics
13. **Orbital-dependent correlation functionals**

A. Heßelmann and A. Görling


13.4. The role of orbital transformations in coupled-pair functionals

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- Brueckner orbitals
- orbital optimisation
- size extensivity
- configuration interaction
- spectroscopic constants
The role of orbital transformations in coupled-pair functionals

Christian Kollmar • Andreas Heßelmann

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Abstract The replacement of single excitations by orbital transformations in coupled-pair functionals derived from a single double configuration interaction approach is discussed. It is demonstrated that this modification leads to considerably improved density matrices and better agreement with results from coupled cluster singles doubles calculations taken as a reference. A comparison between the variationally optimized orbitals and the Brueckner orbitals shows that these two sets of orbitals are different.

Keywords Configuration interaction • Coupled-pair functional • Orbital optimization • Brueckner orbitals • Size extensivity

1 Introduction

The method of configuration interaction (CI) is one of the standard approaches for the treatment of electron correlation in molecules. However, a serious problem exhibited by any limited CI expansion of an electronic wave function is its lack of size extensivity. Size extensivity is here defined as the additivity of electronic energies for an ensemble of molecules separated by an infinite distance from each other. There are several approaches compensating for the lack of size extensivity, such as correction terms added a posteriori to the energy of a limited CI wave function [1–6], many-body perturbation theory as formulated by Möller and Plesset (MP) [7], various coupled electron pair approximations (CEPA) [8–11], the coupled cluster (CC) method [12–14], and the quadratic CI (QCI) method [15]. None of these methods is variational in the sense that the electronic energy is obtained by variational optimization of an energy functional.

Instead, they might be denoted as projective methods because the equations for the amplitudes of the excited states are obtained by projecting with determinants on the Schrödinger equation as in the case of the MP, CEPA, CC, and QCI methods. In general, these methods employ Hartree–Fock (HF) orbitals. Alternatively, one can use Brueckner orbitals [16] which are obtained from a projective elimination of the amplitudes of the single excitations as for example in the Brueckner CCD (BCCD) [17] method.

There are also methods where the excitation amplitudes are obtained from a variational condition for an energy functional. These are in general derived from the CI singles doubles (CISD) energy expression which is modified such that the energy becomes at least approximately size extensive. The first of these functionals developed by Pulay [18] has been followed by the coupled-pair functional (CPF) [19], the averaged coupled-pair functional (ACPF) [20], and the averaged quadratic CC (AQCC) functional [21]. None of these methods corresponds to a wave function approach but the variables to be optimized are still CI-like singles and doubles excitation amplitudes. HF orbitals are used in general so that the functionals are not optimized with respect to the orbitals. Thus, fully relaxed density matrices can only be obtained by solving coupled-perturbed HF equations. Nonetheless, the variational optimization with respect to the amplitudes leads to a
considerable simplification in the evaluation of response properties, e.g., energy gradients [18].

Most of the approaches just mentioned seem to have been forgotten to a large extent after CCSD has evolved as a kind of standard method for correlation calculations of small molecules. This is a consequence of the fact that CCSD is generally accepted as the most rigorous method among those limited to the amplitudes of double excitations. However, the evaluation of response properties in CCSD requires the solution of Z-vector equations [22] which is as expensive as the solution of the CCSD equations thus doubling the computational cost as compared to CISD-based methods allowing direct variational optimization of an energy functional. Hence, the interest in coupled-pair methods and related approaches has been revived just recently [23–25]. The present contribution has to be situated in this context.

Apart from simplified gradients, there is yet another reason for the renewed interest in coupled-pair methods. It is generally recognized that CCSD(T), i.e., CCSD with perturbative inclusion of triple excitations sets the standard for the calculation of ground state properties in the single reference case yielding atomization energies and reaction energies within chemical accuracy [26]. However, CCSD(T) calculations are expensive due to the unfavorable scaling behavior of this method ($N^6$ if $N$ is a measure for the size of the molecule). Thus, there is clearly a need for cheaper methods restricted to the amplitudes of single and double excitations which scale as $N^4$ (CCSD) or $N^3$ (MP2).

It has been found that atomization and reaction energies obtained from CCSD calculations are only slightly superior to the corresponding MP2 results [26]. On the other hand, it has been demonstrated that coupled-pair and CEPA methods (also scaling as $N^3$) outperform CCSD with respect to reaction energies and other energetic properties [25, 27]. This is surprising given the fact that CCSD is in principle the more rigorous method. It has been speculated that CEPA and coupled-pair functionals simulate the effect of connected triples to some extent [8, 10, 28] but the phenomenon is perhaps not well-understood. Nonetheless, these encouraging results stimulate the further development of coupled-pair methods thus strengthening their position in a hierarchy between the less rigorous but cheap density functional approaches and the accurate but expensive CCSD(T) method.

There is, however, one aspect where CCSD is clearly superior to the coupled-pair methods. The exponential treatment of the single excitations ($e^{\epsilon_i}$ with $T_1$ being the single excitation operator) in the wave function makes CCSD relatively insensitive to the underlying orbital basis and thus capable to deal with cases where orbital relaxation effects are important. It has been shown that QCISD [15] which employs a linear instead of an exponential ansatz for the singles fails in such cases whereas CCSD is well-behaved [29]. The coupled-pair methods suffer from the same drawback. This difficulty has led to modified versions of the averaged coupled-pair functional (ACPF) [20] which have been denoted as ACPF-2 [30] and NACPF [25] and differ just by a different treatment of the singles from the original ACPF approach. Although it would in principle be possible to employ the exponential $e^{\epsilon_i}$ ansatz in conjunction with CEPA, there are alternatives which avoid the appearance of single excitations at the outset. First, there is the concept of Brueckner orbitals [16] which is based on a projective condition for the elimination of the singles. Second, if the energy is given in the form of a functional, it can also be variationally optimized with respect to the orbitals which necessitates the elimination of the single excitations to avoid a redundant parametrization. As far as we know, this possibility has not yet been explored for the coupled-pair and related functionals. The present contribution is intended to fill this gap. An analogous procedure has already been applied in a recently proposed energy functional based on a CID approach [23]. Since orbital optimized versions of coupled-pair methods dispense with the single excitations altogether the abovementioned ambiguity with respect to the treatment of the singles in the ACPF method is avoided. Another important advantage of the replacement of single excitations by orbital optimization is the fully variational nature of the resulting energy functional in the sense that the electronic energy is optimized with respect to all variables, i.e., both the orbital coefficients and the amplitudes of the excited states. Thus, fully relaxed density matrices are obtained directly without solving any type of coupled-perturbed equations.

In the present contribution the replacement of the single excitations by orbital transformations will be discussed focussing on the ACPF method and a variational analogue to the CEPA(1) approach. The variationally optimized orbitals will also be compared to Brueckner orbitals.

2 CISD-based energy functionals

Formal aspects concerning CISD-based energy functionals will be discussed in this section. The general form of the functional, its variational optimization with respect to the excitation amplitudes and orbitals, and the corresponding density matrices will be presented. A comparison with the coupled-pair functional of Ahlrichs et al. [19] and the CEPA approach points to the close relationship with these methods. The main aspect of this contribution, i.e., the replacement of single excitations by orbital optimization will be elucidated. Finally, a comparison of the orbital gradient with the Brueckner condition shows that the optimized orbitals differ from the Brueckner orbitals.
2.1 The form of the functional

The following considerations will be restricted to the single reference closed-shell case. A spin-adapted notation first suggested by Pulay et al. [31] is used in a slightly modified version of Hampel et al. [32]. The spin-adapted CISD wave function on which the functionals considered in the following are based reads

\[ |\Psi\rangle = b_0|\Phi_0\rangle + \sum_a B_a^i|\tilde{\phi}_i^a\rangle + \frac{1}{2} \sum_{ij} B_{ij}^a|\tilde{\phi}_i^a\tilde{\phi}_j^b\rangle \]

\[ = b_0|\Phi_0\rangle + \sum_a \tilde{B}_a^i|\tilde{\phi}_i^a\rangle + \sum_{ij} \tilde{B}_{ij}^a|\tilde{\phi}_i^a\tilde{\phi}_j^b\rangle \]  \hspace{1cm} (1)

where the spin-adapted singly and doubly excited configurations

\[ |\phi_i^a\rangle = E_i^a|\tilde{\phi}_i^a\rangle = |\phi_i^a\rangle + |\phi_j^b\rangle \]

and their contravariant counterparts

\[ |\tilde{\phi}_i^a\rangle = \frac{1}{2}|\phi_i^a\rangle \]

\[ |\tilde{\phi}_j^b\rangle = \left( \frac{1}{2} E_i^a E_j^b + \frac{1}{6} E_{ij}^a E_{ij}^b \right) |\Phi_0\rangle = \frac{1}{6} \left( 2|\phi_i^a\rangle + |\phi_j^b\rangle \right) \]  \hspace{1cm} (2)

are obtained by application of the excitation operators

\[ E_i^a = \tilde{a}_i^a\tilde{a}_i^a + \tilde{a}_i^a\tilde{a}_i^a. \]  \hspace{1cm} (4)

As can be seen from Eq. (1), the contravariant amplitudes are given by

\[ \tilde{B}_a^i = 2B_a^i \]

\[ \tilde{B}_{ij}^a = 2B_{ij}^a - B_{ba}^i. \]  \hspace{1cm} (5)

The introduction of contravariant configurations leads to the orthogonality relations

\[ \langle \tilde{\phi}_i^a | \tilde{\phi}_j^b \rangle = \delta_{ij}\delta_{ab} \]

\[ \langle \tilde{\phi}_i^a | \tilde{\phi}_j^b \rangle = \delta_{ij}\delta_{ab}\delta_{ad} + \delta_{ij}\delta_{ak}\delta_{bd} \]  \hspace{1cm} (6)

and thus to a simplification of the wave function algebra [31].

The wave function equation (1) is assumed to be conventionally normalized, i.e., \( \langle \Psi | \Psi \rangle = 1 \). This distinguishes the present approach from the coupled-pair functional of Ahlrichs et al. [19] which is based on an intermediate normalized wave function, i.e., \( \langle \Phi_0 | \Psi \rangle = 1 \) with \( |\Phi_0\rangle \) being the reference determinant. \( b_0 \) is the corresponding CI coefficient. The symbol \( B \) refers to excitation amplitudes in conventional normalization whereas \( C \) is reserved for the corresponding amplitudes in intermediate normalization.

The two possible spin orientations are distinguished by attaching a bar for \( \beta \) spins (\( m_s = \frac{1}{2} \)) to the corresponding orbital index. If the bar is missing the corresponding spin function refers to spin \( \alpha \) (\( m_s = -\frac{1}{2} \)). In the doubly excited determinant \( |\Psi_{ab}\rangle \) the orbitals \( \psi_i \) and \( \psi_j \) of the reference determinant \( |\Phi_0\rangle \) are replaced by the unoccupied orbitals \( \psi_a \) and \( \psi_b \). Subscripts \( i,j, \ldots \) and \( a,b, \ldots \) refer to the occupied and virtual orbitals, respectively, and subscripts \( p,q,r,s, \ldots \) denote general indices. The symmetry relation

\[ B_{ab}^0 = B_{ba}^0 \]

has been used in Eq. (1).

The modified energy functional suggested for CID [23] and supplemented with single excitations by DePrince and Mazzotti [33] reads in a simplified version adapted to the coupled-pair functionals:

\[ E = E_0 + \langle \Phi_0 | \hat{H} | \sum_a b_{0,ai}^a \tilde{\phi}_i^a + \sum_{ij} b_{0,ij} \tilde{B}_{ij}^a \tilde{\phi}_i^a \tilde{\phi}_j^b \rangle \]

\[ + \sum_k \tilde{B}_k^a \tilde{\phi}_k^a | \hat{H} - E_0 | b_{0,k0}^a \Phi_0 \]

\[ + \sum_{ij} \tilde{B}_{ij}^a \tilde{\phi}_k^a | \hat{H} - E_0 | b_{0,j0}^a \Phi_0 \]  \hspace{1cm} (7)

with

\[ E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle. \]  \hspace{1cm} (8)

The crucial modification of the energy functional arises from the introduction of the factor \( f_{ijkl} \) in the modified normalization condition

\[ b_{0,ij}^2 + \sum_k \tilde{B}_k^a \tilde{B}_k^{aj} f_{ijkl} + \sum_{cd} \tilde{B}_{cd}^{ij} \tilde{B}_{cd}^{kl} f_{ijkl} = 1 \]  \hspace{1cm} (9)

with \( b_{0,ij} > 0 \). The various methods considered in this contribution differ by the choice of the factor \( f_{ijkl} \). If this factor were chosen equal to one, the energy functional equation (7) would simply correspond to the energy of the CISD wave function equation (1) and Eq. (9) would just represent the normalization condition for this wave function. In this case the energy obtained from Eq. (7) would not be size extensive. Thus, one wishes the factor \( f_{ijkl} \) to be chosen in accordance with the requirement of size extensivity. This corresponds to the condition that this factor must vanish whenever the index sets \{\( ij \)\} and \{\( kl \)\} are completely disjoint [23] which leads to the appearance of Kronecker deltas such as \( \delta_{ik}\delta_{jl} \). Thus, \( f_{ijkl} \) has the form of a contraction factor reducing the sum on the left-hand side of Eq. (9) from four to three or less indices. It has also been denoted as a topological factor by Ahlrichs et al. [19]. There have been efforts to derive contraction factors \( f_{ijkl}^{abcd} \) including indices of virtual orbitals in accordance with \( N \) representability conditions [23, 34, 35]. Similar factors without indices of virtual orbitals are known from the CEPA methods [8–11]. They lead to size extensivity if the orbitals are localized on
the individual subsystems. The most popular of these methods is CEPA(1) for which the contraction factor reads
\[ f_{ijkl} = \frac{1}{4}(\delta_{ik} + \delta_{il} + \delta_{jk} + \delta_{jl}). \] (10)

Employing this factor in Eq. (9) leads to a kind of variational CEPA method (a comparison with the original CEPA method and the coupled-pair functional [19] will be given in Sect. 2.4). Note that the functional arising from Eq. (10) is not invariant with respect to unitary transformations within the subset of the occupied orbitals. This invariance can be restored by employing a simplified factor corresponding to the averaged coupled-pair functional (ACPF) [20]. In this case the factor does not depend on any orbital index. One has:
\[ f = \frac{2}{N} \] (11)

where \( N \) is the number of correlated electrons. The functional resulting from Eq. (11) is only size extensive for a system of identical molecules. It has the advantage of being invariant with respect to orbital rotations within the subsets of both the occupied and the virtual orbitals.

2.2 Variational optimization with respect to the excitation amplitudes

The variational problem posed by Eqs. (7) and (9) can be solved by forming the Lagrangian
\[ \mathcal{L} \equiv E - \sum_{ij} \epsilon_{ij} g_{ij} \] (12)

with Lagrangian multipliers \( \epsilon_{ij} \) and the constraints
\[ g_{ij} = b_{00}^{ij} + \sum_{k} b_{ik}^{j} b_{jk}^{i} + \sum_{kl} b_{kl}^{ij} b_{kl}^{ij} f_{ijkl} - 1. \] (13)

The gradient components required for the minimization of the energy are obtained as
\[ \frac{\partial \mathcal{L}}{\partial b_{ijk}^{l}} = \langle \Phi_{i}^{j} | H - E_{0} - \Delta_{kl} | b_{00}^{kl} \Phi_{0} \rangle \]
\[ + \sum_{a} b_{ai}^{j} | \rho_{a}^{j}+ \frac{1}{2} \sum_{ab} b_{ab}^{ij} \Phi_{ab}^{ij} \rangle \]
\[ \frac{1}{\kappa_{cd}} \frac{\partial \mathcal{L}}{\partial b_{ijkl}^{cd}} = \langle \Phi_{i}^{j} | H - E_{0} - \Delta_{kl} | b_{00}^{kl} \Phi_{0} \rangle \]
\[ + \sum_{a} b_{ai}^{j} | \rho_{a}^{j}+ \frac{1}{2} \sum_{ab} b_{ab}^{ij} \Phi_{ab}^{ij} \rangle \]
\[ \frac{1}{2 \kappa_{kl}} \frac{\partial \mathcal{L}}{\partial b_{00}^{kl}} = \delta_{kl} \sum_{c} \langle \Phi_{0} | H | b_{00}^{kl} \Phi_{c} \rangle \]
\[ + \sum_{cd} \langle \Phi_{0} | H | b_{00}^{kl} \Phi_{cd}^{kl} \rangle - \epsilon_{kl} b_{00}^{kl} \] (14)

with
\[ \Delta_{kl} = \sum_{ij} \epsilon_{ij} f_{ijkl} \] (15)
\[ \tau_{kl} = 2 - \delta_{kl} \] (16)
\[ \tilde{\tau}_{kl} = \frac{2}{1 + \delta_{kl}}. \] (17)

The factor \( \tau_{kl} \) accounts for the twofold appearance of each coefficient except for \( k = l \) and \( c = d \) as a consequence of the symmetry relation \( b_{kl}^{ij} = b_{kl}^{ij} \). Equation (17) arises from the symmetry relation \( b_{kl}^{ij} = b_{kl}^{ij} \).

Defining a kind of intermediately normalized coefficients as
\[ C_{ab}^{ij} = \frac{b_{ab}^{ij}}{b_{00}^{ij}}, \] (18)

the variational condition
\[ \frac{\partial \mathcal{L}}{\partial b_{ij}^{kl}} = 0 \] (19)

leads to
\[ \langle \Phi_{i}^{j} | H - E_{0} | \Phi_{0} \rangle + \sum_{a} c_{a}^{ij} b_{00}^{kl} | \Phi^{ab}_{a} \rangle + \frac{1}{2} \sum_{ab} c_{ab}^{ij} b_{00}^{kl} | \Phi_{ab}^{ab} \rangle = C_{c}^{ij} \Delta_{kl} \]
\[ \langle \Phi_{i}^{j} | H - E_{0} | \Phi_{0} \rangle + \sum_{a} c_{a}^{ij} b_{00}^{kl} | \Phi^{ab}_{a} \rangle + \frac{1}{2} \sum_{ab} c_{ab}^{ij} b_{00}^{kl} | \Phi_{ab}^{ab} \rangle = C_{c}^{ij} \Delta_{kl} \] (20)

and
\[ \epsilon_{kl} = \delta_{kl} \sum_{c} \langle \Phi_{0} | H | C_{c}^{ij} \Phi_{c}^{ij} \rangle + \sum_{cd} \langle \Phi_{0} | H | C_{c}^{ij} \Phi_{cd}^{kl} \rangle. \] (21)

It can be shown that the sum of the Lagrangian multipliers \( \epsilon_{ij} \) gives the correlation energy \( E - E_{0} \) for the variationally optimized coefficients. Using Eqs. (7) and (14), we have:
\[ \sum_{c} b_{c}^{ij} \frac{\partial \mathcal{L}}{\partial b_{c}^{ik}} + \sum_{kl} b_{kl}^{ij} \frac{\partial \mathcal{L}}{\partial b_{kl}^{ij}} + \frac{1}{2} \langle \Phi_{0} | H | b_{00}^{kl} \Phi_{c}^{ij} \rangle \]
\[ = E - E_{0} - \sum_{kl} b_{kl}^{ij} \Delta_{kl} - \sum_{cd} b_{kl}^{ij} b_{kl}^{ij} \Delta_{kl} - \sum_{cd} \epsilon_{kl} b_{kl}^{ij}. \] (22)

From Eq. (19) it can be seen that the left-hand side of Eq. (22) has to vanish. Using Eq. (15), rearranging some terms and partially renaming the indices, we then obtain from Eq. (22):
The functional form of the energy has the big advantage that first-order and second-order density matrices can be directly extracted from the energy equation (7). Evaluating the matrix elements in Eq. (7) in terms of the integrals

\[
\langle \psi_p | V | \psi_q \rangle = \int \psi_p(r_1) \psi_q(r_2) \frac{\epsilon^2}{|r_1 - r_2|} \times \psi_p(r_1) \psi_q(r_2) d^3r_1 d^3r_2.
\]

(26)

the energy can also be expressed as

\[
E = \sum_{pq} \Gamma_{pq} h_{pq} + \sum_{pqrs} \Gamma_{pqrs} \langle \psi_p | V | \psi_q \rangle \langle \psi_q | V | \psi_r \rangle
\]

(27)

where \( V(r) \) is the external potential and \( \Gamma_{pq} \) and \( \Gamma_{pqrs} \) are the first-order and second-order reduced density matrices (1-RDM and 2-RDM), respectively. Their elements are determined by the coefficients \( b_{0,ij} \), \( B_{ij} \), and \( B^0_{ij} \). The elements of the 1-RDM are given by:

\[
\Gamma_{ij} = 2 (\delta_{ij} - B_{ij}^0)
\]

\[
\Gamma_{ab} = 2B_{ab}
\]

\[
\Gamma_{ia} = 2b_{0,ij}B_{ij}^a + 2 \sum \limits_{k} B_{ik}^a B_{ak}^k
\]

(28)

with

\[
B_{ij} = \sum \limits_{k} B_{ik}^k B_{kj}^k + \sum \limits_{c} B^0_{ij} B^0_{cj}
\]

\[
B_{ab} = \sum \limits_{q} B_{ai}^q B_{bq}^i + \sum \limits_{c} B^0_{ab} B^0_{bc}
\]

(29)

The elements of the 2-RDM read

\[
\Gamma_{ijkl} = 2 \delta_{ik} \delta_{jl} - \delta_{ij} \delta_{kl} - 2B_{ik}^0 \delta_{jl} - 2B_{jl}^0 \delta_{ij} + B_{il}^j \delta_{jk} + \sum \limits_{ab} B_{ik}^a B_{jb}^b
\]

\[
\Gamma_{kldj} = 2B_{kj}^0 \delta_{dj} - \frac{1}{2} \sum \limits_{kc} \left( B_{ik}^k B_{kj}^k + 3B_{ij}^k B_{kj}^k \right) - B_{kj}^d B_{kl}^j
\]

\[
\Gamma_{labj} = -B_{lb} \delta_{ij} + \sum \limits_{kc} B_{bkc}^k B_{iak} - 2B_{lb} B_{ij}
\]

\[
\Gamma_{abcd} = \sum \limits_{ij} B_{iab} B_{jcd}
\]

\[
\Gamma_{ijkl} = 2 \left( \delta_{ij} \delta_{kl} \right) \delta_{jl} - \left( \delta_{ij} C_{ijkl} + \sum \limits_{k} B_{ik}^k B_{kj}^k \right) \delta_{ij} + \sum \limits_{c} B_{ij}^c B_{ik}^c
\]

(30)

Thus, the functional form of the energy leads to a direct availability of the density matrices. Equations (28)–(30) hold for all CISD-based functionals considered in the following and will be used for the evaluation of expectation values. The amplitudes of the singles must be set to zero in the case of orbital optimized functionals (see below). It is only in this latter case that the density matrices given by Eqs. (28) and (30) are fully relaxed. Employing HF orbitals instead of optimized orbitals, one has to solve coupled-perturbed HF equations to obtain fully relaxed density matrices.

2.4 Comparison with CEPA and the coupled-pair functional of Ahlrichs et al.

In contrast to the approach described in Sect. 2.1, the CEPA methods are not based on the variational optimization of an energy functional. Assuming a full CI wave function in intermediate normalization \( \langle \Phi_0 | \Psi \rangle = 1 \), i.e.,

\[
\Psi = \Phi_0 + \sum \limits_{l} C_{il} \Phi_{il}^I + \sum \limits_{i} \sum \limits_{a} \sum \limits_{b} \frac{1}{2} \sum \limits_{ab} C_{ab}^i \Phi_{ab}^{i+} + \cdots
\]

(31)

the equations to be solved for the excitation amplitudes are obtained by projecting with the ground and excited state configurations \( \Phi_0 \) and \( \Phi_{il}^I \) and \( \Phi_{il}^{i+} \) on the Schrödinger equation \( (H - E) \Psi = 0 \). In the case of the ground state \( | \Phi_0 \rangle \), this results in the energy given by Eq. (25). Projection with \( \Phi_{il}^I \) and \( \Phi_{il}^{i+} \) leads to the residuals \( \sigma_{il}^I \) and \( \sigma_{il}^{i+} \), respectively, which are approximated as...
in the case of the CEPA methods. The energy shifts \( \Delta_{ij} \) have to be defined such that they take into account the effects of higher excitation levels, i.e., triples and quadruples in an approximate fashion so that size extensivity is guaranteed. They are given by Eq. (15) where the contraction factor \( f_{ijkl} \) has to be chosen accordingly. The similarity between the conditions \( \sigma_{ij}^f = 0, \sigma_{ij}^b = 0 \) according to Eq. (32) and the variational condition equation (20) is obvious. The only difference is the appearance of the ratio \( f_{ijkl} \) in the latter which can be expected to be close to one. In the case of ACPF, where the factors \( b_{ij} \) do not depend on any orbital index (see Eqs. 9 and 11) it is even exactly equal to one. Note that the CEPA equations \( \sigma_{ij}^b = 0 \) and \( \sigma_{ij}^f = 0 \), in contrast to Eq. (20), do not correspond to a variational condition for an energy functional except for ACPF. The functional form of the energy is a prerequisite for the replacement of single excitations by orbital optimization.

The advantage of a functional form for the electronic energy missing in the CEPA methods is retained in the coupled-pair functional of Ahlrichs et al. [19]. In contrast to the previous approach defined by Eqs. (7) and (9) which is based on a conventionally normalized wave function, Ahlrichs et al. start from a wave function in intermediate normalization. The coupled-pair functional is based on the energy expression \( E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \) with the modification affecting the squared norm \( \langle \Psi | \Psi \rangle \equiv c_0^2 \) of the wave function. The modified energy reads

\[
E = E_0 + \langle \Phi_0 | H \rangle \sum_{i} \frac{1}{c_{i,0,ij}^2} C_{ai}^2 \Phi_i + \sum_{i} \frac{1}{c_{i,0,ii}^2} \frac{1}{2} C_{ii}^2 \Phi_i \Phi_i + \sum_{i} \sum_{j} \frac{1}{c_{i,0,ij}^2} \frac{1}{2} C_{ij}^2 \Phi_i \Phi_j
\]

\[
+ \sum_{i} \sum_{k} \sum_{l} \sum_{m} c_{kl}^2 \langle \Phi_{ij}^c | H - E_0 \rangle \sum_{a} \frac{1}{c_{a,0,ij}^2} C_{ai} \Phi_i + \sum_{i} \sum_{j} \frac{1}{2} C_{ij}^2 \Phi_i \Phi_j
\]

\[
+ \sum_{i} \sum_{k} \sum_{l} \sum_{m} c_{kl}^2 \langle \Phi_{ij}^{cd} | H - E_0 \rangle \sum_{a} \frac{1}{c_{a,0,ij}^2} C_{ai} \Phi_i + \sum_{i} \sum_{j} \frac{1}{2} C_{ij}^2 \Phi_i \Phi_j
\]

(33)

with

\[
c_{0,ij}^2 = 1 + \sum_{k} c_{ik}^2 C_{ik} f_{ijkl} + \sum_{kl} C_{kl} c_{kl} f_{ijkl}.
\]

Equations (33) and (34) should be compared to Eqs. (7) and (9). Whereas the contraction factor leading to size extensivity modifies the coefficient \( b_{ij} \) of the reference determinant in the latter case, it is now introduced to modify the squared norm \( \langle \Psi | \Psi \rangle \) which is recovered by setting \( f_{ijkl} = 1 \) in Eq. (34). In this particular case, the energy equation (33) has the standard form \( E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \) with \( \Psi \) being the CISD wave function in intermediate normalization. Size extensivity can be obtained in complete analogy to the procedure described in Sect. 2.1 by adopting the contraction factor from the CEPA methods. Ahlrichs et al. [19] have chosen the factor corresponding to CEPA(1) as given by Eq. (10) in their coupled-pair functional. Defining

\[
B_{ij}^2 = \frac{C_{ij}^2}{c_{0,ij}^2}
\]

(35)

with analogous definitions for the contravariant coefficients, a comparison of Eqs. (7) and (33) shows that these are strictly equivalent if \( b_{0,ij} = \frac{1}{c_{0,ij}} \). Such an equivalence is only obtained if the contraction factor is constant as, e.g., in the ACPF case, Eq. (11), and for CISD (\( f = 1 \)), but not for the CEPA contraction factor equation (10). This can be seen by inserting Eq. (35) into Eq. (34) leading to

\[
c_{0,ij}^2 B_{0,ij}^2 = 1
\]

(36)

with

\[
B_{0,ij}^2 = 1 - \sum_{k} B_{ik}^e B_{jkl}^e \frac{c_{0,ik}^2}{c_{0,ij}} - \sum_{kl} B_{kl}^e B_{ijkl}^e \frac{c_{0,kl}^2}{c_{0,ij}}.
\]

(37)

A comparison of Eqs. (37) and (9) shows that in general \( b_{0,ij} \neq b_{0,ij} \) so that Eq. (36) is not compatible with the requirement \( b_{0,ij} = \frac{1}{c_{0,ij}} \) except for a constant factor \( f \).

The variational problem for the coupled-pair functional is again solved by forming a Lagrangian including the constraints equation (34) in complete analogy to Eq. (12). The equations for the components of the gradient are a bit more involved than Eqs. (14) and will not be presented here. Moreover, the variational energy obtained by inserting the optimized coefficients in Eq. (33) is in general not exactly equal to the energy obtained with the same coefficients from the projective energy equation (25).

2.5 The replacement of single excitations by orbital rotations and the orbital gradient

The essential new feature of the methods discussed in this contribution is the orbital optimization of the energy. This necessitates the elimination of the single excitations from the energy equation (7) to avoid a redundant parametrization as has already been observed for the orbital optimized CCD method [36]. Thus, the orbital optimized ACPF
approach dispenses with the aforementioned ambiguity with respect to the treatment of single excitations [25, 30].

The redundancy of single excitations in orbital optimized treatments of the correlation problem is due to a close relationship between single excitations and orbital transformations. It can be shown [37] that application of the operator $e^Q$ with

$$\hat{Q} = \sum_{p < q} Q_{pq} \left( a_p^\dagger a_q + a_p^\dagger a_q - a_p a_q^\dagger a_p^\dagger \right)$$

$$= \sum_{pq} Q_{pq} \left( a_p^\dagger a_q + a_p^\dagger a_q \right)$$

(38)

to any Slater determinant built with orbitals $\Psi_q$ is equivalent to forming the same Slater determinant with the orbitals $\Psi_q$ being replaced by the transformed orbitals

$$\tilde{\Psi}_q = \sum_p \Psi_p (e^Q)_{pq}$$

(39)

where $Q$ is an anti-Hermitean matrix so that $e^Q$ is unitary. Assuming $|Q_{pq}| << 1$ the expansion of the exponential $e^Q$ can be terminated after the linear term so that the resulting operator just adds singly excited states to the reference determinant. This linear approximation therefore provides some justification for the replacement of the singly excited states by a unitary transformation of the orbitals as shown in Eq. (39). In contrast to the single excitation operator $T_1 = \sum_{a\neq b} T_a^{ij} (a_a^\dagger a_b + a_b^\dagger a_a)$, however, the anti-Hermiticity of the operator $Q$ leads to the appearance of the corresponding deexcitation operators $-T_a^{ij} (a_a^\dagger a_b + a_b^\dagger a_a)$. Thus, the application of the operator $e^Q$ in the CC method is not completely equivalent to an orbital transformation employing the amplitudes of the singles in the transformation matrix $e^Q$.

The orbital gradient needed for the update of the orbitals in each iteration cycle can be evaluated by employing the exponential ansatz equation (39) for a unitary transformation as suggested a long time ago for orbital optimization in the multiconfiguration self-consistent field (MCSCF) method [38]. The variational condition for the optimized orbitals can be obtained by expanding the exponential in Eq. (39) in a power series. The first order variation of the orbital $\Psi_q$ is then given by

$$\delta \Psi_q = \sum_p \Psi_p Q_{pq}.$$  (40)

Inserting Eq. (40) into Eq. (27), the corresponding first order variation of the electronic energy reads

$$\delta E = 2 \sum_{pq} Q_{pq} (g_{pq} - g_{qp})$$

(41)

with

$$g_{pq} = \frac{1}{2} \sum_r \Gamma_{pr} h_{rq} + \sum_{rst}^{2} \Gamma_{prst} \langle \psi_r | \psi_r | \psi_q | \psi_q \rangle.$$  (42)

Defining

$$f_{pq} \equiv g_{pq} - g_{qp},$$

(43)

the variational condition for the orbitals is simply given by $f_{pq} = 0$. The ACPF energy is invariant with respect to unitary transformations within the subsets of occupied and virtual orbitals so that the equations $f_{ij} = 0$ and $f_{lab} = 0$ are fulfilled identically. Thus, only the matrix elements $F_{ia}$ of the occupied-virtual subblock are of interest. These can be obtained by inserting Eqs. (28) and (30) with vanishing amplitudes of the singles in Eq. (42) and using Eq. (43) as

$$F_{ia} = F_{ia} - \sum_j B^{ij} F_{ja} - \sum_b B_{ab} F_{bi} -$$

$$- \sum_{cd} B^{cd}_{ij} (2 \langle \psi_i | \psi_j | \psi_d | \psi_k \rangle - \langle \psi_i | \psi_j | \psi_d | \psi_d \rangle) -$$

$$+ \sum_{cd} B_{cd} (2 \langle \psi_i | \psi_j | \psi_d | \psi_c \rangle - \langle \psi_i | \psi_j | \psi_d | \psi_d \rangle)$$

$$+ \sum_{cd} \sum_{k,l} B^{cd}_{il} B^{kl}_{cd} \langle \psi_i | \psi_j | \psi_l | \psi_c \rangle -$$

$$- \sum_{cd} \sum_{k,l} B^{cd}_{il} B^{kl}_{cd} \langle \psi_i | \psi_j | \psi_l | \psi_c \rangle -$$

$$- \sum_{k,l} \sum_{cb} B^{cb}_{il} B^{kl}_{cd} \langle \psi_i | \psi_j | \psi_l | \psi_c \rangle -$$

$$- \sum_{k,l} \sum_{cb} B^{cb}_{il} B^{kl}_{cd} \langle \psi_i | \psi_j | \psi_l | \psi_c \rangle$$

(44)

with

$$F_{pq} = \langle \psi_p | \hat{H} | \psi_q \rangle + \sum_i (2 \langle \psi_p | \psi_q | \psi_i \rangle - \langle \psi_p | \psi_i | \psi_q \rangle) +$$

$$+ \langle \chi_p | \hat{F} | \chi_q \rangle.$$  (45)

$\hat{F}$ is the HF operator.

Orbital invariance within the subspace of occupied orbitals is no longer guaranteed if the contraction factor equation (10) corresponding to CEPA(1) is employed so that $f_{ij} \neq 0$ (note, however, that orbital invariance within the subspace of virtual orbitals is still preserved in this case ($f_{lab} = 0$)). To avoid convergence problems the orbital optimization must still be restricted to orbital rotations between occupied and virtual orbitals. A unique set of
orbitals can then be obtained by diagonalizing the occupied–occupied subblock of the Fock matrix defined in Eq. (45) such that \( F_{ij} = F_{ii} \delta_{ij} \).

2.6 Brueckner orbitals

Singly excited states can be removed from a correlated wave function by employing the concept of Brueckner orbitals first introduced by Nesbet into quantum chemistry [16]. In contrast to the optimized orbitals, the Brueckner orbitals do not arise from a variational criterion but from the projective condition \( \langle \Phi^e_i | \hat{H} | \Psi \rangle = 0 \) which eliminates the amplitudes of the singles rather than omitting them a priori as in orbital optimized methods. It has been shown that the Brueckner condition yields a reference determinant which has maximum overlap with the exact wave function in the full CI case [39]. For methods limited to the amplitudes of double excitations like CID (BCID) or CCD (BCCD) the Brueckner condition reads

\[
\langle \Phi^e_i | \hat{H} | \Phi_0 \rangle + \frac{1}{2} \sum_{c,d} C_{cd}^{(2)} \Phi^{(2)}_{cd} = 0. \tag{46}
\]

Evaluating the matrix elements, Eq. (46) can be rewritten as

\[
f_{ia}^{B} = 0 \tag{47}
\]

with

\[
f_{ia}^{B} = F_{ia} + \sum_{b} C_{ab}^{(2)} \frac{\langle \psi_{ib} | \psi_{ia} \rangle}{\langle \psi_{ib} | \psi_{ia} \rangle} + \sum_{b} C_{ca}^{(2)} \frac{\langle \psi_{ai} | \psi_{ba} \rangle}{\langle \psi_{ai} | \psi_{ba} \rangle} - \sum_{b} C_{ab}^{(2)} \frac{\langle \psi_{ja} | \psi_{kb} \rangle}{\langle \psi_{ja} | \psi_{kb} \rangle}. \tag{48}
\]

Although the functionals discussed in this contribution do no longer correspond to a wave function approach, one can still determine Brueckner orbitals according to Eq. (48) if the definition Eq. (18) for intermediated normalized coefficients is used.

Noting that the matrix elements \( F_{ia} \) which vanish for HF orbitals are still rather small for Brueckner orbitals, it can be assumed that the first, third, and fourth term dominate the right-hand side of Eq. (48). Comparing the Brueckner condition equation (48) with the variational condition equation (44) for the optimized orbitals, it can be seen that these terms reappear in the latter if we assume \( b_{0,ij} \approx 1 \) which is a reasonable approximation for the single-reference case. Since the remaining terms in Eq. (44) are of higher order in the amplitudes of the doubles, there is some similarity between the Brueckner condition equation (48) and the variational condition equation (44). That projected Brueckner orbitals might be close to variationally optimized orbitals has been conjectured by Kutzelnigg and Smith [40] and, in the case of the CCD method, by Sherill et al. [41].

The difference between Brueckner and variationally optimized orbitals has been discussed by several authors [16, 42, 43]. First, it should be noted that the two sets of orbitals are completely identical for a full CI wave function which is invariant with respect to any orbital transformation. Thus, an orbital rotation eliminating the singles will still correspond to the variational minimum of the energy so that the Brueckner orbitals are also variationally optimized in this case. It may also be argued that the orbital optimization is no longer clearly defined if the wave function approaches the exact wave function while the Brueckner condition \( \langle \Phi^e_i | \hat{H} | \Psi \rangle = 0 \) always uniquely defines a certain reference determinant. For limited CI wave functions, however, the Brueckner orbitals are different from the variationally optimized orbitals. Dykstra [42] has compared the stability conditions for CISD wave functions including and excluding single excitations and has found that in the former case the fulfillment of the Brueckner condition would be a poorer approximation to the variational condition for the orbitals than for wave functions without the explicit inclusion of singles. Moreover, he has shown that the energy of the BCID method is always slightly higher than the energy obtained from the CISD method based on a HF reference determinant. Orbital optimization in CC theory can be performed by defining a Lagrange function including the equations for the CC amplitudes as constraints in the CC energy expression [36, 41, 43, 44]. The Lagrangian can be considered as a kind of CC energy functional [44]. For a truncated cluster operator, one can expect the optimized orbitals to be different from the Brueckner orbitals [43]. Moreover, Köhn and Olsen [43] found that orbital optimized CC, in contrast to Brueckner CC, does not converge to the full CI limit. In the light of these discussions, it might be of interest to compare the optimized orbitals to Brueckner orbitals.

3 Numerical results

Various formalisms based on Eqs. (7) and (9) with and without orbital optimization have been implemented in the MOLPRO program package [45] for the single-reference case. To distinguish the versions including orbital optimization from those without orbital relaxation, the suffix “O” is appended (ACPFO, VCEPAO). The optimized orbitals are determined in complete analogy to the Brueckner orbitals as described by Hampel et al. [32] except that the matrix elements arising from the Brueckner condition equation (48) have been replaced by those corresponding to the orbital gradient (see Eq. (44). In the case of CEPA, the
prefix “V” indicates that a variational version is used. The difference to the original CEPA approach has been discussed in Sect. 2.4. In the following, all references to CEPA tacitly assume that the contraction factor equation (10) corresponding to CEPA(1) has been used.

The geometrical data for a small test set of molecules have been taken from the Computational Chemistry Comparison and Benchmark Database. These geometries have been used in all tables referring to single point calculations in the following sections. Core electrons are kept frozen in all calculations and the aug-cc-pVQZ basis set has been used throughout [46].

The following results are mainly intended to demonstrate the advantage arising from the replacement of single excitations by orbital optimization and are obtained using the functionals ACPF and VCEPA. The difference between the optimized and the Brueckner orbitals will also be illustrated by numerical results.

3.1 Energies and dipole moments

The electronic energies obtained from both ACPF and VCEPA as well as from their modified counterparts ACPFO and VCEPAO with the single excitations being replaced by orbital rotations are shown in Table 1. The CCSD values are given as a reference. The energies obtained from the orbital optimized approaches are consistently higher than those resulting from the original methods thus being slightly closer to the CCSD energy. Nonetheless, the effect of the replacement of single excitations by orbital optimization is rather small for these simple molecules.

The dipole moments for the same set of molecules are shown in Table 2. They point in the direction of the z axis which represents the rotation axis for all molecules shown in Table 2. Assuming this axis to point from the left to the right, the H atoms are located to the right of the heavy atoms for H₂O, NH₃, and HF. The same holds for Li in LiF. The C atom is to the left of the O atom in both CO and H₂CO and to the left of the N atom in HCN. For the original CISD and ACPF methods the dipole moments are calculated both as an expectation value using the density matrices equation (28) and a response to an external electric dipole field using a finite field approach with the dipole field strength being set to 0.005 a.u. in all calculations. The distinction between expectation values and response values is not necessary for the modified method ACPFO where the expectation and response values are identical because the density matrix from which the expectation value is calculated is fully relaxed in this case. This statement does not hold strictly for VCEPAO where the orbital invariance of the energy is violated for the space spanned by the occupied orbitals. In practice, however, we did not observe a significant difference between response and expectation values for VCEPAO. This difference can get quite large for VCEPA and ACPF in some cases, e.g., CO and formaldehyde. This indicates that the first-order density matrices obtained from Eq. (28) can deviate significantly from the relaxed density matrices determining properties in the case of HF orbitals. Thus, the former are often not very accurate given for example the relatively large deviation of the expectation value of the dipole moment of CO from the experimental value of 0.04 a.u. Note the fairly good agreement of the dipole moments obtained from ACPFO and VCEPAO with the CCSD reference values. This observation is corroborated if the dipole moment of CO is considered as a function of the bond length as presented in Fig. 1 which shows only the ACPF values. The ACPFO results agree well with CCSD in contrast to the ACPF expectation values. The ACPF response values are closer to CCSD than the ACPF expectation values but the corresponding relaxed density matrices can only be obtained after solving coupled-perturbed HF equations.

CO is just one example to demonstrate the superiority of the orbital optimized methods with respect to molecular properties. The sensitivity of the dipole moment of CO with respect to the orbitals has already been noted by Ernzerhof et al. who conclude that the orbitals should carefully be tuned to the electron correlation treatment which is used [47]. However, there are molecules where orbital relaxation plays an even more pronounced role. A remarkable example of this kind is CuF. It has been shown that the QCI method [15] which in most cases gives results very close to those obtained from CCSD calculations fails for CuH and to an even larger extent for CuF [29]. This indicates the importance of orbital relaxation because QCI

### Table 1: Electronic energies in atomic units for some small molecules

<table>
<thead>
<tr>
<th></th>
<th>CCSD</th>
<th>VCEPA</th>
<th>VCEPAO</th>
<th>ACPF</th>
<th>ACPFO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>−76.354</td>
<td>−76.355</td>
<td>−76.355</td>
<td>−76.356</td>
<td>−76.355</td>
</tr>
<tr>
<td>NH₃</td>
<td>−56.487</td>
<td>−56.489</td>
<td>−56.488</td>
<td>−56.489</td>
<td>−56.488</td>
</tr>
<tr>
<td>HF</td>
<td>−100.369</td>
<td>−100.370</td>
<td>−100.369</td>
<td>−100.370</td>
<td>−100.369</td>
</tr>
<tr>
<td>LiF</td>
<td>−107.294</td>
<td>−107.295</td>
<td>−107.294</td>
<td>−107.295</td>
<td>−107.294</td>
</tr>
<tr>
<td>CO</td>
<td>−113.172</td>
<td>−113.176</td>
<td>−113.174</td>
<td>−113.177</td>
<td>−113.174</td>
</tr>
<tr>
<td>H₂CO</td>
<td>−114.354</td>
<td>−114.358</td>
<td>−114.356</td>
<td>−114.359</td>
<td>−114.357</td>
</tr>
<tr>
<td>HCN</td>
<td>−93.284</td>
<td>−93.288</td>
<td>−93.287</td>
<td>−93.289</td>
<td>−93.287</td>
</tr>
<tr>
<td>RMS</td>
<td>3.0</td>
<td>1.9</td>
<td>3.7</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>MAE</td>
<td>2.6</td>
<td>1.5</td>
<td>3.3</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

The last two lines display the route mean square (RMS) error and the mean absolute error (MAE) with respect to the CCSD reference results for each method in units of 10⁻³ a.u.

---

linearizes the single excitation operator whereas CCSD uses the full exponential thus being much less sensitive to the choice of the underlying MO basis than QCI. The relationship between application of the exponential of a single excitation operator and orbital relaxation has already been discussed in Sect. 2.5. The example of CuF shows that the linear approximation of the exponential is not always appropriate. This molecule should therefore be well-suited to demonstrate the effect of orbital optimization. The cc-pVQZ-PP basis set in connection with an effective core potential has been used for Cu [48]. The electronic energy and the dipole moment as a function of the Cu–F bond length for various methods are shown in Fig. 2. It can be seen that the energy curve obtained from ACPF runs nicely parallel to the CCSD curve. The deviation of the conventional ACPF from the CCSD results is more pronounced and the energy minimum is shifted to the left. Much more interesting is again the dipole moment also shown in Fig. 2 with the Cu atom being located to the left of the F atom. We note the very good agreement between the CCSD and ACPF results for all bond lengths. The conventional ACPF method, on the other hand, fails completely. The deviation is so large that even the calculation as a response property instead of an expectation value does not lead to a significant improvement. The error is particularly pronounced in the region near the equilibrium bond distance of about 3.25 Å. QCISD results are also shown in Fig. 2 indicating the failure of this method.

### 3.2 Geometries

Geometry optimizations for the molecular test set already shown in the preceding tables have also been performed. The results are given in Table 3. The differences between the orbital optimized methods and their unmodified counterparts are not very pronounced. Note, however, the excellent agreement of the bond lengths obtained from the orbital optimized methods with the CCSD reference values, especially for VCEPAO.

### 3.3 Spectroscopic constants for diatomic molecules

Spectroscopic constants for some diatomic molecules are presented in Table 4 which also shows the experimental values given by Huber and Herzberg [49]. We have also added results obtained from the perturbative inclusion of triples. These can be taken into account in analogy to

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**Table 2** Dipole moments in atomic units for some small molecules as obtained from the CCSD, VCEPA, VCEPAO, ACPF, and ACPF methods with the aug-cc-pVQZ basis set

<table>
<thead>
<tr>
<th></th>
<th>CCSD</th>
<th>VCEPA</th>
<th>VCEPAO</th>
<th>ACPF</th>
<th>ACPF</th>
<th>ACPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.736</td>
<td>0.722</td>
<td>0.732</td>
<td>0.735</td>
<td>0.722</td>
<td>0.732</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.605</td>
<td>0.597</td>
<td>0.601</td>
<td>0.604</td>
<td>0.596</td>
<td>0.601</td>
</tr>
<tr>
<td>HF</td>
<td>0.714</td>
<td>0.700</td>
<td>0.711</td>
<td>0.714</td>
<td>0.700</td>
<td>0.711</td>
</tr>
<tr>
<td>LiF</td>
<td>2.495</td>
<td>2.473</td>
<td>2.490</td>
<td>2.498</td>
<td>2.472</td>
<td>2.490</td>
</tr>
<tr>
<td>CO</td>
<td>0.023</td>
<td>0.105</td>
<td>0.028</td>
<td>0.022</td>
<td>0.116</td>
<td>0.033</td>
</tr>
<tr>
<td>H₂CO</td>
<td>0.963</td>
<td>0.885</td>
<td>0.948</td>
<td>0.951</td>
<td>0.868</td>
<td>0.942</td>
</tr>
<tr>
<td>HCN</td>
<td>1.202</td>
<td>1.165</td>
<td>1.194</td>
<td>1.195</td>
<td>1.161</td>
<td>1.192</td>
</tr>
<tr>
<td>RMS</td>
<td>46.5</td>
<td>7.4</td>
<td>5.4</td>
<td>53.9</td>
<td>10.0</td>
<td>8.1</td>
</tr>
<tr>
<td>MAE</td>
<td>36.4</td>
<td>6.3</td>
<td>3.6</td>
<td>41.3</td>
<td>8.1</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The last two lines display the RMS error and the MAE with respect to the CCSD reference results for each method in units of 10⁻³ a.u. Atoms on the negative half of the z-axis are marked with an overline.

a Expectation value
b Response property
CCSD(T) [50] for the coupled-pair functionals. In the case of orbital optimization, the perturbation theory treatment requires a block diagonalization of the occupied-occupied and virtual–virtual subblocks of the Fock matrix. Except for F2, the replacement of single excitations by orbital optimization in the coupled-pair functionals shifts all results close to the corresponding CCSD or CCSD(T) reference values. This effect is again particularly pronounced for CuF where orbital relaxation plays an important role. Moreover, the perturbative inclusion of the triples leads to very good agreement with the experimental results. The case of F2 is critical because this molecule exhibits an increased multireference character. While all methods considered here refer to a single reference determinant, the coupled-pair functionals deteriorate apparently faster than CCSD with increasing multireference character of the wave function. This deterioration is more pronounced for ACPF than for VCEPA. In the case of ACPF(T), the energy curve for F2 does not even exhibit a minimum in the range of bond lengths considered here.

3.4 Are the variationally optimized orbitals close to Brueckner orbitals?

The orbital optimized and the Brueckner approach share the common feature that single excitations do not appear. The differences between the two sets of orbitals have been discussed in Sects. 2.5 and 2.6. Both approaches refer to the same form of the energy functional which is obtained by omitting the singly excited states from Eq. (7) so that it might be of interest to compare the two sets of orbitals. It follows from the variational principle that the orbital optimized methods yield a lower electronic energy than the Brueckner method but the difference is very small and does not exceed 1 mH for our small test set of molecules. A possible difference between the two orbital sets may be detected in several ways. If the hypothesis that the Brueckner orbitals are close to the optimized orbitals is correct the total density matrices (Eqs. 28 and 29) obtained with the former should be almost fully relaxed, i.e., the dipole moments calculated as an expectation value should not deviate strongly from the corresponding value obtained as a response to an external dipole field. These values along with the Brueckner CCD (BCCD) results are given in Table 5. It can be seen that there is a considerable difference between the response and the expectation value in the case of CO.

The difference between Brueckner and optimized orbitals must also show up in the dipole moments obtained as
Table 4 Spectroscopic constants for some diatomic molecules as obtained from various methods with the aug-cc-pVQZ basis set

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy</th>
<th>r_e</th>
<th>B_e</th>
<th>z_e</th>
<th>(\omega_e)</th>
<th>(\omega_e^2_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_2</td>
<td>-109.386848</td>
<td>1.093</td>
<td>2.015</td>
<td>0.0160</td>
<td>2.434.5</td>
<td>12.9</td>
</tr>
<tr>
<td>CCSD</td>
<td>-109.392460</td>
<td>1.096</td>
<td>2.005</td>
<td>0.0166</td>
<td>2.401.5</td>
<td>13.8</td>
</tr>
<tr>
<td>ACPF</td>
<td>-109.390492</td>
<td>1.094</td>
<td>2.011</td>
<td>0.0163</td>
<td>2.423.0</td>
<td>13.4</td>
</tr>
<tr>
<td>ACPFO</td>
<td>-109.391467</td>
<td>1.095</td>
<td>2.008</td>
<td>0.0164</td>
<td>2.412.5</td>
<td>13.4</td>
</tr>
<tr>
<td>VCEPA</td>
<td>-109.389574</td>
<td>1.093</td>
<td>2.014</td>
<td>0.0161</td>
<td>2.432.5</td>
<td>13.1</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-109.407243</td>
<td>1.101</td>
<td>1.988</td>
<td>0.0170</td>
<td>2.354.6</td>
<td>13.9</td>
</tr>
<tr>
<td>ACPF(T)</td>
<td>-109.414832</td>
<td>1.105</td>
<td>1.972</td>
<td>0.0184</td>
<td>2.293.5</td>
<td>15.9</td>
</tr>
<tr>
<td>ACPFO(T)</td>
<td>-109.412220</td>
<td>1.102</td>
<td>1.981</td>
<td>0.0177</td>
<td>2.328.5</td>
<td>15.2</td>
</tr>
<tr>
<td>VCEPA(T)</td>
<td>-109.413551</td>
<td>1.104</td>
<td>1.976</td>
<td>0.0179</td>
<td>2.310.7</td>
<td>15.2</td>
</tr>
<tr>
<td>VCEPAO(T)</td>
<td>-109.411047</td>
<td>1.101</td>
<td>1.985</td>
<td>0.0173</td>
<td>2.343.1</td>
<td>14.5</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td>1.098</td>
<td>1.998</td>
<td>0.0173</td>
<td>2.358.6</td>
<td>14.3</td>
</tr>
<tr>
<td>CO</td>
<td>-113.171641</td>
<td>1.125</td>
<td>1.944</td>
<td>0.0163</td>
<td>2.231.4</td>
<td>12.1</td>
</tr>
<tr>
<td>CCSD</td>
<td>-113.176800</td>
<td>1.128</td>
<td>1.934</td>
<td>0.0172</td>
<td>2.193.0</td>
<td>13.4</td>
</tr>
<tr>
<td>ACPF</td>
<td>-113.174071</td>
<td>1.125</td>
<td>1.944</td>
<td>0.0163</td>
<td>2.234.5</td>
<td>12.0</td>
</tr>
<tr>
<td>ACPFO</td>
<td>-113.176225</td>
<td>1.127</td>
<td>1.936</td>
<td>0.0171</td>
<td>2.199.7</td>
<td>13.2</td>
</tr>
<tr>
<td>VCEPA</td>
<td>-113.173647</td>
<td>1.124</td>
<td>1.945</td>
<td>0.0162</td>
<td>2.237.2</td>
<td>12.0</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-113.190371</td>
<td>1.132</td>
<td>1.920</td>
<td>0.0173</td>
<td>2.160.3</td>
<td>13.1</td>
</tr>
<tr>
<td>ACPF(T)</td>
<td>-113.198363</td>
<td>1.139</td>
<td>1.895</td>
<td>0.0203</td>
<td>2.062.6</td>
<td>17.7</td>
</tr>
<tr>
<td>ACPFO(T)</td>
<td>-113.194096</td>
<td>1.133</td>
<td>1.917</td>
<td>0.0174</td>
<td>2.152.5</td>
<td>13.3</td>
</tr>
<tr>
<td>VCEPA(T)</td>
<td>-113.197515</td>
<td>1.138</td>
<td>1.899</td>
<td>0.0198</td>
<td>2.077.1</td>
<td>16.9</td>
</tr>
<tr>
<td>VCEPAO(T)</td>
<td>-113.193520</td>
<td>1.132</td>
<td>1.918</td>
<td>0.0174</td>
<td>2.157.6</td>
<td>13.2</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td>1.128</td>
<td>1.931</td>
<td>0.0175</td>
<td>2.169.8</td>
<td>13.3</td>
</tr>
<tr>
<td>HF</td>
<td>-100.369106</td>
<td>0.915</td>
<td>21.046</td>
<td>0.7786</td>
<td>4.189.4</td>
<td>88.2</td>
</tr>
<tr>
<td>CCSD</td>
<td>-100.370065</td>
<td>0.916</td>
<td>21.012</td>
<td>0.7898</td>
<td>4.169.6</td>
<td>90.3</td>
</tr>
<tr>
<td>ACPF</td>
<td>-100.369265</td>
<td>0.915</td>
<td>21.046</td>
<td>0.7860</td>
<td>4.183.7</td>
<td>89.8</td>
</tr>
<tr>
<td>ACPFO</td>
<td>-100.369900</td>
<td>0.915</td>
<td>21.020</td>
<td>0.7866</td>
<td>4.174.1</td>
<td>89.6</td>
</tr>
<tr>
<td>VCEPA</td>
<td>-100.369111</td>
<td>0.915</td>
<td>21.053</td>
<td>0.7831</td>
<td>4.188.0</td>
<td>89.2</td>
</tr>
<tr>
<td>VCEPAO</td>
<td>-100.377384</td>
<td>0.918</td>
<td>20.918</td>
<td>0.7877</td>
<td>4.142.1</td>
<td>89.5</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-100.378840</td>
<td>0.919</td>
<td>20.859</td>
<td>0.8044</td>
<td>4.110.4</td>
<td>92.5</td>
</tr>
<tr>
<td>ACPF(T)</td>
<td>-100.377807</td>
<td>0.918</td>
<td>20.907</td>
<td>0.7972</td>
<td>4.131.5</td>
<td>91.4</td>
</tr>
<tr>
<td>ACPFO(T)</td>
<td>-100.378645</td>
<td>0.919</td>
<td>20.868</td>
<td>0.8001</td>
<td>4.116.1</td>
<td>91.6</td>
</tr>
<tr>
<td>VCEPA(T)</td>
<td>-100.377628</td>
<td>0.918</td>
<td>20.915</td>
<td>0.7933</td>
<td>4.136.7</td>
<td>90.6</td>
</tr>
<tr>
<td>VCEPAO(T)</td>
<td></td>
<td>0.917</td>
<td>20.956</td>
<td>0.7980</td>
<td>4.138.3</td>
<td>89.9</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td>1.390</td>
<td>0.918</td>
<td>0.0104</td>
<td>1.016.8</td>
<td>8.7</td>
</tr>
<tr>
<td>F_2</td>
<td>-199.344390</td>
<td>1.428</td>
<td>0.871</td>
<td>0.0192</td>
<td>813.9</td>
<td>22.8</td>
</tr>
<tr>
<td>CCSD</td>
<td>-199.354609</td>
<td>1.424</td>
<td>0.875</td>
<td>0.0200</td>
<td>818.5</td>
<td>25.4</td>
</tr>
<tr>
<td>ACPF</td>
<td>-199.352395</td>
<td>1.407</td>
<td>0.897</td>
<td>0.0121</td>
<td>941.0</td>
<td>10.8</td>
</tr>
<tr>
<td>ACPFO</td>
<td>-199.351272</td>
<td>1.404</td>
<td>0.901</td>
<td>0.0122</td>
<td>949.2</td>
<td>11.1</td>
</tr>
<tr>
<td>VCEPA</td>
<td>-199.349153</td>
<td>1.413</td>
<td>0.889</td>
<td>0.0125</td>
<td>921.5</td>
<td>11.4</td>
</tr>
<tr>
<td>VCEPAO</td>
<td>-199.365737</td>
<td>2.083</td>
<td>0.409</td>
<td>-0.0041</td>
<td>2.527.4</td>
<td>39.8</td>
</tr>
<tr>
<td>ACPS(T)</td>
<td>-199.507134</td>
<td>1.450</td>
<td>0.844</td>
<td>0.0207</td>
<td>747.1</td>
<td>23.7</td>
</tr>
<tr>
<td>VCEPAO(T)</td>
<td>-199.376055</td>
<td>1.443</td>
<td>0.853</td>
<td>0.0204</td>
<td>768.1</td>
<td>24.4</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td>1.412</td>
<td>0.890</td>
<td>0.0138</td>
<td>916.6</td>
<td>11.2</td>
</tr>
</tbody>
</table>
an expectation value from the corresponding reference determinants. These are given in Table 6 including the dipole moments arising from the Brueckner coupled cluster doubles (BCCD) reference determinant. The good agreement of the latter with the BACPF values indicates a close resemblance between the BACPF and the BCCD orbitals. The fairly large difference between the ACPFO and BACPF values in cases like CO leads again to the conclusion that the difference between the two sets of orbitals can not in general be neglected.

It may also be noted that the dipole moments obtained from the Brueckner determinants are clearly superior to the HF values. The agreement of the values obtained from the BCCD reference determinant shown in Table 6 and the corresponding CCSD values in Table 2 is fairly good. In the case of CO, there is not only a sign change but also the largest difference between HF and BCCD values for all molecules shown in Table 6. It has been observed before that Brueckner orbitals are more appropriate for the calculation of molecular properties than HF orbitals [51]. This can be ascribed to the fact that the Brueckner determinant is the determinant which has maximum overlap with the total wave function thus being closer to it than the determinant formed with any other set of orbitals.

### 4 Conclusion

The role of orbital transformations in coupled-pair energy functionals has been discussed. The most striking property of the orbital optimized ACPF functional is its fully variational nature with respect to all variables, i.e., both the

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**Table 6** Dipole moments in atomic units for some small molecules as obtained from single determinant wave functions formed with the HF, BCCD, BACPF, and ACPFO orbitals

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF</th>
<th>BCCD</th>
<th>BACPF</th>
<th>ACPFO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>0.780</td>
<td>0.741</td>
<td>0.740</td>
<td>0.751</td>
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<tr>
<td>NH\textsubscript{3}</td>
<td>0.637</td>
<td>0.610</td>
<td>0.609</td>
<td>0.614</td>
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<tr>
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<td>0.756</td>
<td>0.717</td>
<td>0.716</td>
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<tr>
<td>LiF</td>
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<td>2.491</td>
<td>2.491</td>
<td>2.508</td>
</tr>
<tr>
<td>CO</td>
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<td>−0.961</td>
<td>−0.949</td>
<td>−0.993</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>−1.295</td>
<td>−1.209</td>
<td>−1.202</td>
<td>−1.227</td>
</tr>
</tbody>
</table>

Atoms on the negative half of the z-axis are marked with an overline.
orbital coefficients and the amplitudes of the double excitations. Thus, fully relaxed density matrices are directly obtained without the necessity to solve coupled-perturbed equations. This advantage can hardly be overestimated with respect to the calculation of response properties. It has also been demonstrated that orbital optimized coupled-pair functionals lead to improved results as compared to their unmodified counterparts including single excitations. This improvement is particularly pronounced in cases with strong orbital relaxation effects. Taking CuF as an example, it has been shown that the conventional ACPF method fails completely in this case whereas the ACPF with orbital optimization is still well-behaved. The agreement with the CCSD reference values is in general very good and clearly better than for the conventional ACPF method. Moreover, the elimination of the single excitations removes an ambiguity indicated by the difference between the ACPF \cite{20}, the ACPF-2 \cite{30}, and the NACPF \cite{25} methods. Since the solution of the Z-vector equations \cite{22} necessary to obtain relaxed density matrices for CCSD is as costly as solving the CCSD equations itself, we conclude that the orbital optimized methods presented here offer a considerably cheaper alternative for obtaining relatively accurate density matrices. The direct availability of correlated densities and first and second-order density matrices is not only advantageous for the calculation of molecular properties but could also be exploited to determine intermolecular electrostatic and first-order exchange energies in the framework of intermolecular perturbation theories, see e.g., Refs. \cite{52, 53}.

Finally, a word with respect to the computational efficiency of the orbital optimized methods might be appropriate. The scaling is the same as for the conventional methods with the most expensive step scaling as $m^2N^4$ if $N$ is the number of basis functions and $m$ the number of valence orbitals. However, it has to be admitted that our present implementation is rather slow. For the small molecules considered here, the CPU times are increased by a factor of roughly 2.5 as compared to the corresponding methods without orbital optimization. The bottleneck is the integral transformation of the electron repulsion integrals which has to be performed in each iteration cycle in the case of orbital optimized methods and takes more than one half of the time per iteration cycle for all molecules considered here. In particular, our present implementation performs the integral transformation for integrals with up to three external indices leading to $mN^3$ scaling of this step. This seems to be cheap compared to the aforementioned $m^2N^4$ scaling arising from the most unfavorable term in the residuals, i.e., the one involving integrals with four external indices but the prefactor is apparently very unfavorable. Thus, the integral transformation has to be avoided for the integrals with three external indices in an efficient implementation. This can be achieved by performing the corresponding contractions in the AO basis as described by Hampel et al. \cite{32} and will be considered in future implementations. Moreover the additional cost in orbital optimized methods due to the integral transformation step can greatly be reduced with density-fitting methods, see e.g. Ref. \cite{54}.

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References

10. Ahlrichs R (1979) Comp Phys Commun 17:31
13. Orbital-dependent correlation functionals

13.5. Correct Description of the Bond Dissociation Limit without Breaking Spin Symmetry by a Random-Phase-Approximation Correlation Functional

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- static correlation
- exact exchange
- hydrogen molecule
- exchange kernel
Correct Description of the Bond Dissociation Limit without Breaking Spin Symmetry by a Random-Phase-Approximation Correlation Functional

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A correlation functional that is termed exact-exchange random phase approximation (EXX-RPA) functional and is obtained with the exact frequency-dependent exchange kernel via the fluctuation-dissipation theorem is shown to correctly describe electron pair bonds in the dissociation limit without the need to resort to symmetry breaking in spin space. Because the functional also yields more accurate electronic energies for molecules in their equilibrium geometry than standard correlation functionals, it combines accuracy at equilibrium bond distances and in dissociation processes with a correct description of spin, something all commonly employed correlation functionals fail to do. The reason why the EXX-RPA correlation functional yields distinctively and qualitatively better results than RPA approaches based on Hartree-Fock and time-dependent Hartree-Fock is explained.

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Despite their ubiquitous application, present density-functional methods or more precisely Kohn-Sham (KS) methods, i.e., methods based on density functionals in the generalized gradient approximation or hybrid methods like the B3LYP method, suffer from severe shortcomings. The most serious problem of present KS methods, besides their inability to treat van der Waals interactions, is that they cannot correctly treat bond dissociation in molecules. The prototype dissociation of a chemical bond is the dissociation of the H₂ molecule. Standard nonspin-polarized KS calculations, as well as nonspin-polarized Hartree-Fock calculations, do yield qualitatively wrong electronic energies for larger bond distances and, in the limit of infinite distances, do not yield an electronic energy equal to twice the energy of an isolated hydrogen atom. By resorting to spin-polarized calculations, a qualitatively correct electronic energy is obtained at large distances which leads to a qualitatively correct potential energy curve, however, at the price of a qualitatively wrong spin-density. From a certain bond length on, termed the Coulson-Fisher point, alpha and beta electron densities in a spin-polarized calculation no longer are equal as they should be for an electronic state which, at all bond distances, is a singulet.

The problem occurs generally when dissociating electron pair bonds. Therefore, a lot of work has been attributed to it [1–8], with the goal to devise a KS approach that is generally applicable, performs well at equilibrium bond distances, and at the same time describes qualitatively correct bond breaking. We here show that a recent correlation functional [9] obtained within the framework of the random phase approximation (RPA) with the frequency-dependent exact-exchange (EXX) kernel [10] of time-dependent density-functional theory (TDDFT) leads to a correct dissociation of the H₂ molecule as well as other molecules.

RPA correlation functionals have attracted considerable interest in recent years [3,4,9,11–18]. The EXX-RPA correlation functional considered here is unique because it not only describes the dissociation limit correctly but also leads to electronic energies of molecules at equilibrium distances and to reaction energies that are more accurate than those from standard generalized gradient approximation or hybrid DFT methods [9] and because it enables a description of van der Waals interactions. Moreover, the basic EXX-RPA correlation functional can easily be modified and further developed; see below. Therefore, this EXX-RPA functional seems to be a highly promising starting point for a new family of functionals.

As usual in KS methods, an EXX-RPA calculation consists of two steps. (i) The KS orbitals and eigenvalues are calculated. This is done by an EXX-KS calculation [19] which means treating exactly the local multiplicative KS exchange potential, which must not be confused with the nonlocal HF exchange potential, but neglects the correlation potential. (ii) The electronic energy is calculated. It is the sum of the EXX energy plus the correlation energy from the EXX-RPA correlation functional obtained with the EXX kernel. One can easily imagine modifications of this approach by including a correlation potential in step (i) or a correlation contribution to the EXX kernel in step (ii). Here we concentrate on the basic EXX-RPA correlation functional.

An important, however, unexplained finding in Ref. [9] is that for the molecules considered in that work (molecules in their equilibrium geometry) the results from the EXX-RPA approach are distinctively better than those from an RPA method based on HF and time-dependent HF (TDHF), which shall be denoted as HF-RPA here. The EXX-KS and the HF determinants and thus the EXX and the HF electronic energies are known to be very close to each other [20]. Moreover, the excitation energies from a
TDDFT calculation with the EXX kernel, i.e., a TDEXX calculation, and a TDHF calculation are known to be very similar [21,22]. Therefore, one might also assume that the RPA correlation energies and the resulting complete electronic energies are close. This, however, was found in Ref. [9] not to be the case. Here we make the same finding in the case of H2 dissociation [see Fig. 1], which is even more striking. Because H2 is a two-electron system, the occupied EXX and HF orbital and thus the EXX and HF electronic energies are exactly identical. Moreover the TDEXX and the TDHF excitations energies are exactly identical. Nevertheless, the HF-RPA approach leads to a potential energy curve of H2 that differs strongly from the exact one while the EXX-RPA approach yields a potential energy curve approaching the correct dissociation energy [see Fig. 1], which is even more striking. Because

\[
E_c = -\frac{1}{2\pi} \int_0^1 \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty d\omega \chi_0(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega)
\]

(1)

The central quantity required in expression (1) for the correlation energy is the frequency- and coupling-strength-dependent response function \(\chi_0\). For a coupling constant of \(\alpha = 0\), \(\chi_0\) is the KS response function which is known in terms of the KS orbitals and eigenvalues. For all other values of the coupling strength \(\alpha\) the response function \(\chi_0\), or its frequency integral, is calculated by TDDFT. For the EXX-RPA correlation energy the coupling-strength-dependent TDEXX equation

\[
\left[ \mathbf{e}^2 + \alpha \mathbf{e}^{1/2}(\mathbf{A} + \mathbf{B} + \Delta) \mathbf{e}^{-1/2} \right] z_n(\alpha) = \Omega^2_n(\alpha)[1 - \alpha \mathbf{e}^{-1/2}(\mathbf{A} - \mathbf{B} + \Delta) \mathbf{e}^{-1/2}] z_n(\alpha)
\]

(2)

is solved. Equation (2) is obtained from the TDEXX equation derived in Refs. [21,22] for the full coupling strength \(\alpha = 1\) by simply multiplying all terms originating from the sum of the Coulomb and exchange kernel by the coupling strength \(\alpha\) exploiting the fact that these kernels are linear in \(\alpha\). The matrices \(\mathbf{A}, \mathbf{B}, \Delta\), and \(\mathbf{e}\) with a dimension equal to the number of occupied times unoccupied KS orbitals contain the matrix elements \(A_{ia,jb} = 2a_{ia}b_{jb} - a_{ia}b_{ji}, B_{ia,jb} = 2a_{ia}b_{jb} - (a_{ia}b_{jb})\), \(\Delta_{ia,jb} = \delta_{ij}\langle \Phi_a | \hat{V}^N - \hat{\nu}_1 | \Phi_b \rangle - \delta_{ab}\langle \Phi_i | \hat{V}^N - \hat{\nu}_1 | \Phi_j \rangle\), and \(\epsilon_{ia,jb} = \delta_{ia,jb}(\epsilon_i - \epsilon_a)\) with \(\Phi_i\) and \(\Phi_j\) being occupied KS orbitals with eigenvalues \(\epsilon_i\) and \(\epsilon_j\), \(\epsilon_a\) and \(\epsilon_b\) being unoccupied KS orbitals with eigenvalues \(\epsilon_a\) and \(\epsilon_b\), and with integrals of the type \(a_{ia}b_{jb}\) being defined according to \(\int d\mathbf{r} d\mathbf{r}' \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}') \varphi_j(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|\). The indices \(ia\) and \(jb\) are superindices labeling the columns and rows of the matrices. The operator \(\hat{V}^N\) is a nonlocal exchange operator of the form of the HF exchange operator but is constructed from KS orbitals, while \(\hat{\nu}_1\) is the operator corresponding to the local multiplicative KS exchange potential. The eigenvectors \(z_n(\alpha)\) and the eigenvalues \(\Omega_n(\alpha)\) of the TDEXX equation [9] then yield the EXX-RPA correlation energy according to

\[
E_c = \int_0^1 d\alpha V_c(\alpha)
\]

(3)

with the sum-over-excitations integrand

\[
V_c(\alpha) = \left[ \sum_n z_n^2(\alpha) e^{1/2} C z_n(\alpha)/\Omega_n(\alpha) \right] - Tr[C]
\]

(4)

with the matrix \(C\) containing the matrix elements \(C_{ia,jb} = \langle i|a\rangle \langle j|b\rangle\). The coupling strength integration in Eq. (3) is carried out numerically.

For the HF-RPA correlation energy instead of the TDEXX Eq. (2) the TDHF equation is solved. The latter can be written in the form [20,22]
in Eq. (4) differs for $\alpha \neq 1$ and $\alpha \neq 0$. [For $\alpha = 0$ $V_c(\alpha)$ in any case equals zero.]

In Fig. 2 $V_c(\alpha)$ is displayed for EXX-RPA and HF-RPA for different H$_2$ bond distances. Figure 2 shows that the differences in $V_c(\alpha)$ are significant. Such strong differences in the $\alpha$ dependence of $V_c(\alpha)$ not only occur for H$_2$ but are present in general; see, e.g., $V_c(\alpha)$ curves for the water molecule in the supporting information. The differences between the TDEXX Eqs. (2) and (7) and the TDHF equation expressed in EXX orbitals, Eqs. (6) and (8), that are responsible for most (all, in the H$_2$ case) of the differences between EXX-RPA and HF-RPA arise from the fact that the matrix $\Delta$ resulting from the transformation of HF to EXX eigenvalue differences is not scaled by the coupling constant in the HF-RPA case. This leads to terms $(1 - \alpha)\Delta$ in the TDHF equations not present in the TDEXX equations.

The differences between HF-RPA and EXX-RPA can also be rationalized as follows. The RPA correlation energy according to Eq. (1) depends on the response function $\chi_n$ at all values $0 \leq \alpha \leq 1$. At $\alpha = 1$ TDHF and TDEXX excitation energies $\Omega_n$ and the associated eigenvalues $z_n$ are quite similar (identical for H$_2$) and, therefore, the corresponding response functions $\chi_{n=1}$ are quite similar. However, at $\alpha = 0$ the response function is given by a sum-over-states expression containing occupied and unoccupied orbitals and differences of the orbital eigenvalues. The unoccupied HF and EXX orbitals and their

![FIG. 2. Coupling strength integrand [Eq. (4)] for HF-RPA (top panel) and EXX-RPA (bottom panel) plotted for several H-H bond distances.](image)
eigenvalues differ strongly and as a result the response function $\chi_\alpha$ is also strongly different at $\alpha = 0$. Indeed, in most cases, unoccupied HF orbitals have positive eigenvalues and individually have little physical meaning in contrast to EXX orbitals and their eigenvalues. Because the response function changes continuously along the adiabatic connection, i.e., along $\alpha$, the response functions are strongly different for all values of $\alpha$ that are not close to 1. The resulting better performance of EXX-RPA compared to HF-EXX correlation functionals, in this sense, to some extent is a consequence of the physically more meaningful EXX orbital and eigenvalue spectrum.

Figure 2 shows that for increasing H$_2$ bond distance the electron-electron contribution $V_\gamma$ to the correlation energy as a function $V_\gamma(\alpha)$ of the coupling constant $\alpha$ jumps immediately next to $\alpha = 0$ from zero to a lower energy that equals the static correlation energy given by the integral $-\langle i|a|a \rangle$ with $i$ referring to the occupied and $a$ referring to the lowest unoccupied orbital. This static correlation correction exclusively arises from the contribution of the energetically lowest excitation (excitation from bonding to the antibonding linear combination of $1s$ orbitals) to the total EXX-RPA correlation energy of Eqs. (4) and (3); see supplementary material for details [26]. The jump of $V_\gamma$ is in agreement with the finding of Ref. [8] where the exact $V_\gamma(\alpha)$ was determined for small systems using a full configuration interaction method. The exact curve for $V_\gamma(\alpha)$ of Ref. [8] jumps to a horizontal line which shows that the static correlation energy is independent of the coupling constant. The fact that the EXX-RPA $V_\gamma(\alpha)$ curve after the jump shows a slight slope can be attributed to dynamic correlation which arises from the contributions of other excitations to the correlation energy. This dynamic correlation corrects contributions to the EXX energy arising because the EXX orbitals are not linear combinations of the exact atomic hydrogen 1s orbitals (see supplementary material for details [26]).

For H$_2$ bond distances around 6 a.u., a hump occurs in the EXX-RPA potential energy curve; see Fig. 1. The reason is that for this distance $V_\gamma(\alpha)$ does not yet jump to the full static correlation energy [see Fig. 2] and, therefore, the EXX-RPA correlation functional does not yet yield the full static correlation energy $-\langle i|a|a \rangle$ of $-0.178$ a.u. but only $-0.108$ a.u., which is the contribution from the energetically lowest excitation energy to $V_\gamma(\alpha)$; see supplementary material for details [26].

The EXX-RPA method not only describes the dissociation limit of H$_2$ correctly, but of molecular bonds in general. Results for molecules like N$_2$, CO, or HF will be presented elsewhere. The EXX-RPA functional, therefore, is a general purpose functional that seems to be superior to commonly employed correlation functionals.

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In Fig. 1 $V_c(\alpha)$ curves for the EXX-RPA and the HF-RPA case are compared for the water molecule at equilibrium geometry. The almost invisible differences in $V_c(\alpha)$ at $\alpha = 1$ are due to the fact that the EXX and the KS determinants are not exactly equal and due to the fact that even for $\alpha = 1$ the right hand sides of the EXX-TDDFT equation (2) and the TDHF equation expressed in EXX orbitals, Eq. (6) are different. However, the differences in the right hand sides of the equations for $\alpha = 1$ were shown to be of second order in $\varepsilon^{-1/2}[\alpha (A - B) + \Delta]|\varepsilon^{-1/2}$ and to have only a quite small effect. Because also the differences in EXX and HF determinants are small, $V_c(\alpha)$ differs only very little in the EXX-RPA and the HF-RPA case for $\alpha = 1$. For $\alpha \neq 1$ also the left hand sides of Eqs. (2) and (6) differ, as for the H$_2$ molecule, by a term containing $(1 - \alpha)\Delta$ and furthermore the differences in the right hand sides no longer are of the second order in $\alpha$ also due to the occurrence of a term $(1 - \alpha)\Delta$. Fig. 1 shows that these differences lead to significant differences in $V_c(\alpha)$ for $\alpha \neq 1$ (and $\alpha \neq 0$).
FIG. 2. Contribution $V^{HL}_c(\alpha)$ of the HOMO-LUMO excitation to the electron-electron interaction part $V_c(\alpha)$ of the RPA correlation energy in the H$_2$ molecule for various bond distances $r$, upper panel refers to HF-RPA, lower panel to EXX-RPA.
Fig. 2, for the H_2 molecule at various bond distances, shows the contribution $V^\text{HL}_c(\alpha)$ to the electron-electron interaction part $V_c(\alpha)$ of the RPA correlation energy that arises form the energetically lowest excitation $\Omega_1(\alpha)$, see Eq. (4) of the main text for $V_c(\alpha)$ given as a sum-over-excitations expression. An analysis of the eigenvectors $z_n(\alpha)$ of the TDEXX or TDHF equations (7) and (8) of the main text, respectively, reveals that the lowest excitation is a pure HOMO (Highest Unoccupied Molecular Orbital) LUMO (Lowest Unoccupied Molecular Orbital) excitation, i.e., an excitation from the occupied bonding linear combination of hydrogen 1s-orbitals to the corresponding unoccupied antibonding linear combination. Indeed for large bond distances $r$ beyond 20 $a_0$ the eigenvector $z_1(\alpha)$ in the TDHF as well as in the TDEXX case for all values of $\alpha$ is an almost perfect unit vector (in the TDHF case multiplied by a normalization factor, see below). In this case the corresponding excitation energy $\Omega_1(\alpha)$ is given by those diagonal elements of the TDEXX and TDHF equations, Eqs. (7) and (8) of the main text, that belong to the superindex $ia$ with $i$ and $a$ referring to the HOMO and LUMO, respectively. In other words in this case a single pole approximation yields the exact excitation energy. The lowest TDEXX excitation energy $\Omega_1(\alpha)$ then is given by

$$\Omega_1(\alpha) = \sqrt{\epsilon_{ia}^2 + 2\alpha \epsilon_{ia}^{1/2} (ia|ia) \epsilon_{ia}^{1/2}}.$$  

(1)

For the remainder of the Supporting Informations the indices $i$ and $a$ shall refer to the HOMO and LUMO, respectively, as in Eq. (1). The contribution $V^\text{HL}_c(\alpha)$ according to Eq. (4) of the main text then is given by

$$V^\text{HL}_c(\alpha) = \left[ \frac{x^{1/2}}{\sqrt{x + 2\alpha}} - 1 \right] (ia|ia)$$  

(2)

with $x = \epsilon_{ia}/(ia|ia)$ if it is exploited that the vector $z_1(\alpha)$ is a unit vector. If the HOMO-LUMO gap $\epsilon_{ia}$ is small enough such that the ratio $x = \epsilon_{ia}/(ia|ia)$ is small compared to the coupling constant $\alpha$ then the expression in the large square brackets of Eq. (2) approaches $-1$ and $V^\text{HL}_c(\alpha)$ approaches $-(ia|ia)$. For large bond distances $r$ the HOMO LUMO gap is vanishing and therefore $\epsilon_{ia}/(ia|ia)$ is small compared to $2\alpha$ for all values of $\alpha$ except in the immediate vicinity of $\alpha = 0$. This explains the jump in $V^\text{HL}_c(\alpha)$ and subsequently in the complete coupling constant integrand $V_c(\alpha)$.

The coupling constant integration, see Eq. (3) of the main text, of the contribution $V^\text{HL}_c(\alpha)$ given in Eq. (2) can easily be carried out analytically and yields the contribution
$E_{c}^{HL}$ of the HOMO-LUMO excitation to the complete EXX-RPA correlation energy $E_c$,

$$E_{c}^{HL} = \left[ x^{1/2} \sqrt{x + 2} - x - 1 \right] (ia|ia).$$

(3)

If the HOMO-LUMO gap $\epsilon_{ia}$ is small compared to $(ia|ia)$ such that $x = \epsilon_{ia}/(ia|ia)$ is small compared to one then it follows from Eq. (3) that the contribution $E_{c}^{HL}$ of the HOMO-LUMO excitation to the EXX-RPA correlation energy $E_c$ equals $-(ia|ia)$, i.e., the complete static correlation energy.

The EXX total energy for H$_2$ at large bond distances $r$ equals $2\epsilon_{\text{atomic}} + (ii|ii) - 1/r$ with $\epsilon_{\text{atomic}}$ denoting the energy expectation value of an atomic hydrogen Hamiltonian operator with the 1$s$-like atomic orbitals forming as bonding and antibonding linear combinations the H$_2$ HOMO and LUMO. The term $-1/r$ arises from the interaction of the atomic orbitals with the other nucleus, i.e., the nucleus they are not centered on, and the repulsion of the two nuclei. If the static correlation $-(ia|ia)$ is added to the EXX total energy, then the energy $2\epsilon_{\text{atomic}}$ is obtained because $(ii|ii) - (ia|ia) = 1/r$ for large $r$. If the EXX orbitals were the exact Kohn-Sham orbitals then $\epsilon_{\text{atomic}} = \epsilon_{H1s}$ with $\epsilon_{H1s}$ being the atomic hydrogen 1$s$ energy because the atomic orbitals building the H$_2$ HOMO and LUMO would equal the exact atomic hydrogen 1$s$-orbitals. As a result the sum of the EXX total energy plus the static correlation, i.e., the EXX total energy plus the contribution of the HOMO-LUMO excitation to the EXX-RPA energy, would yield exactly twice the energy of the hydrogen atom. However, the EXX orbitals are not equal to the exact Kohn-Sham orbitals. The sum of the Coulomb and the exchange potential is not canceled by a correlation potential in the EXX case and therefore the EXX orbitals are not linear combinations of the exact hydrogen 1$s$-orbitals but of somewhat more diffuse atomic 1$s$-like orbitals. This leads to a contribution in the EXX total energy which, however, is canceled, at least to the most part, by contributions to the EXX-RPA energy from higher excitations. The sum of these contributions, which shall be denoted dynamic EXX-RPA correlation energy, is reflected in the differences of $V_{c}^{HL}(\alpha)$ and the complete $V_{c}(\alpha)$, i.e., in the differences of the adiabatic connection curves of Fig. 2 of the supplementary information and of Fig. 2 in the main text. The latter figure shows that these dynamic correlation contributions to $V_{c}(\alpha)$ depend on the coupling constant $\alpha$ as pointed out in the main text.

Fig. 2 shows that at a bond distance of $r = 6$ a$_0$ the HOMO-LUMO contribution $V_{c}^{HL}(\alpha)$ to the electron-electron interaction part $V_{c}(\alpha)$ of the RPA correlation energy of the H$_2$...
molecule still shows a sizeable $\alpha$-dependence. As a result the corresponding contribution $E^{\text{HL}}_c$ to the EXX-RPA correlation energy with -0.108 a.u. does not yet equal the full static correlation energy $-(ia|ia)$ which equals -0.178 a.u. for this bond distance. If the difference of 0.070 a.u. to the full static correlation was subtracted from the sum of the EXX total energy plus the EXX-RPA correlation energy then the hump in the $H_2$ EXX-RPA potential energy curve of Fig. 1 of the main text would completely vanish, the potential energy curve would actually lie 0.022 a.u. below the CI curve. This means the hump in the EXX-RPA potential energy curve of $H_2$ at a bond distance around 6 $a_0$ is caused by an incomplete accounting of the static correlation energy. This has two reasons. First, the EXX HOMO-LUMO gap is too large compared to the exact KS HOMO-LUMO gap, 0.027 a.u. compared to 0.0098 a.u. The latter value was obtained via a reconstruction of the exact KS potential from the CI density. According to Eq. (2) and (3) a too large HOMO-LUMO gap leads to a static correlation energy too small in magnitude. Second, the EXX-RPA correlation energy even if evaluated for the exact Kohn-Sham orbitals and eigenvalue differences does not recover the full static correlation energy at bond distance around 6 a.u. If $E^{\text{HL}}_c$ is evaluated with the recalculated exact Kohn-Sham orbitals and eigenvalues a value of -0.179 a.u. is obtained while the static correlation in this case has a value of -0.235 a.u.

Finally we consider the contribution $V^{\text{HL}}_c(\alpha)$ of the first excitation to the HF-RPA correlation energy, upper panel of Fig. 2. In the HF-RPA case like in the EXX-RPA case the single pole approximation for the lowest excitation energy becomes exact for large bond distances. Instead of Eq. (2) we obtain

$$V^{\text{HL}}_c(\alpha) = \left[ \sqrt{\frac{x + (1 - \alpha)[\Delta_{ia}/(ia|ia)]}{x + (1 - \alpha)[\Delta_{ia}/(ia|ia)] + 2\alpha - 1}} - 1 \right] (ia|ia) \tag{4}$$

for $V^{\text{HL}}_c(\alpha)$ in the HF-RPA case. For a better comparison with the EXX-RPA case given in Eq. (2) we have expressed the contribution $V^{\text{HL}}_c(\alpha)$ to the HF-RPA correlation energy in Eq. (4) in terms of EXX orbitals and eigenvalue differences. To that end we considered the single pole expression of the HF HOMO-LUMO excitation energy following from Eq. (8) of the main text, i.e., the TDHF equation for a two electron system expressed in EXX orbitals and eigenvalues. Moreover, when evaluating the single pole expression we have taken into account that the eigenvectors $z_n(\alpha)$ of Eq. (8) of the main text have to be normalized with respect to the matrix occurring on the right hand side of the equation before they are substituted in the sum-over-excitations expression of Eq. (4) of the main text. Furthermore,
note that the eigenvalue differences occuring in the sum-over-excitation expression (4) of the main text always have to be those occuring in the TDEXX or TDHF equations used to calculate the eigenvectors $z_n(\alpha)$. In case of the TDHF equation expressed in EXX orbitals and eigenvalues, Eq. (8) of the main text, these are the EXX eigenvalue differences.

In contrast to Eq. (2) of the EXX case, in Eq. (4) it is not enough that $x = \epsilon_{ia}/(ia|ia)$ is small compared to the coupling constant $\alpha$ for $V^{\text{HL}}_c(\alpha)$ to jump to the static correlation energy $-(ia|ia)$. It is furthermore necessary that $(1 - \alpha)|\Delta_{ia}/(ia|ia)|$ is small compared to $2\alpha$. Because $\Delta_{ia}$, i.e., the difference of the HF and EXX HOMO-LUMO gap, approaches $1/r$ for large bond distances $r$ this happens, however, only for very large bond distances. Therefore HF-RPA describes the dissociation of $H_2$ much worse than EXX-RPA. Comparison of Eqs. (2) and (4) shows that the reason for the differences of HF-RPA and EXX-RPA is the occurrence of terms that depend on the difference of the HF and EXX HOMO-LUMO gap given by $\Delta_{ia}$.


13.6. Third-order corrections to random-phase approximation correlation energies

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- adiabatic connection
Third-order corrections to random-phase approximation correlation energies

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Several random-phase approximation (RPA) correlation methods were compared in third order of perturbation theory. While all of the considered approaches are exact in second order of perturbation theory, it is found that their corresponding third-order correlation energy contributions strongly differ from the exact third-order correlation energy contribution due to missing interactions of the particle-particle—hole-hole type. Thus a simple correction method is derived which makes the different RPA methods also exact to third-order of perturbation theory. By studying the reaction energies of 16 chemical reactions for 21 small organic molecules and intermolecular interaction energies of 23 intermolecular complexes comprising weakly bound and hydrogen-bridged systems, it is found that the third-order correlation energy correction considerably improves the accuracy of RPA methods if compared to coupled-cluster singles doubles with perturbative triples as a reference. © 2011 American Institute of Physics.

I. INTRODUCTION

The description of electron correlation plays an important role in the theoretical study of molecular systems. This perhaps becomes most obvious when one considers molecular systems that are far from their ground-state equilibrium or in case of weakly bound molecular complexes where the Hartree-Fock method completely fails. However, even for nonproblematic systems Hartree-Fock theory fails to deliver the chemical accuracy of 1 kcal/mol for binding energies, 0.01 Å for bond distances, or 10 cm⁻¹ for vibrational frequencies. Because of this the electron correlation effects missing in Hartree-Fock theory have to be accounted for. Usually this is done using standard ab initio correlation methods like configuration interaction, Møller-Plesset perturbation theory, or coupled-cluster theory. Since these methods are conventionally much more computationally expensive than Hartree-Fock, Kohn-Sham density-functional methods (DFT) have become very popular as a compromise between accuracy and cheapness since they are commonly even cheaper than Hartree-Fock methods but usually less accurate than standard ab initio correlation methods.

However, the development of new computational algorithms like density fitting and Cholesky decomposition (see also Refs. 25 and 26 for singular value decomposition approaches in coupled-cluster theory), the transformation into local basis functions or the exploitation of parallel computer architectures has lead to an increase of the feasibility of standard ab initio methods also for extended molecular systems so that electron correlation effects can nowadays also be accounted for quite large systems that formally could be described only on the density functional theory level. However, though in contrast to DFT standard ab initio correlation methods have the advantage that they can systematically be improved, one usually has to restrict oneself to those methods that have the lowest scaling behaviour with respect to the molecular size, that is, second-order Møller-Plesset perturbation theory (MP2) scaling as $N^5$ or coupled-cluster singles-doubles (CCSD) which has a scaling behaviour of $N^6$.

Among these methods one can also classify random-phase approximation (RPA) correlation methods which, as was recently shown by Scuseria et al., are related to coupled cluster doubles theory in which one only keeps terms of the particle-hole type (see also Ref. 2; in fact, it has been shown that the dispersion interaction energy on the coupled-cluster doubles level is identical to the dispersion energy described by RPA response propagators of the monomers, see Ref. 53). Because of this they are generally computationally less expensive than corresponding coupled-cluster methods restricted to doubles excitations but have in comparison with, e.g., Møller-Plesset perturbation theory methods the advantage that certain types of correlation energy diagrams, namely, those with a ring structure, are summed up to infinity. In spite of this feature of RPA methods one may now ask why they have rarely been used in the past to calculate the electron correlation energy for molecular ground states. In Sec. II it will be shown that the extraction of the correlation energy from the RPA is by far not unique and a number of RPA methods were developed that are exact in second order of perturbation theory, but differ in third-order. We here refer to these methods as “normal” RPA (NRPA) methods in order to point out the difference to so called higher RPA methods (like SOPPA, second-order polarization propagator approximation) in which the wave function that enters the RPA equations also contains double excitations.

In recent years RPA methods have become more popular in the framework of density functional theory. The use of

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the Kohn-Sham determinant instead of the Hartree-Fock determinant as the reference determinant in RPA methods might be advantageous in order to account implicitly for single excitations that are commonly absent in Hartree-Fock based RPA methods. It has been shown for some small molecules that, depending however on the underlying exchange-correlation potential, Kohn-Sham orbitals are closer to Brueckner orbitals than Hartree-Fock orbitals \(^{77}\) (see, however, Ref. \(^{78}\)) and therefore might be closer to variationally optimised orbitals in RPA approaches. It has also been demonstrated recently that an adiabatic-connection RPA method based on exact Kohn-Sham exchange is superior for the description of bond dissociation than the corresponding Hartree-Fock based approach.\(^ \text{79} \)

RPA correlation functionals also appear to be attractive candidates in range-separated DFT methods in which the short-range electron correlation is described by standard DFT methods and the long-range correlation, that is poorly described on the standard DFT level, is described with RPA.\(^ {68, 69, 71, 73, 80-82}\)

The advantage of such range-separated methods is that they are less basis set dependent than common \(ab\) initio correlation methods since the interelectronic cusp problem is screened out by using a DFT description for small interelectronic distances.

In this work several random-phase approximation correlation methods based on the Hartree-Fock reference determinant will be considered. In Sec. II the explicit expressions for the correlation energies of the different RPA methods will be presented. In Sec. III the third-order contributions to the correlation energy for these RPA methods will be investigated numerically and a simple correction approach will be derived that enforces correctness in third order for the different RPA methods. Section IV shows the performance for the RPA methods for total correlation energies (Subsection IV A), reaction energies (Subsection IV B), and intermolecular interactions (Subsection IV C). It will be shown that the third-order correction to RPA correlation energies considerably improves their accuracy if compared to coupled-cluster singles doubles with perturbative triples (CCSD(T)) reference values. Finally, Sec. V discusses the results and concludes.

II. CORRELATION ENERGY IN THE RANDOM PHASE APPROXIMATION

The RPA equations determining the excitation energies \(\omega_n\) and the amplitudes \(X_n, Y_n\) are given by\(^ {1, 46, 83, 84}\)

\[
\begin{pmatrix}
  e + A & B \\
  -B & -e - A
\end{pmatrix}
\begin{pmatrix}
  X \\
  Y
\end{pmatrix}
= \omega
\begin{pmatrix}
  0 & \lambda \\
  \lambda & 0
\end{pmatrix}
\begin{pmatrix}
  X \\
  Y
\end{pmatrix},
\]

(1)

where the matrices \(A, B, X,\) and \(Y\) have the dimension \(n_{\text{occ}} \times n_{\text{virt}}\) with \(n_{\text{occ}}\) and \(n_{\text{virt}}\) being the number of occupied and unoccupied spin orbitals, respectively. The matrix \(\omega\) collects the positive eigenvalues of the Hessian matrix in its diagonal. Here and in the following the orbitals are assumed to be real-valued. Note that Eq. (1) has the complementary solution

\[
\begin{pmatrix}
  Y \\
  X
\end{pmatrix}
\]

corresponding to an eigenvalue \(-\omega_n\). The Hessian and overlap matrices occurring in Eq. (1) are defined as

\[
(\varepsilon + A)_{ia,jb} = \langle \Psi^a_{ij} | \hat{H} - E_0 | \Psi^b_{ij} \rangle,
\]

(2)

\[
\lambda_{ia,jb} = \langle \Psi^a_{ij} | \hat{\lambda} | \Psi^b_{ij} \rangle.
\]

(4)

\(\hat{H}\) is the electronic Hamiltonian, \(E_0\) the Hartree-Fock ground-state energy, and \(\Psi^a_{ij}, \Psi^b_{ij}\) are singly and doubly excited wave functions, respectively. Indices \(i, j, k, \ldots\) label occupied and \(a, b, c, \ldots\) label unoccupied orbitals. If the wave function \(\Psi\) in Eqs. (2)–(4) is approximated by the Hartree-Fock wave function, then the NRPA approach\(^ {46, 55}\) is obtained and the Hessian and overlap matrices are given by

\[
(\varepsilon + A)_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + \langle ij | ab \rangle - \langle ia | jb \rangle,
\]

(5)

\[
B_{ia,jb} = \langle ij | ab \rangle - \langle ij | ba \rangle,
\]

(6)

\[
\lambda_{ia,jb} = \delta_{ij} \delta_{ab},
\]

(7)

with \(\varepsilon_i\) and \(\varepsilon_a\) being occupied and virtual orbital energies and \(\langle ij | tu \rangle\) defines a two-electron repulsion integral in physicist’s notation.

Originally correlation energies within the RPA were obtained for infinite systems like the homogeneous gas.\(^ {48, 51, 54, 85-87}\) For finite systems, however, it was found that the RPA correlation energy is wrong by a prefactor of two in second order. Because of this several “normal” RPA approaches exist which enforce the correct behaviour in second order.

McLachlan and Ball derived an expression for the RPA correlation energy by multiplying the corresponding expression from the RPA correlation energy for the homogeneous electron gas by a factor of one half.\(^ {53, 85}\) The RPA correlation energy, which will be termed as NRPA1 correlation energy in the following and which is identical to the ring coupled-cluster doubles correlation energy (rCCD),\(^ {52}\) is then given by

\[
E_c^{\text{NRPA1}} = \frac{1}{4} \text{Tr}(B \mathbf{T}) = \frac{1}{4} \text{Tr}(B^1 \mathbf{T} + 3B^2 \mathbf{T}).
\]

(8)

In Eq. (8) the final expression on the right-hand side is written in spatial orbitals. The amplitudes \(\mathbf{T}\) are given by \(\mathbf{T} = \mathbf{Y}^{-1}\) and the matrices \(B^1, B^2\) and \(3B^2\) define singlet and triplet Hessian matrices and amplitudes, respectively.

In the RPA correlation energy expression from Fukuda \textit{et al.}\(^ {49}\) termed as NRPA2 here, the correct second-order behaviour is enforced by subtracting the second-order energy from the electron-gas formula:

\[
E_c^{\text{NRPA2}} = \frac{1}{4} \text{Tr}(B \mathbf{T}) - E_c^{(2)}.
\]

(9)

Since the Hartree-Fock determinant is used as the reference determinant here, \(E_c^{(2)}\) is identical to the second-order Möller-Plesset (MP2) correlation energy.

It has been shown by Oddershede and Jørgensen\(^ {47, 59}\) that if the Hartree-Fock wave function is used to solve the RPA Eq. (1), then there is an inconsistency in the corresponding two-particle density matrix since the Hartree-Fock ground state is not the ground state for the RPA excitation operators.\(^ {90-92}\) Namely, the condition that \(\mathbf{Y}^\dagger \mathbf{Y} = 3 \mathbf{Y}^\dagger \mathbf{X}^\dagger\), which arises from the condition that the wave function is an eigenfunction of the spin-squared operator \(S^2\) with eigenvalue zero, is not...
fulfilled. Because of this triplet excitation energies, in contrast to singlet excitation energies, within the NRPA (time-dependent Hartree-Fock) are often poor and it has been stated by Chambaud et al. that in fact triplet instabilities occur in any \(\pi\)-electronic system like ethylene or benzene. While one possibility to overcome this deficiency is to use higher-order RPA approaches, Oddershede proposed to enforce the condition \(1^Y\mathbf{X}^T = -3^Y\mathbf{X}^T\) in the RPA correlation energy and arrives at

\[
E_{\text{c}}^{\text{dRPA}} = \frac{1}{2} \text{Tr}(\mathbf{1}\mathbf{B}^3 - 3\mathbf{B}^2 \mathbf{Y}^T \mathbf{X}^T)
\approx \frac{1}{2} \text{Tr}(\mathbf{1}\mathbf{B}^3 - 3\mathbf{B}^2 \mathbf{Y}^T)
\tag{10}
\]

where it has been used that \(\mathbf{Y} \mathbf{X}^T \approx \mathbf{Y} \mathbf{X}^{-1}\) since the two expressions differ only in second order in the small vector component \(\mathbf{Y}\).\cite{47, 98}

Szabo and Ostlund have shown that none of the above given expressions for the RPA correlation energy fulfill the desired criterion that the long-range behaviour of the dispersive part of the interaction energy between two separate closed-shell molecules is described on the coupled Hartree-Fock level, i.e., the interaction contribution does not reduce to the dispersion energy on the time-dependent Hartree-Fock level for the methods NRPA1, NRPA2, and NRPA3.\cite{46, 99} Because of this Szabo and Ostlund proposed the following expression for the RPA correlation energy:

\[
E_{\text{c}}^{\text{NRPA3}} = \frac{1}{2} \text{Tr}(\mathbf{1}\mathbf{B}^3 - 3\mathbf{B}^2 \mathbf{Y}^T \mathbf{X}^{-1}) + \mathbf{X}^1_T
\tag{11}
\]

which again is exact to second order and describes the long-range correlation energy on the coupled Hartree-Fock level.\cite{46}

It can be shown that the desired long-range behaviour of the RPA correlation energy as well as correctness in second order can also be obtained by using an adiabatic connection approach.\cite{85, 100, 102} In the adiabatic connection method the electron-electron interactions (here all interactions that are not described on the Hartree-Fock level) are switched on by multiplication with a coupling-strength parameter \(\alpha\) which varies between 0 (interaction turned off) and 1 (interaction fully turned on). The electron correlation energy is then obtained by an integral over the coupling strength and is given by

\[
E_{\text{c}}^{\text{AC-RPA}} = \frac{1}{2} \int_0^1 d\alpha \text{Tr}(C(\mathbf{X}_a + \mathbf{Y}_a)(\mathbf{X}_a + \mathbf{Y}_a)^T - 1)
\tag{12}
\]

where \(C_{ia,jb} = (ij)ab\) and \(\mathbf{P}\) is the correlation part of the pair density within the RPA. The RPA eigenvector components \(\mathbf{X}_a\) and \(\mathbf{Y}_a\) at the coupling strength \(\alpha\) are the solutions of a modified RPA Eq. (1) in which the matrices \(\mathbf{A}\) and \(\mathbf{B}\) are scaled by the coupling strength \(\alpha\).

Recently Kresse et al. have derived another RPA variant which requires only the solution vectors \(\mathbf{X}\) and \(\mathbf{Y}\) of the direct RPA (dRPA) equation which has the same form as Eq. (1) but in which all exchange integrals in Eqs. (5) and (6) are neglected. While dRPA misses the exchange part of the second order correlation energy (diagram 1b in Figure 1), it can be obtained if the dRPA amplitudes \(\mathbf{T}^{\text{dRPA}} = \mathbf{Y}^{\text{dRPA}} \mathbf{X}^{-1}^{\text{dRPA}}\) are contracted with antisymmetrised two-electron integrals. The method is termed as second order screened exchange (SOSEX) and the correlation energy reads

\[
E_{\text{c}}^{\text{SOSEX}} = \frac{1}{2} \text{Tr}(\mathbf{B}^{\text{dRPA}})
\tag{13}
\]

The advantage of the SOSEX method over the other RPA methods discussed in this section is that the amplitudes \(\mathbf{T}^{\text{dRPA}}\) can be obtained with a lower computational cost, see, e.g., Refs. 67, 103, and 104.

III. THIRD-ORDER CORRECTIONS TO NORMAL RANDOM-PHASE APPROXIMATION CORRELATION ENERGIES

While all RPA approaches discussed in Sec. II, namely, NRPA1 (rCCD), NRPA2, NRPA3, NRPA4, AC-RPA, and SOSEX are exact to second-order of perturbation theory, they differ in third order. A corresponding third order analysis of RPA correlation energies has already been made by Szabo and Ostlund, Oddershede, and very recently by Jansen et al.\cite{102} (see also Ref. 105). The third order correlation energy is given in diagrammatical form in Figure 1, more precisely it is given by the sum of the diagrams (2a)–(2l) in Figure 1. The corresponding algebraic expressions can be looked up in Ref. 1. All normal RPA methods (including SOSEX and AC-RPA) contain only those third order contributions that are of the particle-hole (ph) type, i.e., diagrams (2a)–(2h). The individual prefactors for each perturbation theory diagram for the different RPA methods are displayed in Table I. It can be seen that the NRPA1 method accounts for all third order ph contributions, but with a wrong prefactor of one half. This is corrected by the NRPA2 method which includes all ph diagrams with the correct prefactor of one. In contrast to this all other RPA methods displayed in Table I only contain fractions of the total ph correlation contribution. For example, the NRPA4 method from Szabo and Ostlund excludes the diagrams (2g) and (2h) from Figure 1 and the NRPA3 method contains even less third order correlation contributions than NRPA4. The SOSEX method contains, in addition to the direct RPA diagram (2a), only one further exchange type contribution, namely, diagram (2e). The AC-RPA method misses only one ph third-order contribution, but has wrong prefactors of \(\frac{1}{2}\) and \(\frac{1}{2}\) for the other ph diagrams, as can be seen in Table I.

In order to investigate the importance of the third-order correlation contributions numerically, the individual third order contributions from Figure 1 were calculated for a range of small molecules (see Sec. IV A for details). In Figure 2 the correlation energy contributions are shown for the three molecules \(\text{H}_2\text{O}, \text{CO},\) and \(\text{HCOOH}\). It can be seen that in spite of quantitative differences for all three cases the relative magnitudes of the individual contributions are very similar and this observation also transfers to all other systems studied in this work. It is apparent from Figures 2(a), 2(c), and 2(e) that diagrams (2d) and (2g) as well as (2e) and (2f) are identical, which is due to the fact that real valued orbitals were used. The direct third-order ring diagram (2a) always gives a strong positive contribution to the third-order correlation
energy, but it is more than compensated by the ph-exchange diagrams (2b) and (2h). The sum of all other ph-exchange diagrams leads to a small positive correlation energy contribution, so that the total third order ph-correlation energy is always a significant negative contribution, as shown by the green bars in Figure 2. In contrast to this the pp-hh-correlation contributions that are missing in the NRPA methods, displayed by the blue bars in Figures 2(a), 2(c), and 2(e), always sum up to a positive correlation contribution, see orange bars in Figure 2. As a consequence, the ph and pp-hh correlation diagrams of third order always cancel each other to a large extent and so the total third order correlation contribution is

\[ \text{FIG. 1. Second- and third-order Goldstone diagrams. Diagrams (1a) and (1b) correspond to the direct and exchange term of the second order correlation energy, diagrams (2a)-(2h) are particle-hole diagrams and diagrams (2i)-(2l) are particle-particle and hole-hole diagrams. Note that only particle-hole diagrams of the type (2a)-(2h) are contained in conventional RPA correlation methods, see Table I.} \]

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Table I. Comparison of the third order expansions of various RPA correlation methods. The diagram labels correspond to the ones displayed in Figure 1. The column values correspond to the respective prefactor for each perturbation diagram.

<table>
<thead>
<tr>
<th>Diagram</th>
<th>Exact</th>
<th>dRPA</th>
<th>SOSEX</th>
<th>NRPA1(rCCD)</th>
<th>NRPA2</th>
<th>NRPA3</th>
<th>NRPA4</th>
<th>AC-RPA</th>
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always very small, as shown in Figure 2. Because of this all RPA methods usually yield third order correlation energy contributions that largely deviate from the exact total third order energy, as can be seen in the Figures 2(b), 2(d), and 2(f). For example, the SOSEX method contains only the third order exchange diagram (2e) in addition to the direct ring diagram (2a) and strongly overestimates the third order correlation energy on magnitude. The NRPA1 and NRPA2 methods give too strong negative third order contributions, because they contain all ph diagrams which sum up to a large negative value as discussed above. The best description of the correlation energy at the third order level is given by the NRPA3, NRPA4,
and AC-RPA methods since in these methods at least partially the strong positive and negative ph contributions quench each other, as can be observed in Figures 2(b), 2(d), and 2(f). In this way one can argue that the NRPA3, NRPA4, and AC-RPA methods can mimic the missing pp-hh contributions.

Figure 3 shows the sum of the second- and third-order \( E_c^{(2+3)} \) correlation contributions as well as the total correlation energies \( E_c^{(2−∞)} \) for the three molecules \( \text{H}_2\text{O}, \text{CO}, \) and \( \text{HCOOCH}_3 \) for the different RPA methods. It can be seen that in all cases the higher order correlation contributions given by the difference \( E_c^{(4−∞)} = E_c^{(2−∞)} - E_c^{(2+3)} \) have a negative value. With exception of NRPA3 and AC-RPA, this higher order contribution is relatively strong, especially for NRPA2 where \( E_c^{(4−∞)} \) amounts to 20% to 40% of the total correlation energy. The perturbation expansions underlying the methods dRPA, SOSEX, NRPA1, NRPA2, and NRPA4 are thus not well converged at the third-order level. In contrast to this the higher order correlation energies for NRPA3 and AC-RPA are very small on magnitude. In case of NRPA3 Figures 3(a)–3(c) show that the total correlation energies of this method are very close to the MP3 correlation energies marked by the horizontal dashed lines.

Because of the generally poor description of the correlation energy of the various RPA methods at third order of perturbation theory, here the following simple correction scheme is proposed:

\[
E_c^{\text{total}}(M[3]) = E_c^{\text{total}}(M) - E_c^{(3)}(M) + E_c^{(3)}(\text{exact}),
\]

where \( M \) stands for SOSEX, NRPA1-4, and AC-RPA (excluding dRPA which is not even exact in second order). The third order correlation contribution \( E_c^{(3)}(M) \) for each method is given by the respective sum of individual terms of Figure 1 with the corresponding prefactors from Table I. The exact third order correlation contribution \( E_c^{(3)}(\text{exact}) \) corresponds to the sum of of all diagrams (2a)–(2l) in Figure 1 and is, de facto, identical to the third-order Møller-Plesset correlation contribution since a Hartree-Fock orbital basis is used in this work. In Sec. IV the performance for total correlation energies, reaction energies, and intermolecular interaction energies of the standard RPA methods as well as the third-order corrected methods will be investigated.

IV. RESULTS

A. Total correlation energies

Total energies were calculated for a range of small organic molecules displayed in Figure 4 using the aug-cc-pVTZ basis set of Dunning. The geometries for the molecules were optimised at the MP2 level using the aug-cc-pVTZ basis set and are taken from Ref. 107. In addition to the RPA calculations at the various levels described in Sec. II, correlation energies for the standard methods MP2 and MP3 (second- and third-order Møller-Plesset perturbation theory), CCSD, and CCSD(T) have been made. The latter method will serve as a reference in the following. Core electrons were correlated in the calculations. All calculations were done using the developers version of the Molpro quantum chemistry program.

Figure 4 shows the correlation energy differences of the different correlation methods to CCSD(T) correlation energies. In the upper panel in Figure 4 the energy differences are shown for the standard RPA methods described in Sec. II. For SOSEX, NRPA1, and NRPA2 one can observe relatively
strong deviations to the CCSD(T) energies which can be explained with the findings from Sec. III and the analysis of Figure 3. In case of SOSEX the strong underestimation of the CCSD(T) correlation energies can be explained with the too small contribution of the exchange diagram (2e) from Figure 1 so that the sum of diagrams (2a)+(2e) (3rd order contribution in the SOSEX method) is always a quite large positive value, see Figure 2. Contrary to this, NRPA1 and NRPA2 strongly overestimate the CCSD(T) correlation energy because half the total (NRPA1) respectively the total sum (NRPA2) of the third-order ph diagrams always yield a large negative contribution, see Figure 4. The dRPA, NRPA4, and AC-RPA methods yield correlation energies much closer to the accurate CCSD(T) ones, but still there are significant differences if compared to the standard correlation methods MP2/3 or CCSD shown in the bottom diagram in Figure 4.

The best performance for the standard RPA methods regarding correlation energy differences is obtained with the NRPA3 method which shows similar deviations to the CCSD(T) values as CCSD, see upper diagram of Figure 4.

In the bottom diagram of Figure 4 the correlation energy differences for the third-order corrected RPA methods according to Eq. (14) are shown in addition to MP2, MP3, and CCSD differences. As the scale of the ordinate axis is the same for the top and bottom diagram in Figure 4, it can clearly be seen that the correction approach of Eq. (14) leads to strong improvements for all RPA methods (the dRPA method has been excluded here, see above). If compared to CCSD correlation energies, however, the methods SOSEX[3], NRPA1[3], NRPA4[3], and especially NRPA2[3] still
overestimate the correlation energies to a large extent. In contrast to this for NRPA3[3] and AC-RPA[3] the correlation energies are extremely close to the CCSD(T) reference values, see bottom panel in Figure 4. Indeed, both for NRPA3[3] and AC-RPA[3] the absolute correlation energy differences to CCSD(T) do not exceed 10 millihartree and in all cases, with exception of the H2 molecule where NRPA3[3] overestimates the CCSD correlation energy by 0.6 millihartree, the total energies of NRPA3[3] and AC-RPA[3] lie slightly above the CCSD(T) energies. It can also be observed in Figure 4 that the NRPA3[3] and AC-RPA[3] energies are constantly closer to the CCSD(T) reference values than the corresponding MP2, MP3, and CCSD energies. It can therefore be argued that the higher than third order correlation energy contributions contained in the NRPA3[3] and AC-RPA[3] energies can effectively approximate the correlation energy differences between the CCSD(T) and MP3 method. In Subsections IV B and IV C it will be investigated whether the strong improvements of total energies using the correction approach of Eq. (14) also leads to improvements for energy differences, namely, reaction energies and intermolecular interaction energies that are usually two or more orders of magnitude smaller than total energies.

B. Reaction energies

The reaction energies of the 16 chemical reactions displayed in Table II were calculated using the various RPA methods with and without the third-order correction from Eq. (14), MP2, MP3, and CCSD without and with perturbative triples. The geometries and basis sets are the same as given in Sec. IV A. The total reaction energies for each chemical reaction can be found in the supporting information.109

Figure 5 shows the root-mean squared errors (rms), the mean absolute errors (mae), and the relative percentual deviations (|Δ|/E) from the CCSD(T) reference reaction energies for each method for the 16 chemical reactions of Table II. Note that the methods NRPA1, NRPA2, and NRPA4 are excluded due to their very poor performance for the chemical reactions, see Table II in the supporting information.109 The red bars in Figure 5 display the respective errors of Hartree-Fock theory and the standard correlation methods MP2, MP3, and CCSD. It can be observed that MP2 and MP3 theory give strong corrections to Hartree-Fock, however there is little improvement from MP2 to MP3. A further clear improvement of MP3 is
obtained with CCSD which reduces the rms error of MP3 from 2.2 kcal/mol to 1.1 kcal/mol on average.

The standard RPA methods shown in Figure 5 (blue bars) all to some extent improve Hartree-Fock theory, but with exception of NRPA3 their absolute or relative errors to the CCSD(T) reference values are not smaller than with MP2 or MP3. The NRPA3 approach gives a clearly smaller rms error for the chemical reactions than MP2 and MP3 theory, but its performance is worse than CCSD.

The errors for the third-order corrected RPA methods are displayed by the green bars in Figure 5. While one can see that for the SOSEX method the third-order correction leads to even larger errors in comparison with CCSD(T), in case of NRPA3 and AC-RPA the corresponding corrected methods NRPA3[3] and AC-RPA[3] strongly improve the performance of the underlying uncorrected methods. With NRPA3[3] the rms error to the CCSD(T) reference values is only 1.0 kcal/mol and with AC-RPA[3] it is even only 0.6 kcal/mol for the chemical reactions considered. Thus one can observe not only a clear improvement of the original NRPA3 and AC-RPA methods, but the errors of NRPA3[3] and AC-RPA[3] are also significantly smaller than with CCSD.

FIG. 6. Root-mean squared errors (rms), mean absolute errors (mae), and total relative deviations (∆|/Δ|) from CCSD(T) reference interaction energies for 8/23 different intermolecular complexes/structures, see text.

13. Orbital-dependent correlation functionals
Therefore the exceptionally good description of total correlation energies with NRPA3[3] and AC-RPA[3], see Figure 4, transfers also to the description of reaction energies.

C. Intermolecular interaction energies

Compared to chemical reaction energies intermolecular interaction energies present an even stronger challenge for correlation methods since the absolute energy differences are again one or two orders of magnitude smaller. In order to analyse the performance of electron correlation methods for the description of intermolecular interaction energies we have developed a small database of eight different dimers comprising the rare gas dimers He₂, Ne₂, Ar₂, NeAr, the dimers NeHF, ArHF, (H₂)₂ and the hydrogen-bridged dimers (HF)₂ and (H₂O)₂ in 23 different orientations altogether. The geometries for the different intermolecular complexes can be found in Ref. 110. For the rare-gas dimers and the hydrogen molecule dimer the aug-cc-pVQZ basis set was used106,111,112 while in all other cases the aug-cc-pVTZ basis set was used.106 The core electrons were correlated in all calculations. The individual values for the interaction energies can be found in the Tables IV-VI in the supporting information.109

Here we again only consider the overall performance of the different correlation methods represented by the average statistical errors to CCSD(T) reference interaction energies for the 23 intermolecular complexes. These are shown in the diagrams in Figure 6. Note that due to strong differences in the performance of the respective methods the diagrams in Figure 6 are splitted into two parts: the left-hand side of the diagrams shows the methods with a larger deviation from the CCSD(T) values and the right-hand side comprises the methods that have a smaller deviation from the CCSD(T) interaction energies. The maximal scale of the ordinate axis of the diagrams on the right-hand side is marked by dashed horizontal lines in the respective diagrams on the left-hand side for comparison.

The left-hand parts of the diagrams in Figure 6 comprise the statistical errors for Hartree-Fock (red bar) and NRPA1, NRPA2, and NRPA4 (blue bars) together with their third-order corrected methods (green bars). It can be seen that the errors for the respective corrected approaches are smaller than with the standard RPA methods, however not significantly. The improvements over the Hartree-Fock interaction energies is limited, regarding the rms errors one can even see that the NRPA2 and NRPA2[3] methods yield errors that are about two times larger.

As expected, a clear improvement over the Hartree-Fock interaction energies is obtained by MP2, MP3, and CCSD, see right-hand side of Figure 6. It can be seen that among these standard correlation methods the MP3 method gives the smallest errors to the CCSD(T) reference values with an rms error of only 0.07 kcal/mol. The CCSD method is slightly worse than MP2 for the intermolecular complexes considered. This is partially because the CCSD interaction energies are less accurate for the ArHF complex than MP2, see Table IV in the supporting information.109 The dRPA, SOSEX, and SOSEX[3] method yield interaction energies that are worse than with the standard correlation methods, as can be seen in Figure 6. Similar to the findings for the reaction energies in Sec. IV B the SOSEX[3] approach does not improve the SOSEX interaction energies for the rms and mae errors, but it gives a smaller relative error which is due to the much smaller error for the T-shaped structure III of the hydrogen molecule dimer, see Tables V and VI in the supporting information.109

The best performance among the RPA methods for the intermolecular interaction energies is obtained with the NRPA3, AC-RPA, and corresponding third-order corrected methods. In the top diagram in Figure 6 one can observe that the rms deviations for these methods are similar to those from MP2 theory and they are clearly better than CCSD, but the interaction energies are less accurate than the MP3 interaction energies on average. Contrary to the results for the reaction energies, here the third-order correlation energy correction does not lead to considerable improvements of the uncorrected approaches. Using the rms and mae errors as measure the NRPA3[3] values are even slightly worse than the NRPA3 interaction energies. For the relative errors, which more assess the weakly bound dimers of the intermolecular complexes considered, the third-order correlation energy corrected approaches NRPA3[3] and AC-RPA[3] are clearly better than the uncorrected counterparts and the relative average deviation for AC-RPA[3] is even almost as good as with MP3 (12% and 11%, respectively, see bottom diagram in Figure 6).

V. DISCUSSION AND CONCLUSION

Several random-phase approximation correlation methods were presented and tested for total energies, reaction energies, and intermolecular interactions. It has been shown that the earliest RPA methods, termed in this work NRPA1 (and which is identical to the ring coupled-cluster doubles method) from McLachlan and Ball43, 88 and NRPA2 from Fukuda et al.86, yield very poor total energies and energy differences, though, among the other “normal” RPA methods presented they are the most complete from the perturbation theory point of view since they contain half of (NRPA1) respectively all (NRPA2) particle-hole (ph) contributions in third order of perturbation theory. The numerical analysis from Sec. III shows, however, that the missing third-order particle-particle−hole-hole (pp-hh) contributions to the correlation energy are large and their sum has an opposite sign compared to the sum of all third-order ph terms. As a consequence the third-order correlation energies of the NRPA1 and NRPA2 methods are largely in error in comparison with the exact third-order correlation energy. This might explain why RPA methods have rarely been used to describe molecular ground-state correlation energies since their introduction in quantum chemistry in the mid sixties. The NRPA4 method from Szabo and Ostlund,46,99 which describes long-range electron correlation energies on the coupled Hartree-Fock level, indeed has been shown to yield intermolecular interactions that are better than with NRPA1 and NRPA2, but its accuracy is still much worse in comparison with standard correlation methods like MP2 or CCSD.

The best performance among the standard RPA approaches considered for reaction energies and intermolecular
interactions is found for the NRPA3 and AC-RPA methods. It has been shown in Sec. III that for these methods a partial cancellation of third-order correlation energy contributions occurs so that these methods contain a smaller error in third order than the corresponding NRPA1 and NRPA2 methods. One can also argue that in contrast to NRPA1,2 and 4 the NRPA3 and AC-RPA methods do not require triplet amplitudes. The triplet amplitudes are obtained from the solution of RPA equations for the triplet excited states and these can be very poorly described on the normal RPA or time-dependent Hartree-Fock level, see Sec. II. Indeed, the NRPA3 and AC-RPA methods yield similar statistical errors to CCSD(T) reference values for the set of chemical reactions and intermolecular interactions as the standard correlation methods MP2, MP3, or CCSD.

While all RPA methods (excluding direct RPA) considered in this work are exact to second order but not in third order of perturbation theory, a correction scheme is proposed (Eq. (14)) that enforces correctness also in third order for the several RPA methods. It has been shown that this almost always leads to improvements of the corresponding uncorrected RPA methods. For NRPA3 and AC-RPA the deduced NRPA[3] and AC-RPA[3] methods yield total correlation energies which are extremely close to accurate CCSD(T) values for a range of 21 small organic molecules. It has been shown that this high accuracy also transfers to a set of 16 chemical reactions built from this set of molecules. The statistical errors for NRPA3[3] and AC-RPA[3] are all smaller than with CCSD both for the set of chemical reactions and also for the intermolecular interaction energies of a set of 23 small dimer systems. Overall the third-order corrected AC-RPA[3] method yields the highest accuracy of the correlation methods considered in this work if compared with CCSD(T) reference values. This result is important from the point of view that formally all methods (excluding MP2, SOSEX and dRPA; $\mathcal{N}^2$) have a computational cost that grows as $N^6$ with the molecular size measured by $N$. In praxis the NRPA3[3] and AC-RPA[3] methods should be even more efficient than CCSD since the expensive integral transformations required for the four-external integrals occurring in the third-order pph correlation energy contributions (diagrams (2i) and (2f) in Figure 1) can be done on the fly since these integrals are only required once for the third-order correction.

In summary this work presents a simple yet accurate scheme to improve common RPA methods that is based on perturbation theory. For some RPA methods, namely, NRPA3 and AC-RPA, the correction approach significantly improves the performance for the chemical reaction energies and intermolecular interactions that exceeds the accuracy of MP2 and CCSD. Therefore, while certainly the new methods should be further tested for other molecular properties, these RPA methods might become more attractive for describing electron ground-state correlation in chemical applications in the future.

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ARTICLE

Random-phase approximation correlation methods for molecules and solids

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Random-phase approximation (RPA) correlation methods based on Kohn-Sham density-functional theory and Hartree-Fock are derived using the adiabatic-connection fluctuation dissipation theorem. It is shown that the correlation energy within the adiabatic-connection fluctuation dissipation theorem is exact in a Kohn-Sham framework while for Hartree-Fock reference states this is not the case. This shows that Kohn-Sham reference states are probably better suited to describe electron correlation for use in RPA methods than Hartree-Fock reference states. Both, Kohn-Sham and Hartree-Fock RPA methods are related to each other both by comparing the underlying correlation functionals and numerically through the comparison of total energies and reaction energies for a set of small organic molecules.

Keywords: random-phase approximation, density functional theory, time-dependent density-functional theory, correlation energy, RPA

1. Introduction

In the early 1950’s Bohm and Pines published a series of seminal papers that studied the collective properties of the electron gas [1–3]. They described the density fluctuations within the electron gas by separating a collective long-range (plasma) oscillation and a short-range thermal or random motion of the individual electrons. In their quantum mechanical treatment [3], the many-electron Hamiltonian was expressed through a Fourier transformation by a series of momentum transfers between the electrons and it was found that terms with a random phase, corresponding to different momentum transfers, have a zero mean value and can be neglected if the electrons interact rather weakly via screened Coulomb forces. Thus, within this random-phase approximation (RPA), the electrons are assumed to respond only to the total electric potential, which is the sum of an external potential and a screening potential produced by the electron clouds surrounding the electrons, as has been shown later on by Nozieres and Pines [4]. A relation between the RPA and the perturbed self-consistent field theory describing the interaction of a many-electron system with an electromagnetic field was then established by Ehrenreich and Cohen [5].

Using the plasmon model that describes the many-body system in terms of collective excitations, Sawada et al. derived an expression for the (exchange-)correlation energy that arises from the plasma oscillations which is given by the zero-point
energy of the oscillations and the value this energy approaches as the coupling between the oscillators is switched off [6]:

$$E_{xc} = \frac{1}{2} \sum \left[ \omega_i - \omega_0^i \right]$$  \hspace{1cm} (1)

While this result differed from the corresponding expression of Bohm and Pines, since in their work the zero point energy alone appears explicitly [3], Sawada et al. showed that both approaches are identical in the high density limit. Thus the correlation energy within the random-phase approximation can also be connected with the zero-point energy of a set of harmonic oscillators which have the same oscillation frequencies as the electrons. This model is also closely related to a Drude model firstly introduced by London [7, 8] describing the dispersion interaction between atoms. In the Drude model the electron interactions are described by coupled harmonic oscillators such that, in a quantum mechanical picture, a zero-point energy exists describing a lowering of the energy due to correlations. Gell-Mann and Brueckner [9] have shown that the RPA correlation energy of an electron gas in the high density limit is represented by the sum of all Feynman diagrams with a ring structure and therefore the RPA also is sometimes referred to as ring approximation in many-particle physics.

Originally, electron exchange effects were neglected in early works using the RPA. This RPA method neglecting exchange effects shall be designated direct RPA (dRPA) here. However, it has been found later on, e.g., in the work of Brener and Fry, [10, 11] that an extension of the RPA dielectric function [12] using exchange interactions leads to improvements for the description of the properties of the electron gas. McLachlan and Ball derived an expression for the correlation energy of the electron gas within the framework of time-dependent Hartree-Fock (TDHF) theory [13, 14] that, however, differed from the original expression from Sawada et al. [6] by a factor of one half. While the TDHF approach itself has been used extensively for the description of excited states and dynamic response properties [15–20], the TDHF RPA variant from McLachlan and Ball has rarely been used for describing correlated molecular ground states in contrast to the original RPA method excluding exchange interactions. On the one hand, the reason for this may stem from the fact that the TDHF method often is affected by triplet instabilities due to an incompatibility of the wave function ansatz and the excitation operators [14, 21–25]. On the other hand, it turned out that alternative correlation methods like many-body perturbation theory or coupled-cluster theory are more accurate for the description of the correlation energy of molecules.

The RPA approach for determining the correlation energy of a many-body system can be derived from a very general theorem, termed adiabatic-connection fluctuation-dissipation theorem (AC-FDT) [26–29] which apparently first was first discovered by Pauli (see remarks in Refs. [4, 26]). The fluctuation-dissipation theorem was originally derived by Callen and Welton [30] and is used to study the properties of non-equilibrium thermodynamic systems. It relates the internal random motions of the particles in a many-body system to the response to small externally applied perturbations since both, the fluctuation forces and the dissipative forces (that is the density-density response) have their origin in the interactions between the particles. The AC-FDT theorem within the framework of the Kohn-Sham (KS) formalism of density-functional theory (DFT) [28, 29] provides an exact expression for the exchange- and correlation-energy, while an approximate expression for the exchange- and correlation-energy is provided on the basis of the Hartree-Fock (HF) method. The AC-FDT requires as input the response function of the
electronic system. The latter has to be approximated. If this response function is determined via TDHF then TDHF RPA methods are obtained. If the response function is determined within time-dependent density-functional theory (TDDFT) then KS based RPA correlation energies result.

While RPA methods based on HF have rarely been used in molecular applications since their invention (see also a recent work by Klopper et al. which suggests that RPA variants including Hartree-Fock exchange seem to be less suitable to describe electron ground-state correlation than direct RPA methods [31]), see above, in recent years Kohn-Sham based RPA methods have gained an increase in popularity [32–55]. Apart from presenting efficient computational implementations of direct RPA methods for solids and molecules [39, 40, 45], it was shown that direct RPA methods using KS orbitals yield quite accurate results for atomisation energies and even describe to some extent static correlation effects in molecules [33]. This finding is somewhat surprising in view of the fact that direct RPA methods violate the Pauli exclusion principle since they treat on an unequal footing so called exclusion-principle violating diagrams, i.e., diagrams of equal magnitude and opposite sign that cancel each other in a complete perturbation series expansion. Because of this it has been argued [56] that direct RPA methods may fail especially for small systems and small basis sets while they should produce better results for extended systems, e.g., the electron gas. Indeed the direct RPA exhibits the shortcoming of yielding a nonzero correlation energy in one-electron systems while it has been demonstrated recently that direct RPA calculations of a set of 24 solids yield excellent lattice constants and good relative energies [46, 57].

In spite of recent developments that make RPA methods more efficient for molecular systems, they are still computationally more demanding than standard Kohn-Sham DFT methods. This stems from the fact that within the RPA one has to accurately model the interelectronic cusp, a problem that is common in all orbital based correlation methods. Usually this requires large basis sets with high angular momentum functions. A potential remedy of this problem are range-separated methods [42, 43, 49, 50, 58–63] in which the short-range electron correlation is treated via conventional DFT methods and the long-range correlation via orbital based methods. While such methods originally treated the long-range part or the correlation with configuration-interaction [58] or second-order Møller-Plesset [59] methods, it was found in a number of recent studies that range-separated methods including long-range RPA (including or excluding exchange) perform well for a number of molecular properties [42, 43, 49, 50, 62, 63].

The TDDFT methods used in KS based RPA approaches to calculate the response function require approximations for the exchange-correlation potential and kernel (more precisely, for the exchange potential and kernel, while KS methods that include electron correlation effects in the potential and kernel go beyond the random-phase approximation, see, e.g., Ref. [64]). The exchange-correlation kernel is the frequency-dependent functional derivative of the KS exchange-correlation potential with respect to the electron density. The quality of the approximations for the exchange-correlation potential and kernel determines the accuracy of the KS based RPA approaches. Initially conventional exchange-correlation density-functional within the local density or generalized gradient approximation were employed in RPA methods [64] and the frequency-dependence of the kernel is neglected, an approximation called adiabatic approximation. Recently methods were introduced [52, 53, 55, 65] that neglect the correlation contribution to the potential and kernel but use the exact exchange potential and the exact frequency-dependent exchange kernel [66–68]. Such methods were named exact exchange (EXX) RPA methods. Hellgren et al. [65] have used this approach to study the correlation ener-
gies for some atoms using a cubic spline representation for the radial basis sets and found a very good agreement with accurate configuration interaction results. In Ref. [52] Hellgren et al. also investigate a self-consistent exact-exchange RPA method in which the EXX potential is accompanied by a correlation potential derived from an (approximate) functional derivative of the RPA correlation functional. While this led to only small changes for atomic correlation energies compared to the non-iterative approach, clear improvements were obtained for the exchange-correlation potentials and thus single-particle spectrum in the KS calculations.

In Ref. [53] we presented the first exact Kohn-Sham exchange RPA method that could be generally applied to molecular systems using an exchange kernel which was derived from a reformulation of the TDDFT response equations omitting the numerically problematic inverses of the noninteracting response functions [69–71]. This new method, termed as EXX-RPA (note that the acronym RPA(EXX) was used in Ref. [53]), has been shown to yield accurate correlation energies and chemical reaction energies if compared to coupled-cluster singles doubles with perturbative triples reference results. In Ref. [55] we have furthermore shown that this EXX-RPA correlation functional also correctly describes the bond dissociation of the hydrogen molecule in the asymptotic limit in contrast to the corresponding HF based adiabatic-connection RPA method. Therefore RPA methods based on the exact KS exchange kernel offer new correlation methods that surpass the accuracy of common density functionals.

While the RPA method including electron exchange effects was originally only defined using Hartree-Fock reference states, in this work it will be shown that the corresponding RPA method on the basis of exact KS exchange (EXX), the EXX-RPA method, directly relates to the adiabatic-connection fluctuation dissipation theorem of the KS formalism. The ansatz to determine the KS correlation energy via the adiabatic-connection fluctuation-dissipation theorem, which leads to methods commonly denoted KS based RPA methods, is an exact one, approximations then are made if the exchange-correlation potential and kernel required within this ansatz are chosen. In the EXX-RPA case the approximation of neglecting correlation in potential and kernel is made as only approximation. In HF based RPA methods, on the other hand, the ansatz itself is an approximation, see section 3.1. Moreover, HF based RPA approaches that invoke a coupling constant integration lack a straightforward formal justification for performing this integration because an adiabatic connection between the reference wave function, the HF determinant, and the exact wave function, can not be straightforwardly constructed in a simple way in this case. A further general differences between KS and HF based RPA methods, that shall be elucidated within this work, is the fact that within KS based RPA methods due to their root in the adiabatic-connection fluctuation-dissipation theorem only singulet-singulet excitations need to be considered whereas RPA methods on the basis of HF often require to also consider singulet-triplet excitations.

This work is organized as follows. In section 2 KS RPA methods, i.e., methods that calculate the KS correlation energy via the adiabatic-connection fluctuation-dissipation theorem will be introduced. In subsection 2.1 of section 2 we consider the integration of response functions along imaginary frequencies leading to the basic fluctuation-dissipation theorem. In subsection 2.2 the adiabatic connection and the coupling strength integration of the KS formalism are presented and in subsection 2.3 the coupling strength integration and the fluctuation-dissipation theorem are combined to the adiabatic-connection fluctuation-dissipation theorem. Finally in the last subsection of section 2 the EXX-RPA method is introduced. In section 3 we will then review ‘standard’ RPA methods that include exchange interactions and that are based on the HF reference determinant. In the first subsection of
section 3 the general relation between response functions and correlation energies is discussed and in this way the formal basis of HF based RPA methods is analysed. In the second subsection of section 3 various variants of HF based RPA methods are introduced and related to perturbation theory. In section 4 relations between HF based RPA methods and the EXX-RPA method are discussed and approaches combining elements from both types of methods are considered. An analysis of results from the various RPA methods for total energies and chemical reaction energies is given in sections 5 and 6, respectively. Section 7 summarises the results.

2. RPA correlation energy in density-functional theory

2.1. Integration of response functions along imaginary frequencies

The causal response function $\chi$ that yields the response of the electron density of an electronic system in its ground state with wave function $\Psi_0$ on a frequency-dependent perturbation is given by

$$\chi(r, r', \nu) = \sum_{n \neq 0} \left[ \frac{\langle \Psi_0 | \hat{\rho}(r) | \Psi_n \rangle \langle \Psi_n | \hat{\rho}(r') | \Psi_0 \rangle}{E_0 - E_n + \nu} \right. + \left. \frac{\langle \Psi_n | \hat{\rho}(r) | \Psi_0 \rangle \langle \Psi_0 | \hat{\rho}(r') | \Psi_n \rangle}{E_0 - E_n - \nu} \right]. \tag{2}$$

The variable $\nu = \omega + i\eta$ shall combine the real-valued frequency $\omega$ of the perturbation and the imaginary convergence factor $i\eta$. In practical applications the limit $\eta \rightarrow 0$ of a vanishing convergence factor is considered. The summation in Eq. (2) runs over all excited states $\Psi_n$. The density operator $\hat{\rho}(r)$ is given by

$$\hat{\rho}(r) = \sum_{i=1}^{N} \delta(r_i - r) \tag{3}$$

with $N$ denoting the number of electrons and $\delta$ designating the delta function. For real-valued Hamiltonian operators the eigenfunctions $\Psi_n$ can be chosen real-valued. In this case Eq. (2) for the response function turns into

$$\chi(r, r', \nu) = -2 \sum_{n \neq 0} \frac{E_n - E_0}{(E_n - E_0)^2 - \nu^2} \frac{\langle \Psi_0 | \hat{\rho}(r) | \Psi_n \rangle \langle \Psi_n | \hat{\rho}(r') | \Psi_0 \rangle}{E_0 - E_n - \nu} \tag{4}.$$

Next we consider an integration of the response function with respect to the variable $\nu$ along the imaginary axis by integrating along an integration variable $\omega$ and setting $\nu = i\omega$. With the integral

$$\int_0^\infty d\omega \frac{\omega}{\omega^2 + a^2} = \frac{\pi}{2a}$$

for $a > 0$, implying

$$\int_0^\infty d\omega \frac{\omega}{\omega^2 + a^2} = \frac{\pi}{2a} \tag{5}.$$
Eq. (6), by $ds_1 ds_2 ... ds_N$ the integration over spin variables shall be denoted, $\rho_2(r, r')$ designates the pair density, the diagonal of the second order spinless density matrix defined according to

$$
\rho_2(r, r') = \frac{1}{2} \int dr_1 dr_2 ... dr_N ds_1 ds_2 ... ds_N \Psi_0(r_1 r_2 ... r_N)
$$

$$
\times \left[ \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r_i - r) \delta(r_j - r') \right] \Psi_0(r_1 r_2 ... r_N). \quad (7)
$$

In the step from the second to the third equality of Eq. (6) it is exploited that $\sum_n |\Psi_n\rangle\langle\Psi_n|$ represents the identity operator.

Next we multiply Eq. (6) by a function $g(r, r')$ which, at this point, shall be arbitrary and later will be set equal to $1/|r - r'|$. Furthermore we integrate over
the variables \( r \) and \( r' \)

\[
    -\frac{1}{2\pi} \int_0^\infty d\omega \int dr \, dr' \, g(r, r') \, \chi(r, r', i\omega) = \int dr \, dr' \, g(r, r') \left[ \rho_2(r, r') - \frac{1}{2} \rho(r) \rho(r') \right]
    + \int dr \, dr' \frac{1}{2} \int dr_1 \, dr_2 \ldots dr_N \, ds_1 \, ds_2 \ldots ds_N \, \Psi_0(r_1 \ldots r_N)
    \times g(r, r') \left[ \sum_{i=1}^N \delta(r_i - r) \delta(r_i - r') \right] \Psi_0(r_1 \ldots r_N)
    = \int dr \, dr' \, g(r, r') \left[ \rho_2(r, r') - \frac{1}{2} \rho(r) \rho(r') \right]
    + \int dr \, dr' \frac{1}{2} \int dr_1 \, dr_2 \ldots dr_N \, ds_1 \, ds_2 \ldots ds_N \, \Psi_0(r_1 \ldots r_N)
    \times g(r, r') \left[ \sum_{i=1}^N \delta(r_i - r) \delta(r_i - r') \right] \Psi_0(r_1 \ldots r_N)
    = \int dr \, dr' \, g(r, r') \left[ \rho_2(r, r') - \frac{1}{2} \rho(r) \rho(r') \right]
    + \frac{1}{2} \int dr \, dr' \, g(r, r') \, \rho(r) \, \delta(r - r') .
\]  

(8)

In the step form the first to the second equality in Eq. (8) we used the relation

\[
    \int dr \, dr' \, dr_i \, g(r, r') \, f(r_i) \, \delta(r_i - r) \, \delta(r_i - r') = \int dr \, dr_i \, g(r, r_i) \, f(r_i) \, \delta(r_i - r)
    = \int dr_i \, g(r_i, r_i) \, f(r_i)
    = \int dr \, g(r, r) \, f(r)
    = \int dr \, dr_i \, g(r, r_i) \, f(r_i) \, \delta(r_i - r)
    = \int dr \, dr' \, dr_i \, g(r, r') \, f(r_i) \, \delta(r_i - r) \, \delta(r' - r)
\]  

(9)

which holds true for arbitrary functions \( f(r_i) \) and thus also for \( f(r_i) = \Psi_0(r_1 \ldots r_i \ldots r_N) \Psi_0(r_1 \ldots r_i \ldots r_N) \).

For \( g(r, r) = 1/|r - r'| \) the first integral on the right hand side of equation (8) yields

\[
    \int dr \, dr' \, \frac{1}{|r - r'|} \left[ \rho_2(r, r') - \frac{1}{2} \rho(r) \rho(r') \right] = V_{ee} - U ,
\]  

(10)
i.e., the sum of the electron-electron interaction energy

\[ V_{ee} = \int \! \! \int \rho_2(r, r') \frac{1}{|r - r'|} = \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle \]  

(11)

with the operator of the electron-electron interaction given by

\[ \hat{V}_{ee} = \sum_{i=1}^{N} \sum_{j=1 \atop j \neq i}^{N} \frac{1}{|r_i - r_j|} \]  

(12)

minus the Coulomb energy

\[ U = \frac{1}{2} \int \! \! \int \rho(r) \rho(r') \frac{1}{|r - r'|} . \]  

(13)

The second integral on the right hand side of equation (8) diverges for \( g(r, r) = 1/|r - r'| \). Later on we will consider differences of expressions of the form given on the right hand side of Eq. (8). In these differences the divergent contributions will cancel each other and therefore will not lead to problems.

### 2.2. Coupling strength integration

An adiabatic connection [28, 72, 73] between the Kohn-Sham model system, a system of hypothetical noninteracting electrons, and the corresponding real electronic system is defined with the help of the Schrödinger equation

\[ [\hat{T} + \alpha \hat{V}_{ee} + \hat{v}(\alpha)] \Psi_0(\alpha) = E_0(\alpha) \Psi_0(\alpha) \]  

(14)

that contains a coupling constant \( \alpha \) with \( 0 \leq \alpha \leq 1 \) scaling the electron-electron interaction operator \( \hat{V}_{ee} \) defined in Eq. (12) and a coupling-constant-dependent potential

\[ \hat{v}(\alpha) = \sum_{i}^{N} v(\alpha, r_i) . \]  

(15)

The operator of the kinetic energy in Eq. (14) is given by

\[ \hat{T} = - \sum_{i}^{N} \frac{1}{2} \nabla_i^2 \]  

(16)

The potential \( v(\alpha, r_i) \) is defined up to an additive constant by the requirement that the ground state wave functions \( \Psi_0(\alpha) \) for all values of the coupling constant \( \alpha \) yield the same electron density \( \rho(r) \), i.e.,

\[ \langle \Psi_0(\alpha) | \hat{\rho}(r) | \Psi_0(\alpha) \rangle = \rho(r) . \]  

(17)

The Hohenberg-Kohn theorem guarantees that up to an additive constant the potential \( v(\alpha, r_i) \) is uniquely defined by this density condition. For vanishing coupling...
constants the potential $v(\alpha, r_i)$ equals the effective KS potential $v_s(r)$, i.e.,

$$v(\alpha = 0, r) = v_s(r)$$ (18)

and for a coupling constant $\alpha = 1$ the potential $v(\alpha, r_i)$ equals the external potential

$$v(\alpha = 1, r) = v_{\text{ext}}(r)$$ (19)

of the considered real electron system, usually the electrostatic potential of the nuclei.

The eigenfunctions $\Psi_n(\alpha)$ of the adiabatic connection Schrödinger equation (14), for a vanishing coupling constant $\alpha = 0$, are the ground and excited KS wave functions $\Phi_n$,

$$\Psi_n(\alpha = 0) = \Phi_n,$$ (20)

and, for coupling constant $\alpha = 1$, equal the eigenstates $\Psi_n$ of the real electron system

$$\Psi_n(\alpha = 1) = \Psi_n.$$ (21)

Note that the Hohenberg-Kohn theorem guarantees only the uniqueness of the coupling-constant-dependent potentials $v(\alpha, r)$ but not their existence. For the fully interacting case, i.e., $\alpha = 1$, the potential $v(\alpha = 1, r) = v_{\text{ext}}(r)$ is given by the considered real electronic system. For other values of the coupling constant $\alpha$ the existence of $v(\alpha, r)$ has to be assumed, an assumption that is called $v$-representability assumption and that underlies the KS formalism and thus most applications of DFT. The KS formalism only requires that with a given external potential $v(\alpha = 1, r) = v_{\text{ext}}(r)$ also the KS potential $v(\alpha = 0, r) = v_s(r)$ exists, for an adiabatic connection as it is defined here potentials $v(\alpha, r)$ for all values $0 \leq \alpha \leq 1$ need to exist.

The ground state wave function $\Phi_0$ of the KS system defines the noninteracting kinetic energy

$$T_s = \langle \Phi_0 | \hat{T} | \Phi_0 \rangle$$ (22)

by its expectation value with the kinetic energy operator and the KS exchange energy

$$E_x = \langle \Phi_0 | \hat{V}_{\text{ex}} | \Phi_0 \rangle - U$$ (23)

by its expectation value with the electron-electron interaction operator minus the Coulomb energy $U$ of Eq. (13). Both the noninteracting kinetic energy as well as the exchange energy only depend on the KS wave function $\Phi_0$ and thus are independent of the coupling constant $\alpha$. That is $T_s$, $E_x$, and $U$ are given by the starting point of the adiabatic connection at $\alpha = 0$. The definition of the KS exchange energy, i.e., the exchange energy in DFT, thus differs from the definition of the exchange energy as it is common in wave function based methods. In the latter case the exchange energy is defined as the electron-electron interaction energy of the HF determinant minus the Coulomb energy $U$. For nondegenerate ground states the KS wave function $\Phi_0$ like the HF wave function is a single Slater determinant. The exchange energy then in both cases is given by the well-known expression for the
exchange energy of a Slater determinant in terms of the orbitals building the Slater determinant. However, the orbitals entering the expression in the one case are KS orbitals and in the other are HF orbitals and therefore the values of the KS and HF exchange energies are different. In practice the differences are small because KS and HF determinants turn out to be surprisingly similar [70, 74–76].

A coupling-constant-dependent correlation energy \( E_c(\alpha) \) shall be defined according to

\[
E_c(\alpha) = \langle \Psi_0(\alpha)|\hat{T}+\alpha \hat{V}_{ee}|\Psi_0(\alpha)\rangle - \langle \Phi_0|\hat{T}+\alpha \hat{V}_{ee}|\Phi_0\rangle. \tag{24}
\]

The correlation energy \( E_c = E_c(\alpha = 1) \) for \( \alpha = 1 \) is the KS or DFT correlation energy which differs in its definition and its value from the correlation energy as it is commonly defined in wave function based methods. Because, by construction, the wave functions \( \Psi_0(\alpha) \) and \( \Phi_0 \) that enter the definition of the correlation energy \( E_c(\alpha) \) yield the same electron density we can turn Eq. (24) into

\[
E_c(\alpha) = \langle \Psi_0(\alpha)|\hat{T}+\alpha \hat{V}_{ee} + \hat{v}(\alpha)|\Psi_0(\alpha)\rangle - \langle \Phi_0|\hat{T}+\alpha \hat{V}_{ee} + \hat{v}(\alpha)|\Phi_0\rangle. \tag{25}
\]

For \( \alpha = 1 \) Eq. (25) yields the KS or DFT correlation energy as the difference of the expectation values of the electronic Hamiltonian operator with the full ground state wave function \( \Psi_0 = \Psi_0(\alpha = 1) \), i.e. the full ground state energy, minus the expectation values of the electronic Hamiltonian operator with the KS wave function \( \Phi_0 = \Psi_0(\alpha = 0) \). The HF based correlation energy, on the other hand, is the difference of the expectation values of the electronic Hamiltonian operator with the full ground state wave function and the HF determinant.

The correlation energy \( E_c(\alpha) \) of Eq. (24) is the sum

\[
E_c(\alpha) = T_c(\alpha) + \alpha V_c(\alpha) \tag{26}
\]

of a kinetic contribution,

\[
T_c(\alpha) = \langle \Psi_0(\alpha)|\hat{T}|\Psi_0(\alpha)\rangle - \langle \Phi_0|\hat{T}|\Phi_0\rangle. \tag{27}
\]

and an electron-electron interaction contribution

\[
V_c(\alpha) = \langle \Psi_0(\alpha)|\hat{V}_{ee}|\Psi_0(\alpha)\rangle - \langle \Phi_0|\hat{V}_{ee}|\Phi_0\rangle. \tag{28}
\]

multiplied by the coupling constant \( \alpha \).

The derivative of the correlation energy \( E_c(\alpha) \) with respect to the coupling constant is given by \( V_c(\alpha) \) because taking the derivative of Eq. (25) yields

\[
\frac{dE_c(\alpha)}{d\alpha} = \langle \Psi_0(\alpha)|\hat{V}_{ee} + \frac{d\hat{v}(\alpha)}{d\alpha}|\Psi_0(\alpha)\rangle - \langle \Phi_0|\hat{V}_{ee} + \frac{d\hat{v}(\alpha)}{d\alpha}|\Phi_0\rangle
\]

\[
= \langle \Psi_0(\alpha)|\hat{V}_{ee}|\Psi_0(\alpha)\rangle + \int d\mathbf{r} \frac{dv(\alpha, \mathbf{r})}{d\alpha} \rho(\mathbf{r})
\]

\[
- \langle \Phi_0|\hat{V}_{ee}|\Phi_0\rangle - \int d\mathbf{r} \frac{dv(\alpha, \mathbf{r})}{d\alpha} \rho(\mathbf{r})
\]

\[
= \langle \Psi_0(\alpha)|\hat{V}_{ee}|\Psi_0(\alpha)\rangle - \langle \Phi_0|\hat{V}_{ee}|\Phi_0\rangle
\]

\[
= V_c(\alpha). \tag{29}
\]
For the first line of Eq. (29) the Hellmann-Feynman theorem was invoked, for the second line it was exploited that $\Psi_0(\alpha)$ as well as $\Phi_0$ yield the electron density $\rho$.

From Eq. (29) follows immediately the coupling strengths integration for the DFT correlation energy $E_c = E_c(\alpha = 1)$,

$$
E_c = E_c(\alpha = 1) = E_c(\alpha = 1) - E_c(\alpha = 0)
$$

$$
= \int_0^1 d\alpha \left( \frac{dE_c(\alpha)}{d\alpha} \right)
$$

$$
= \int_0^1 d\alpha V_c(\alpha),
$$

if we exploit that definition (24) of the correlation energy $E_c(\alpha)$ implies $E_c(\alpha = 0) = 0$.

### 2.3. Adiabatic-connection fluctuation-dissipation theorem

By combining the coupling strength integration, Eq. (30), with the integration of causal response functions along complex frequencies, Eq. (8), we obtain the adiabatic connection fluctuation dissipation theorem for the DFT correlation energy $E_c$ [28, 29, 35, 64, 77]. In Eq. (8) the integration of the response function $\chi(\mathbf{r}, \mathbf{r}', i\omega)$ of the real electron system is considered. A generalization to a coupling-strength-dependent response function $\chi(\alpha, \mathbf{r}, \mathbf{r}', i\omega)$ is straightforward by replacing the wave functions $\Psi_n$ in Eqs. (2) - (11) by the wave functions $\Psi_0(\alpha)$ and by introducing the coupling-strength-dependent pair density $\rho_2(\alpha, \mathbf{r}, \mathbf{r}')$, the diagonal of a coupling-strength-dependent second order spinless density matrix obtained by a generalization of definition (7). The coupling strength integration for $E_c$ then can be expressed as

$$
E_c = \int_0^1 d\alpha V_c(\alpha)
$$

$$
= \int_0^1 d\alpha \left( \langle \Psi_0(\alpha) | \hat{V}_{ee} | \Psi_0(\alpha) \rangle - \langle \Phi_0 | \hat{V}_{ee} | \Phi_0 \rangle \right)
$$

$$
= \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \frac{\rho_2(\alpha, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\rho_2(\alpha = 0, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
$$

$$
= \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \left[ \frac{\rho_2(\alpha, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\rho_2(\alpha = 0, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right].
$$

Only one density $\rho$ that is independent of $\alpha$ occurs in Eq. (31) because the wave functions $\Psi_0(\alpha)$ independently of $\alpha$ yield the same electron density $\rho$. If we now insert twice Eq. (8) with $g(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ and use that the last integral in Eq. (8) is cancelled because it occurs twice with different signs then we obtain the adiabatic-connection fluctuation-dissipation theorem for the DFT correlation energy.
energy $E_c$

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_{0}^{\infty} d\omega \left[ \chi_0(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega) \right]. \quad (32)$$

2.4. RPA correlation energy within Kohn-Sham framework

In order to calculate the Kohn-Sham correlation energy with the adiabatic-connection fluctuation-dissipation theorem the response functions $\chi_0$ and $\chi_0$ are required. The KS response function $\chi_0$ is known in terms of the occupied and unoccupied KS orbitals $\varphi_\alpha$ and $\varphi_\alpha$, respectively, and their eigenvalues $\varepsilon_\alpha$ and $\varepsilon_\alpha$,

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{\alpha, \alpha'}^{\text{occ., unocc.}} \frac{-4\varepsilon_\alpha}{\varepsilon_\alpha^2 + \omega^2} \varphi_\alpha(\mathbf{r}) \varphi_\alpha(\mathbf{r}') \varphi_\alpha(\mathbf{r}) \varphi_\alpha(\mathbf{r}') \quad . \quad (33)$$

In Eq. (33) $\varepsilon_\alpha = \varepsilon_\alpha - \varepsilon_\alpha$ and thus by definition is a positive quantity. Throughout this Section we consider non-sin-polarized systems. By $\varphi_\alpha$ and $\varphi_\alpha$ therefore spatial orbitals are denoted while the spin degree of freedom is taken into account by appropriate prefactors. Throughout this work indices $i$ and $j$ denote occupied, $a$ and $b$ unoccupied, and $p, q, r,$ and $s$ arbitrary orbitals. Summations over the indices run over the occupied, the unoccupied, or all orbitals, respectively.

The integration over the frequency and the spatial variables is straightforward and leads to

$$\frac{-1}{2\pi} \int d\mathbf{r} d\mathbf{r'} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_{0}^{\infty} d\omega \chi_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{ia} \langle ia | ai \rangle = \text{Tr}[C] \quad (34)$$

with $\langle ia | ai \rangle$ denoting a two-electron integral in physicist’s notation and $C$ designating a matrix defined by the matrix elements $C_{ia,jb} = \langle ib | aj \rangle$. The dimension of the matrix $C$ equals the number of occupied times unoccupied KS orbitals, its columns and rows are labeled by the superindices $jb$ and $ia$.

The coupling-strength-dependent response function $\chi_\alpha$ is obtained by time-dependent DFT (TDDFT) in the linear response regime. The basic equation of time-dependent or more precisely frequency-dependent KS response theory is [78–83].

$$\left[ \varepsilon^2 + \varepsilon^{1/2} K_{\text{uxc}}(\alpha, \omega) \varepsilon^{1/2} \right] z_n(\alpha, \omega) = \Omega_n^2(\alpha, \omega) z_n(\alpha, \omega). \quad (35)$$

In Eq. (35) $\varepsilon$ designates a diagonal matrix with elements $\varepsilon_{ia,jb} = \delta_{ia,jb} \varepsilon_{ia} = \delta_{ia,jb} (\varepsilon_\alpha - \varepsilon_\alpha)$. The kernel matrix $K_{\text{uxc}}(\alpha, \omega)$ is defined by its matrix elements $\int d\mathbf{r} d\mathbf{r'} \varphi_\alpha(\mathbf{r}) \varphi_\alpha(\mathbf{r'}) f_{\text{uxc}}(\alpha, \omega, \mathbf{r}, \mathbf{r}') \varphi_\alpha(\mathbf{r'}) \varphi_\alpha(\mathbf{r'}).$ The kernel $f_{\text{uxc}}$ is the frequency- and coupling-strength-dependent functional derivative of the sum of the Hartree and KS exchange-correlation potential.

Eq. (35) is an equation that is nonlinear in the frequency $\omega$. For a given frequency $\omega$ the number of eigenvalues $\Omega_n^2(\alpha, \omega)$ equals the product of occupied times unoccupied orbitals. However, only if a square root $\Omega_n(\alpha, \omega)$ equals the frequency $\omega$ then this $\Omega_n(\alpha, \omega)$ equals an exitation energy. In most TDDFT methods the frequency-dependence of the kernel is neglected, i.e., the adiabatic approximation is employed. In this case the frequency-dependence of the kernel and the eigenvectors $z_n$ vanishes, Eq. (35) becomes linear, and the square roots $\Omega_n$ of the eigenvalues equal the exitation energies. In this work, however, we construct the response
function \( \chi_\alpha \) within an exact-exchange TDDFT (TDEXX) framework, that is we neglect the correlation contribution to the kernel \( f_{\text{aux}} \) but we treat the exchange contribution exactly including its frequency dependence. The exact exchange kernel is given by a quite complicated integral expression \([66–68]\) which is not well suited for numerical implementations. It is, however, possible to derive an equation for the frequency-dependent response of the effective KS potential and not, as usually in TDDFT, of the electron density \([69]\). The corresponding eigenvalue equation for the excitation energies is better suited for an exact treatment of exchange. At first, the eigenvalue equation is again nonlinear in the frequency \( \omega \) but it can be rearranged into the linear generalized eigenvalue equation \([71]\), the TDEXX equation

\[
\begin{align*}
\left( \varepsilon^2 + \alpha \varepsilon^{1/2} [A + B + \Delta \varepsilon^{1/2}] \right) z_n(\alpha) &= \\
\Omega_n^2(\alpha) \left[ 1 - \alpha \varepsilon^{-1/2} [A - B + \Delta \varepsilon^{-1/2}] \right] z_n(\alpha).
\end{align*}
\]

The matrices \( A, B, \Delta \) with a dimension equal to the number of occupied times unoccupied KS orbitals contain the matrix elements \( A_{ia,jb} = 2\langle ij | ab \rangle - \langle ia | jb \rangle, B_{ia,jb} = 2\langle ij | ab \rangle - \langle ij | ba \rangle, \Delta_{ia,jb} = \delta_{ij} \langle \varphi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_b \rangle - \delta_{ab} \langle \varphi_b | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_j \rangle \).

The indices \( ia \) and \( jb \), again, are superindices labeling the rows and columns of the matrices. The operator \( \hat{v}_x^{\text{NL}} \) is a nonlocal exchange operator of the form of the HF exchange operator but is constructed from KS orbitals while \( \hat{v}_x \) is the operator corresponding to the local multiplicative KS exchange potential. Because the exact exchange kernel as well as the Hartree kernel are linear in the coupling strength \( \alpha \), the coupling strength occurs as linear prefactor in the equation. The price for having arranged Eq.\,(36) in a form that does no longer contain terms depending on \( \omega \) is that Eq.\,(36) in contrast to Eq.\,(35) is a generalized eigenvalue equation.

With the eigenvectors \( z_n(\alpha) \) and the square roots \( \Omega_n(\alpha) \) of Eq.\,(36) the response function \( \chi_\alpha \) can be expressed as \([71]\)

\[
\chi_\alpha(\tilde{\omega}, \mathbf{r}, \mathbf{r'}) = \sum_n \frac{1}{\Omega_n(\alpha)} \sum_{ia} \sum_{jb} \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \left[ \varepsilon^{1/2} z_n(\alpha) \frac{-4 \Omega_n(\alpha)}{\Omega_n(\alpha)^2 + \omega^2 z_n(\alpha)^2} \varepsilon^{1/2} z_n(\alpha)^T \right]_{ia,jb} \times \varphi_b(\mathbf{r'}) \varphi_j(\mathbf{r'})
\]

Integration over the frequency and the spatial variables yields

\[
\frac{-1}{2\pi} \int d\mathbf{r} d\mathbf{r'} \frac{1}{|\mathbf{r} - \mathbf{r'}|} \int_0^\infty d\tilde{\omega} \chi_\alpha(\mathbf{r}, \mathbf{r'}, \tilde{\omega}) = \sum_n z_n^T(\alpha) \varepsilon^{1/2} C \varepsilon^{1/2} z_n(\alpha) / \Omega_n(\alpha)
\]

Finally subtracting Eqs.\,(34) and \(38\) and integration over the coupling constant \( \alpha \) yields the EXX-RPA correlation energy

\[
E_c = \int_0^1 d\alpha \ V_c(\alpha)
\]

with

\[
V_c(\alpha) = \left[ \sum_n z_n^T(\alpha) \varepsilon^{1/2} C \varepsilon^{1/2} z_n(\alpha) / \Omega_n(\alpha) \right] - \text{Tr}[C]
\]
A calculation of the EXX-RPA correlation energy in a straightforward manner requires to solve the TDEXX equation (36) for a number of values of the coupling strength $\alpha$, to construct the integrand $V_c(\alpha)$ and to carry out the coupling strength integration (24) numerically. Typically six or seven integration points in a Gaussian-Legendre integration are sufficient to carry out the coupling strength integration with an accuracy of about $10^{-5}$ Hartree.

3. RPA correlation energy based on Hartree-Fock

3.1. Response functions and correlation energies in RPA based on Hartree-Fock

Following Oddershede [84] the total electronic ground-state energy can be written as

$$E_0 = \sum_{pq} \left[ h_{pq} + \frac{1}{4} \sum_r \langle pr \vert \vert qr \rangle + \frac{1}{4} \sum_{rs} \langle pr \vert \vert qs \rangle \langle \Psi_0 \vert a_r^\dagger a_s \vert \Psi_0 \rangle \right] \langle \Psi_0 \vert a_p^\dagger a_q \vert \Psi_0 \rangle$$

$$- \frac{1}{4\pi} \sum_{pqrs} \langle pr \vert \vert qs \rangle \int_{0}^{\infty} d\omega \chi_{pq,rs}(i\omega)$$

(41)

where the summations over $p$, $q$, $r$ and $s$ run over all, i.e., occupied and unoccupied spin orbitals. This means in this Section, in contrast to the previous one, we consider orbitals including their spin degree of freedom and summations run over spin orbitals, i.e., indices $p$, $q$ etc. shall include possible spin indices. By $\langle pr \vert \vert rs \rangle$ an antisymmetrised two-electron integral in physicist's notation is denoted, $a_s$ and $a_q$ designate annihilation, and $a_r^\dagger$ and $a_p^\dagger$ creation operators. The sum $\sum_{rs} \langle \Psi_0 \vert a_r^\dagger a_s \vert \Psi_0 \rangle$ determines the first order density matrix $\rho(\mathbf{r}, \mathbf{r}')$ according to $\rho(\mathbf{r}, \mathbf{r}') = \sum_{rs} \phi_r(\mathbf{r})\phi_s(\mathbf{r}') \langle \Psi_0 \vert a_r^\dagger a_s \vert \Psi_0 \rangle$ (likewise the sum $\sum_{pq} \langle \Psi_0 \vert a_p^\dagger a_q \vert \Psi_0 \rangle$). The response matrix elements $\chi_{pq,rs}(\nu)$ define the response function $\sum_{pqrs} \phi_p(\mathbf{r}_p)\phi_q(\mathbf{r}_q')\chi_{pq,rs}(\nu)\phi_r(\mathbf{r}_r)\phi_s(\mathbf{r}_s')$ that yields the response of the first order density matrix on a perturbation given by a general one-electron operator. That is in contrast to the response function (2) of the previous Section the perturbation can be a nonlocal operator and the response of the first order density matrix not just of the electron density is considered. By $\phi_p$, $\phi_q$, $\phi_r$, and $\phi_s$ spin orbitals are denoted.

The response matrix elements $\chi_{pq,rs}(i\omega)$ are given by

$$\chi_{pq,rs}(i\omega) = \sum_{n \neq 0} \left[ \frac{\langle \Psi_0 \vert a_r^\dagger a_q \vert \Psi_n \rangle \langle \Psi_n \vert a_s^\dagger a_s \vert \Psi_0 \rangle}{E_0 - E_n + i\omega} + \frac{\langle \Psi_n \vert a_r^\dagger a_q \vert \Psi_0 \rangle \langle \Psi_0 \vert a_s^\dagger a_s \vert \Psi_n \rangle}{E_0 - E_n - i\omega} \right]$$

(42)

In order to extract the correlation energy from Eq. (41) one may now add and subtract the contribution $-\frac{1}{4\pi} \sum_{pqrs} \langle pr \vert \vert qs \rangle \int_{0}^{\infty} d\omega \chi_{pq,rs}^0(i\omega)$ from Eq. (41) where $\chi_{pq,rs}^0(i\omega)$ refers to a general single-particle (e.g. Kohn-Sham or Hartree-Fock) response function that is obtained from Eq. (42) by replacing the exact eigenfunctions $\Psi_0$ and $\Phi_n$ by determinantal wave functions $\Phi_0$ and $\Phi_n$. In this case the expectation
values and the summation over \(n\) are readily carried out in Eq. (42) to obtain

\[
\chi_{pq,rs}^0(\iota\omega) = \begin{cases} 
\frac{1}{\iota\omega - \varepsilon_{ia}} & \text{for } p = s = i \text{ and } q = r = a \\
\frac{1}{-\iota\omega - \varepsilon_{ia}} & \text{for } p = s = a \text{ and } q = r = i \\
0 & \text{else},
\end{cases}
\]

(43)
as usual with \(i\) denoting occupied and \(a\) denoting unoccupied orbitals. Note that by \(i\) in front of the frequency \(\omega\) the imaginary unit not the index \(i\) is denoted. By \(\varepsilon_{ia} = \varepsilon_a - \varepsilon_i\) again differences of single-particle eigenvalues are denoted. With this Eq. (41) then transforms into

\[
E_0 = \sum_{pq} \left[ h_{pq} + \frac{1}{4} \sum_r \langle pr||qr \rangle + \frac{1}{4} \sum_{rs} \langle pr||qs \rangle \langle \Psi_0|a_i^\dagger a_s|\Psi_0 \rangle \right] \langle \Psi_0|a_p^\dagger a_q|\Psi_0 \rangle \\
- \frac{1}{4} \sum_{ia} \langle ia||ia \rangle - \frac{1}{4\pi} \sum_{pqrs} \langle pr||qs \rangle \int_0^\infty d\omega \left[ \chi_{pq,rs}(\iota\omega) - \chi_{pq,rs}^0(\iota\omega) \right]
\]

(44)

where it has been used that, using Eq. (43), the frequency integration over \(\chi_{pq,rs}^0(\iota\omega)\) yields \(-2\pi\delta_{ij}\delta_{ab}\) and leads to \(-\frac{1}{4\pi} \sum_{pqrs} \langle pr||qs \rangle \int_0^\infty d\omega \chi_{pq,rs}(\iota\omega) = \frac{1}{4} \sum_{ia} \langle ia||ia \rangle\). with \(i, j\) denoting occupied and \(a, b\) unoccupied orbitals.

If one now makes the approximation that the exact one-particle density matrices are identical to the density matrices of the determinantal wave function, here a KS or HF wave function, i.e. \(\langle \Psi_0|a_p^\dagger a_q|\Psi_0 \rangle \approx \langle \Phi_0|a_p^\dagger a_q|\Phi_0 \rangle = \delta_{pq}\delta_{qi}\), then Eq. (44) simplifies to

\[
E_0 \approx \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \langle ij||ij \rangle - \frac{1}{4\pi} \sum_{pqrs} \langle pr||qs \rangle \int_0^\infty d\omega \left[ \chi_{pq,rs}(\iota\omega) - \chi_{pq,rs}^0(\iota\omega) \right]
\]

(45)

For the case that \(\Phi_0\) is the Hartree-Fock determinant the first two-terms on the right hand-side of Eq. (45) correspond just to the Hartree-Fock ground-state energy and the remainder

\[
E_c \approx -\frac{1}{4\pi} \sum_{pqrs} \langle pr||qs \rangle \int_0^\infty d\omega \left[ \chi_{pq,rs}(\iota\omega) - \chi_{pq,rs}^{HF}(\iota\omega) \right].
\]

(46)

with \(\chi_{pq,rs}^{HF}(\iota\omega)\) denoting the Hartree-Fock response function, i.e., Eq. (43) in terms of Hartree-Fock orbital energies, is an approximation to the correlation energy.

It is instructive to evaluate the frequency integration in Eq. (46). With Eq. (42) and the integral \(\int_0^\infty d\omega \, \omega/(a^2 + \omega^2) = \pi/2\) we obtain for the frequency integral
over $\chi_{pq,rs}(i\omega)$:

\[
-\frac{1}{4\pi} \sum_{pqr}s \langle pr||qs \rangle \int_{-\infty}^{\infty} d\omega \chi_{pq,rs}(i\omega) \\
= -\frac{1}{4\pi} \sum_{pqr}s \langle pr||qs \rangle \int_{-\infty}^{\infty} d\omega \sum_{n \neq 0} \left[ \frac{\langle \Psi_n | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_n \rangle \langle \Psi_n | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_n \rangle}{E_n - E_n + i\omega} \right. \\
\left. + \frac{\langle \Psi_n | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_0 \rangle \langle \Psi_0 | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_n \rangle}{E_0 - E_n + i\omega} \right] \\
= -\frac{1}{4\pi} \sum_{pqr}s \langle pr||qs \rangle \int_{-\infty}^{\infty} d\omega \sum_{n \neq 0} \left[ \frac{\langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_n \rangle \langle \Psi_n | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle}{E_n - E_0} \right. \\
\left. + \frac{\langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_0 \rangle \langle \Psi_0 | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle}{(E_n - E_0)^2 + \omega^2} \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_n \rangle \langle \Psi_n | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle \right] \\
= \frac{1}{4} \sum_{pqrs} \langle pr||qs \rangle \sum_{n \neq 0} \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle \\
= \frac{1}{4} \sum_{pqrs} \langle pr||qs \rangle \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_0 \rangle \langle \Psi_0 | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle \\
\quad - \frac{1}{4} \sum_{pqrs} \langle pr||qs \rangle \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_0 \rangle \langle \Psi_0 | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle \\
= \frac{1}{4} \sum_{pqrs} \langle rp||qs \rangle \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_r \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle + \frac{1}{4} \sum_{pqrs} \langle pr||qs \rangle \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_s | \Psi_0 \rangle \\
\quad - \frac{1}{4} \sum_{pqrs} \langle pr||qs \rangle \langle \Psi_0 | \hat{a}_{p}^\dagger \hat{a}_q | \Psi_0 \rangle \langle \Psi_0 | \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle \\
= V_{ee} - \frac{1}{4} \int d\mathbf{r} d\mathbf{r}' \left[ \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\rho(\mathbf{r}', \mathbf{r}) \rho(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \\
\quad + \frac{1}{4} \int d\mathbf{r} d\mathbf{r}' \frac{\delta(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{4} \int d\mathbf{r} d\mathbf{r}' \sum_q \frac{\phi_q^\dagger(\mathbf{r}') \phi_q(\mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}.
\]

(47)

In Eq. (47) it was used that the summation indices can be renamed $(r \rightarrow p, p \rightarrow r, s \rightarrow q, q \rightarrow s)$ and $(rp||sq) = \langle pr||qs \rangle$, that $\hat{a}_{q}^\dagger \hat{a}_{p} = \delta_{qr} - \hat{a}_{q}^\dagger \hat{a}_{q}$, that $\langle rp||qs \rangle = -\langle pr||qs \rangle$, that $\frac{1}{4} \sum_{pqrs} \langle rp||qs \rangle \langle \Psi_0 | \hat{a}_{r}^\dagger \hat{a}_q \hat{a}_{s}^\dagger \hat{a}_s | \Psi_0 \rangle$ equals the electron-electron interaction energy $V_{ee}$ of an electronic system, that $\sum_{rs} \phi_{q}^\dagger(\mathbf{r}) \phi_{q}(\mathbf{r}') \langle \Psi_0 | \hat{a}_{r}^\dagger \hat{a}_s | \Psi_0 \rangle$ equals the first order density matrix $\rho(\mathbf{r}, \mathbf{r}')$, and that $\sum_q \phi_{q}(\mathbf{r}) \phi_{q}^\dagger(\mathbf{r}')$ is a representation of the delta function $\delta(\mathbf{r} - \mathbf{r}')$. The last two terms in Eq. (47) are singular and thus, strictly speaking, illdefined.

The frequency integration of the terms in Eq. (46) that contain HF response
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matrix elements $\chi_{pq,rs}^{HF}(i\omega)$ together with Eq. (43) yields

$$-\frac{1}{4\pi} \sum_{pqrs} \langle pr||qs \rangle \int_0^\infty d\omega \chi_{pq,rs}^{HF}(i\omega) = \frac{1}{4} \sum_{ia} \langle ia||ai \rangle$$

$$= \frac{1}{4} \sum_{ij} \langle ji||ji \rangle + \frac{1}{4} \sum_{iq} \langle iq||qi \rangle$$

$$= V_{ee}^{HF} - \frac{1}{4} \int dr dr' \left[ \frac{\rho^{HF}(r)\rho^{HF}(r')}{|r-r'|} - \frac{\rho^{HF}(r',r)\rho^{HF}(r,r')}{|r-r'|} \right]$$

$$+ \frac{1}{4} \int dr dr' \frac{\delta(r-r')\rho^{HF}(r)}{|r-r'|} - \frac{1}{4} \int dr dr' \sum_q \phi_q^\dagger(r')\phi_q(r')\rho^{HF}(r).$$

Here $V_{ee}^{HF}$ denotes the electron-electron interaction energy of the HF determinant and $\rho^{HF}(r,r')$ and $\rho^{HF}(r)$ are the HF first order density matrix and the HF electron density, respectively. Subtraction of Eq. (48) from Eq. (47) yields:

$$E_c \approx -\frac{1}{4\pi} \sum_{pqrs} \langle pr||qs \rangle \int_0^\infty d\omega \left[ \chi_{pq,rs}^{HF}(i\omega) - \chi_{pq,rs}^{HF}(i\omega) \right]$$

$$= V_{ee}^{HF} - V_{ee}^{HF} - \frac{1}{4} \int dr dr' \left[ \frac{\rho(r)\rho(r')}{|r-r'|} - \frac{\rho^{HF}(r)\rho^{HF}(r')}{|r-r'|} \right]$$

$$+ \frac{1}{4} \int dr dr' \frac{\rho(r',r)\rho(r,r')}{|r-r'|} - \frac{\rho^{HF}(r',r)\rho^{HF}(r,r')}{|r-r'|}$$

$$+ \frac{1}{4} \int dr dr' \frac{\delta(r-r')\rho(r)}{|r-r'|} - \frac{1}{4} \int dr dr' \frac{\delta(r-r')\rho^{HF}(r)}{|r-r'|}$$

$$- \frac{1}{4} \int dr dr' \sum_q \phi_q^\dagger(r')\phi_q(r')\rho^{HF}(r) + \frac{1}{4} \int dr dr' \sum_q \phi_q^\dagger(r')\phi_q(r')\rho^{HF}(r).$$

The right hand side of Eq. (49) contains the electron-electron interaction contribution to the correlation energy, i.e., the difference $V_{ee}^{HF} - V_{ee}^{HF}$, plus various difference terms containing the exact and the HF first order density matrix and electron density. In order to associate the right hand side of Eq. (49) with the correlation energy as it is done within the RPA, Eq. (46), the approximation that the HF first order density matrix equals the exact first order density matrix has to be made as has been used above. With this approximation, which implies the equality of the HF and the exact electron density, all the difference terms on the right hand side of Eq. (49) cancel. Moreover, under this approximation there would be no kinetic contribution to the correlation energy and no contribution from the electron nuclei interaction and therefore there would remain only the electron-electron interaction contribution $V_{ee}^{HF} - V_{ee}^{HF}$ to the correlation energy. This indicates that the approximation that the HF and the exact first order density matrices are equal is a quite severe one that could introduce errors of a magnitude comparable to the electron-nuclei interaction contribution and the kinetic contribution to the correlation energy. Here a marked difference to the RPA correlation energy within the KS formalism given by the adiabatic-connection dissipation-fluctuation theorem (32)
shows up. The adiabatic-connection dissipation-fluctuation theorem (32) is exact, it yields the exact correlation energy as defined in the KS formalism. Approximations are introduced with the approximate density-functional, the exchange-correlation potential and kernel when applying the adiabatic-connection dissipation-fluctuation theorem. In HF based RPA, with Eq. (46), right from the start approximations are introduced. It should be noted, however, that the form of the correlation energy of Eq. (49) might be even more inaccurate if KS orbitals and the corresponding KS response function are used instead of HF orbitals and the HF response function because the KS one-particle density matrix is neither identical to the exact density matrix nor can it be expected to be a good approximation to it, even if the exact exchange-correlation potential would have been employed, see Ref. [85], p.47 ff.

If in Eq. (49) the antisymmetrized two-electron integral \( \langle pr|qs \rangle \) is replaced by the simple nonantisymmetrized integral \( \langle pr|qs \rangle \) and the prefactor \( \frac{1}{4\pi} \) is replaced by \( \frac{1}{2\pi} \) then carrying out the frequency integrations in the same way as before leads to

\[
E_c \approx -\frac{1}{2\pi} \sum_{pqrs} \langle pr|qs \rangle \int_0^\infty d\omega \left[ \chi_{pq,rs}(i\omega) - \chi_{HF,rs}(i\omega) \right]
\]

\[
= V_{ee} - V_{ee}^{HF} - \frac{1}{2} \int drdr' \left[ \frac{\rho(r)\rho(r')}{|r-r'|} - \frac{\rho_{HF}(r)\rho_{HF}(r')}{|r-r'|} \right]
\]

\[
+ \frac{1}{2} \int drdr' \frac{\delta(r-r')\rho(r)}{|r-r'|} - \frac{1}{2} \int drdr' \frac{\delta(r-r')\rho_{HF}(r)}{|r-r'|}.
\]

(50)

With the assumption that the HF and the exact electron densities are equal the difference terms in Eq. (50) that contain the exact and the HF density vanish and the electron-electron interaction contribution \( V_{ee} - V_{ee}^{HF} \) to the correlation energy remains. The assumption of an equality of the HF and the exact electron densities is weaker than the assumption of the equality of the corresponding first order density matrices. That is, Eq. (50) compared to Eq. (49) requires a weaker approximation to yield a meaningful quantity, \( V_{ee} - V_{ee}^{HF} \) namely. If the stronger assumption of an equality of the HF and the exact first order density matrices is made then, as before, \( V_{ee} - V_{ee}^{HF} \) can be associated with the complete correlation energy. Eq. (50) therefore is an alternative to Eq. (49).

Alternative to the use of Kohn-Sham orbitals or Hartree-Fock orbitals Eq. (41) could also be written in terms of natural orbitals or Brueckner orbitals. For natural orbitals the transformation from Eq. (44) to Eq. (45) holds true exactly, provided the summations run over all orbitals with nonzero occupation numbers and Eq. (43) is generalized accordingly. Brueckner orbitals, on the other hand, differ from natural orbitals in third order of perturbation theory [86]. Since it has been found that the Brueckner reference determinant of a Brueckner coupled-cluster doubles (BCCD) wave function better approximates the electron density of the unrelaxed full BCCD wave function [87, 88] it can be expected that the correlation energy expressions in Eqns. (46) and (50) are better approximated in terms of Brueckner instead of Hartree-Fock orbitals.

### 3.2. Overview of RPA methods including exchange interactions

In a diagrammatical perturbation expansion of the direct RPA (dRPA) correlation energy it can be seen that only certain types of diagrams occur, namely those
that have a ring form [9, 56, 89]. Because of this the direct RPA is sometimes also termed ring approximation or direct ring coupled-cluster doubles method (drCCD). Moreover, it has been shown that the dispersion interaction energy on the coupled-cluster doubles level is identical to the dispersion energy described by RPA response propagators of the monomers, see Ref. [90].

A simple Hartree calculation suffers from the neglect of electron exchange effects that leads to erroneous self-interactions [56]. This shortcoming is rectified by taking into account the exchange contributions in the Hartree-Fock method. Similarly, dRPA suffers from the neglect of exchange, now in higher orders in the electron-electron interaction. As a result, dRPA methods usually strongly overestimate electron correlation due to self-correlation errors. Most striking is the fact, that dRPA yields non-zero correlation energies in one-electron systems [37]. Because of this, self-correlation in dRPA has to be corrected by including electron exchange effects. There is, however, by no means a unique way to do this. Quite some RPA methods including exchange effects were developed over the years [13, 14, 41, 84, 91–93]. As the standard RPA or 'normal RPA' (NRPA) [92, 93] one may define the variant in which all ring-diagrams in dRPA are supplemented by additional ring-diagrams with the interaction lines replaced by antisymmetrised interaction lines. Such an RPA method sometimes is also referred to as ring coupled-cluster doubles (rCCD) approach [94].

The starting point of the various HF based RPA variants is the time-dependent HF equation [19, 93, 95–97]

\[
\begin{pmatrix}
\varepsilon + A & B \\
- B & -\varepsilon - A
\end{pmatrix}
\begin{pmatrix}
X Y \\
Y X
\end{pmatrix}
= 
\begin{pmatrix}
X Y \\
Y X
\end{pmatrix}
\begin{pmatrix}
\Omega & 0 \\
0 & -\Omega
\end{pmatrix}
\]

(51)

whose solutions and eigenvalues are used to construct an approximation to the response matrix elements \(\chi_{pq,rs}(i\omega)\) required in the basic equation (46). The matrices \(\varepsilon, A, B, X, Y\), and \(\Omega\) have the dimension of the number of products of occupied and unoccupied spin orbitals. The matrix elements are defined analogously as in the KS case, however, with respect to HF spin orbitals instead of KS spatial orbitals, i.e., \(\varepsilon_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_i - \varepsilon_a)\), \(A_{ia,jb} = \langle ij|ab\rangle - \langle ia|jb\rangle\), and \(B_{ia,jb} = \langle ij|ab\rangle - \langle ij|ba\rangle\). Again orbitals and subsequently all occurring matrices are assumed to be real-valued.

In a non-spin-polarized electron system the time dependent HF equation (51) can be decoupled in equations for singlet-singlet and singlet-triplet excitations with matrices \(\varepsilon, A, B, X\) and \(Y\) that have the dimension of the number products of occupied and unoccupied spatial orbitals only, i.e., a dimension that is a factor of four smaller than in the general spin-polarized case. Note that Eq. (51) has pairs of solutions with eigenvalues \(\Omega_n\) and \(-\Omega_n\). The eigenvalues \(\Omega_n\) are the excitation energies within the RPA.

The eigenvectors given by the matrices \(X\) and \(Y\) fulfill the normalisation condition [19]

\[
\begin{pmatrix}
X^T & Y^T \\
Y^T & X^T
\end{pmatrix}
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
X Y \\
Y X
\end{pmatrix}
= 
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\]

(52)

Once Eq. (51) has been solved, the RPA response matrix \(\chi^{RPA}(\nu)\) can be expressed in the spectral form

\[
\chi^{RPA}(\nu) = 
\begin{pmatrix}
X Y \\
Y X
\end{pmatrix}
\begin{pmatrix}
(\nu 1 - \Omega)^{-1} & 0 \\
0 & (-\nu 1 - \Omega)^{-1}
\end{pmatrix}
\begin{pmatrix}
X^T & Y^T \\
Y^T & X^T
\end{pmatrix}
\]

(53)
The elements of \( \chi^{\text{RPA}}(\nu) \) with \( \nu = i\omega \) enter as approximation of the exact response matrix elements \( \chi_{pq,rs}(i\omega) \) Eq. (46) for the RPA correlation energy, leading to

\[
E^{\text{RPA}}_c = -\frac{1}{4\pi} \sum_{pqrs} \int_0^\infty d\omega \; \text{Tr} \left[ W^{\text{RPA}} \left[ \chi^{\text{RPA}}(i\omega) - \chi^{\text{HF}}(i\omega) \right] \right]
\]

with the HF response matrix \( \chi^{\text{HF}}(\nu) \) containing elements given in Eq. (43) and with the interaction matrix \( W^{\text{RPA}} \) defined as

\[
W^{\text{RPA}} = \begin{pmatrix} A & B \\ B & A \end{pmatrix}.
\] (54)

Alternatively the RPA response function can be obtained from the Dyson-like equation

\[
\chi^{\text{RPA}}(\nu) = \chi^{\text{HF}}(\nu) + \chi^{\text{HF}}(\nu) W^{\text{RPA}} \chi^{\text{RPA}}(\nu).
\] (55)

Repeated insertion of Eq. (55) into itself leads to a series expansion of \( \chi^{\text{RPA}}(\nu) \). If this expansion is used to evaluate the RPA correlation energy \( E^{\text{RPA}}_c \), also the latter is obtained in a series expansion. Comparing this expansion of \( E^{\text{RPA}}_c \) with many-body perturbation theory shows that the expansion of Eq. (55) produces wrong prefactors in front of all terms. It has been shown that this can be remedied through the introduction of an interaction strength parameter \( \alpha \) in Eq. (46) \([6, 98, 99]\) which then in the RPA approach is written as:

\[
E^{\text{RPA}}_c = -\frac{1}{8\pi} \sum_{pqrs} \langle pr || qs \rangle \int_0^1 d\alpha \int_0^\infty d\omega \left[ \chi^{\text{RPA}}_{pq,rs}(i\omega, \alpha) - \chi^{\text{HF}}_{pq,rs}(i\omega) \right]
\]

\[
= -\frac{1}{2} \text{Tr} (W^{\text{RPA}} P)
\] (56)

where \( P = -(1/2\pi) \int_0^1 d\alpha \int_0^\infty d\omega \left[ \chi^{\text{RPA}}_{pq,rs}(i\omega, \alpha) - \chi^{\text{HF}}_{pq,rs}(i\omega) \right] \) denotes the correlation part of the pair density. The matrix \( \chi^{\text{RPA}}_{pq,rs}(i\omega, \alpha) \) is obtained by scaling the matrices \( A \) and \( B \) in Eq. (51) or the matrix \( W \) in Eq. (55) by the coupling constant \( \alpha \). Since \( W \) is proportional to the electronic interaction, the RPA response function can then be expanded in a power series of \( \alpha \) via the Dyson Eq. (55). A very crucial point is now, that in the standard RPA method the interaction strength integration is not performed exactly. Instead one assumes that the leading order term \( \chi_0 W^{\text{RPA}}(\alpha) \chi_0 \) of the Dyson type Eq. (55) that is linear in \( \alpha \) is dominating the perturbation expansion and sets:

\[
\int_0^1 d\alpha \; \chi^{\text{RPA}}(\nu, \alpha) \approx \frac{1}{2} \chi^{\text{RPA}}(\nu, \alpha = 1)
\] (57)

which corresponds to a coupling strength average. With this the correlation energy gets

\[
E^{\text{RPA}}_c \approx -\frac{1}{8\pi} \sum_{pqrs} \langle pr || qs \rangle \int_0^\infty d\omega \left[ \chi^{\text{RPA}}_{pq,rs}(i\omega, \alpha = 1) - \chi^{\text{HF}}_{pq,rs}(i\omega) \right]
\]

\[
= -\frac{1}{2} \text{Tr} (W^{\text{RPA}} P)
\] (58)

and the insertion of the spectral representation of the response function (Eq. (53))
yields after integration over $\omega$

$$E_{c}^{\text{RPA}} = \frac{1}{8} \text{Tr} \left\{ \left( \begin{array}{cc} A & B \\ B & A \end{array} \right) \circ \left[ \begin{array}{cc} XX^T & XY^T \\ YX^T & YY^T \end{array} \right] - \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right) \right\}$$

$$= \frac{1}{4} \left[ \text{Tr}(BYX^T) + \text{Tr}(AYY^T) \right]$$

(59)

where the operator $\circ$ here defines an elementwise matrix multiplication and the normalisation condition Eq. (52) has been employed. The second term in Eq. (59) is small compared to the first term since it is of second order in the small eigenvector components $Y$. Thus

$$E_{c}^{\text{RPA}} \cong \frac{1}{4} \text{Tr}(BYX^T)$$

(60)

Using the normalisation condition $XX^T - YY^T = 1$ (see Eq. (52)) it is easy to show that $YY^TX = Y + YY^TY$ and thus [18, 100]

$$YY^T = YX^{-1} + YY^T YX^{-1} = (1 + YY^T)YX^{-1} \approx YX^{-1}$$

(61)

where again it has been made use of the fact that $YY^T \ll 1$. With Eq. (61) the RPA correlation energy in Eq. (60) then can be written as

$$E_{c}^{\text{RPA}} \cong \frac{1}{4} \text{Tr}(BYX^{-1})$$

(62)

This is the RPA correlation energy expression which is identical to the ring-approximation in coupled-cluster doubles theory (rCCD) as recently was shown by Scuseria [94]. The amplitudes defined as $T = YX^{-1}$ can alternatively to the solution of Eq. (51) be obtained from the solution of the Riccati equation [101]

$$B + T \varepsilon + \varepsilon T + TA + AT + TBT = 0$$

(63)

and it can be shown that the RPA correlation energy defined in Eq. (62) can be calculated in terms of a sum over the differences of the RPA and SCI (singles configuration interaction) respectively (TDA) Tamm-Dancoff approximation excitation energies:

$$E_{c}^{\text{RPA}} = \frac{1}{4} \sum_n \Omega_n^{\text{RPA}} - \frac{1}{4} \text{Tr}(\varepsilon + A) = \frac{1}{4} \sum_n \left[ \Omega_n^{\text{RPA}} - \Omega_n^{\text{TDA}} \right]$$

(64)

where it was used that the trace of a matrix does not change under cyclic permutations. Eq. (64) is the plasmon formula expression which has been obtained by McLachlan and Ball [13, 14] who assumed that the RPA excitations should be treated as a set of harmonic oscillators and that Eq. (64) is the zero-point energy of these oscillators. Eqs. (62) and (64) are given in the spin-orbital basis. In the spatial orbital basis the expressions transform into [84, 93]
\[ E_{c}^{\text{RPA}} = \frac{1}{4} \left[ \text{Tr}(1^4 B^1 T) + 3 \text{Tr}(3^3 B^3 T) \right] \]
\[ = \frac{1}{4} \sum_{i} \sum_{S=0}^{1} (2S + 1) \left[ \omega_{i}^{\text{RPA}}(S) - \omega_{i}^{\text{TDA}}(S) \right] \]

(65)

where \( S = 0, 1 \) refer to singlet and triplet excitation energies, respectively (Eq. (51) yields \( n_{\text{o}} \times n_{\text{v}} \) singlet excitations and \( 3 \times n_{\text{o}} \times n_{\text{v}} \) triplet excitations which appear in sets with three-fold degeneracy). The matrices \( 1^4 B \) and \( 3^3 B \) correspond to antisymmetrised integrals for the singlet and triplet case with \( 1^4 B_{ia,jb} = \langle ij|ab \rangle - \langle ij|ba \rangle \) and \( 3^3 B_{ia,jb} = -\langle ij|ba \rangle \) with \( i, j, \ldots \) referring to occupied and \( a, b, \ldots \) to unoccupied spatial orbitals.

It should now be noted that the expression in Eqs. (64) and (65) for the RPA correlation energy is not the only possibility to describe electron correlation on the RPA level. First of all, as explained above, Eq. (62) is only an approximation to Eq. (59). In order to distinguish between the different approaches that will be described below, we will term the approximation according to Eq. (62) rCCD-RPA or ‘normal RPA one’ (NRPA1) as suggested by Szabo and Ostlund [93] (to distinguish it from self-consistent RPA schemes described below). The factor of \( 1/2 \) from the coupling strength average (Eq. (57)) in Eq. (64) makes the NRPA1 correlation energy exact to second order of perturbation theory. Another proposal for obtaining an energy expression that is exact to second order has been given by Fukuda [91] who omits the coupling strength integration and subtracts the correlation energy at second order from the corresponding homogeneous electron gas correlation energy. His expression is thus given by

\[ E_{c}^{\text{NRPA2}} = 2 E_{c}^{\text{NRPA1}} - E_{c}^{(2)} \]

(66)

with \( E_{c}^{(2)} \) being identical to the second-order Møller-Plesset (MP2) correlation energy if a Hartree-Fock reference determinant is used. We call this approach NRPA2.

The motivation for the third variant is related to an inconsistency in the RPA two-particle density matrix in the Hartree-Fock orbital basis set. It should hold that the singlet amplitudes \( 1^4 Y^1 X^T \) must be equal to the negative triplet amplitudes \(-3^3 Y^3 X^T\) (see, e.g., table I in Ref. [84]). This requirement stems from the condition that the wave function is an eigenfunction of the square of the spin operator with eigenvalue zero. As a matter of fact, this condition is not fulfilled if the Hartree-Fock determinant is used to build the RPA response function [14, 16, 84]. The dilemma within the TDHF method is, that the linear combinations of single-excited states are produced in two ways: (1) by exciting from the HF ground-state or (2) by de-exciting from a doubly excited state of the true ground-state [21]. Since, however, the HF wave function approximates the ground-state wave function in TDHF, the de-excitation violates the Pauli exclusion principle and thus there exists an incompatibility between the wave function and the excitation operator in TDHF. Indeed, the HF ground state is often triplet unstable or yields very poor triplet excitation energies as compared to its singlet excitations [21–25]. In order to remedy this deficiency higher order RPA (HRPA) methods have been proposed in which the RPA ground state is the sum of the Hartree-Fock ground state and doubly excited...
\[ \Psi_0^{\text{RPA}} = \left[ 1 + \sum_{ia,jb} T_{ij}^{ab} a_i \dag a_j \right] \Phi_0^{\text{HF}} \]

The HRPA correlation coefficients \( T_{ij}^{ab} \) are then determined by iteration. In the first cycle the generalised RPA eigenvalue equation

\[
\left( \varepsilon + A \right) \left( \begin{array}{c} \mathbf{Y} \\ \mathbf{X} \end{array} \right) = \left( \begin{array}{cc} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & -\mathbf{S} \end{array} \right) \left( \begin{array}{c} \mathbf{Y} \\ \mathbf{X} \end{array} \right) \left( \begin{array}{c} \Omega \\ \mathbf{0} \end{array} \right)
\]

is solved using the approximation \( \Psi_0^{\text{RPA}} \approx \Phi_0^{\text{HF}} \) with

\[
B_{ia,jb} = \langle \Psi_{ia}^{a \dag} | \hat{H} - E_0 | \Psi_{jb}^b \rangle
\]

and

\[
S_{ia,jb} = \langle \Psi_{ia}^a | \Psi_{jb}^b \rangle
\]

where \( \hat{H} \) denotes the electronic Hamiltonian, \( E_0 \) is the Hartree-Fock ground-state energy and \( \Psi_{ia}^a \) and \( \Psi_{jb}^b \) denote singly and doubly excited wave functions, respectively. Note that for the case \( \Psi_0^{\text{RPA}} \approx \Phi_0^{\text{HF}} \) Eq. (68) reduces to Eq. (51) and the NRPA1 correlation energy results as first estimate. Then the correlation coefficients are used to construct the RPA wave function in Eq. (67) which in turn is used to construct the Hessian matrix in Eq. (68) to obtain new amplitudes and so forth. It should be noted that depending on which type of amplitudes are iterated different HRPA schemes will arise. While Shibuya and McKoy iterate on the \( T = \mathbf{YX}^{-1} \) [102–104] Oddershede and Jørgensen [16, 18, 24, 84] use the amplitudes \( T = \mathbf{YX}^T \) which, as described above, differ from the \( T = \mathbf{YX}^{-1} \) in third order of \( \mathbf{Y} \). Other related methods are the self-consistent polarisation propagator approximation (SPPA) [16, 105] and the second-order polarisation propagator approximation (SOPPA) [84, 108] which iterate on the two-particle density matrix until a self-consistency is achieved. All these approaches lead to considerable improvements over TDHF (RPA in the HF basis) for the description of triplet excited states [84]. For example in SOPPA the spin-symmetry conditions of the two-particle density matrix are fulfilled [84]. Also, if the matrices \( \mathbf{A} \) in Eq. (68) are augmented with two-particle two-hole corrections [109–111] such higher order RPA methods will become exact in third-order of perturbation theory which is not true for any normal random-phase approximation approach, see below and Ref. [112].

Here we will not discuss the higher RPA approaches further, but we may assume that the condition \( \mathbf{Y} \mathbf{X}^T = -\mathbf{Y} \mathbf{X} \) holds true and rewrite Eq. (62) solely in terms of the singlet amplitudes to obtain

\[
E_c^{\text{NRPA3}} = \frac{1}{2} \text{Tr} \left( \left[ \mathbf{1} \mathbf{Y} \mathbf{X} \right]^T \right)
\]

This expression, which we term here as NRPA3 correlation energy, has been given by Szabo and Ostlund [93] and also by Oddershede [84]. As in the case of the NRPA1 and NRPA2 approaches (Eqs. (65) and (66)) it is exact to second-order of perturbation theory but has the advantage that it can not be affected by triplet instabilities, since the triplet amplitudes do not enter Eq. (69). However, it has been shown by Szabo and Ostlund [93] that neither of the three approaches have the desirable property that they describe the long-range interaction energy between two molecules on the coupled Hartree-Fock level. In fact they contain erroneous terms that behave as \( R^{-7} \) with the distance \( R \) of the monomers and thus can not be expected to yield accurate intermolecular interaction energies [93]. As shown by Szabo and Ostlund [93, 113], an RPA method which has the correct long-range behaviour, i.e., which describes dispersion interactions on the coupled HF level is
given by the following expression for the correlation energy:

\[
E_{c}^{\text{NRPA4}} = \frac{1}{2} \text{Tr} \left( 1 \mathbf{B} \left[ \mathbf{Y}^{1} \mathbf{X}^{-1} + 3 \mathbf{Y}^{3} \mathbf{X}^{-1} \right] \right)
\] (70)

There also exist RPA approaches which do not explicitly account for electron exchange in the construction of the response function but add exchange effects to the direct RPA such that exactness in second order is fulfilled. Note that the dRPA approach corresponds to the approximation \( \mathbf{A} \approx \mathbf{C} \) and \( \mathbf{B} \approx \mathbf{C} \) in the RPA eigenvalue equation Eq. (51) with \( C_{ia,jb} = \langle ij | ab \rangle \). The first variant is the RPA+SOX method where the exchange contribution in second order given by [38]

\[
E_{c,\text{exchange}}^{(2)} = -\frac{1}{2} \sum_{ia,jb} \frac{\langle ij | ab \rangle \langle ij | ba \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}
\] (71)

is added to the dRPA correlation energy:

\[
E_{c}^{\text{RPA+SOX}} = E_{c}^{\text{dRPA}} + E_{c,\text{exchange}}^{(2)}
\] (72)

A variant to this method uses the corresponding second-order Epstein-Nesbet correlation correction to the RPA and is termed RPA+RSOX [38], motivated by the fact that in RPA+SOX the self-correlation is overcorrected since the Coulomb contribution in SOX is unscreened compared to the dRPA. In another approach by Kresse et al. [41] the dRPA amplitudes \( \mathbf{T}^{\text{dRPA}} \) are contracted with antisymmetrised two-electron integrals:

\[
E_{c}^{\text{RPA-SOSEX}} = \frac{1}{2} \text{Tr}(\mathbf{B}^{\text{dRPA}})
\] (73)

This method is termed RPA with second-order screened exchange and has the big advantage that it can efficiently be implemented in plane-wave basis function programs for solids [41].

None of the RPA methods described in this section so far carries out a coupling strength integration like the methods for the correlation energy derived from the AC-FDT formula, see sections 2.4 and 3.1. While it has been shown in section 3.1 that the AC-FDT is not rigorously defined for Hartree-Fock reference determinants, it nonetheless has the advantage that, as the NRPA4 method, it describes the long-range correlation energy between two molecules on the coupled Hartree-Fock level. It has been argued above that Eq. (46) can be written as

\[
E_{c} = -\frac{1}{2\pi} \sum_{pqrs} \langle pr | qs \rangle \int_{0}^{\infty} \left[ \chi_{pq,rs}(i\omega) - \chi_{pq,rs}^{\text{HF}}(i\omega) \right] d\omega
\]

\[
= \frac{1}{2} \text{Tr}(\mathbf{W}^{\text{P}})
\] (74)

by using the inherent antisymmetry property of the two-particle density matrix. The term \( \mathbf{W} \) in Eq. (74) here defines the interaction matrix containing only nonantisymmetrised integrals. Since now again, within the RPA this equation yields wrong prefactors in the perturbation expansion terms, we introduce an additional integration over the coupling strength to obtain the correlation energy within the
adiabatic-connection fluctuation-dissipation theorem

\[ E_{c}^{\text{AC-FDT}} = -\frac{1}{2\pi} \sum_{pqrs} \langle pq|qs \rangle \int_{0}^{1} d\alpha \int_{0}^{\infty} [\chi_{pq,rs}(i\omega, \alpha) - \chi_{\text{HF}}^{pr,rs}(i\omega)] d\omega \]  

(75)

which corresponds to Eq. (50) and defines the correlation energy in terms of the coupled and uncoupled response functions \( \chi \) and \( \chi_{\text{HF}} \). If here \( \chi \) is approximated as \( \chi \approx \chi_{\text{RPA}} \) one obtains the adiabatic connection RPA method (AC-RPA) which can be written as [53, 114]

\[ E_{c}^{\text{AC-RPA}} = \frac{1}{2} \int_{0}^{1} d\alpha \text{Tr} \left[ C[(X_{\alpha} + Y_{\alpha})(X_{\alpha} + Y_{\alpha})^T - 1] \right] = \frac{1}{2} \int_{0}^{1} d\alpha \text{Tr} \left[ C P_{\alpha} \right] \]  

(76)

where the matrix \( C \) is defined by the two-electron integral matrix elements \( C_{ia,jb} = \langle ij|ab \rangle \). The coefficients \( X_{\alpha} \) and \( Y_{\alpha} \) at coupling strength \( \alpha \) are obtained from the solution of the eigensystem Eq. (51) if the matrices \( A \) and \( B \) are scaled by \( \alpha \). Note that only the singlet excitation vectors need to be computed for calculating the AC-RPA correlation energy of Eq. (76). In order to compare this expression with the NRPA methods we can make use of the identity

\[ (X + Y)(X + Y)^T - 1 = 2YX^{-1} + 2YY^T(1 + YX^{-1}) \]

and find, again since \( YY^T \) is small, that

\[ E_{c}^{\text{AC-RPA}} \approx \int_{0}^{1} d\alpha \text{Tr} \left[ CY_{\alpha}X_{\alpha}^{-1} \right] \]  

(77)

(Basically the same transformation has been used in the derivation of Eq. (60)). The coupling-strength average of this expression is given by

\[ E_{c}^{\text{AC-RPA}} \approx \frac{1}{2} \text{Tr} \left[ CYX^{-1} \right] \]  

(78)

A comparison with expression (60) for the correlation energy shows that expression (78) differs from the former by the contribution \(-\frac{1}{4}\text{Tr} \left[ CYX^{-1} \right] - \frac{1}{4}\text{Tr} \left[ KYX^{-1} \right] \) with the matrix \( K \) defined as \( K_{ia,jb} = \langle ij|ba \rangle \). In case of the direct adiabatic-connection RPA (AC-dRPA) in which \( X \) and \( Y \) are the eigenvector components of the dRPA eigenvalue equation it has recently been shown by Jansen et al. [114] that the expressions in Eq. (76) and Eq. (78) are exactly identical, that is, the coupling-strength average of the AC-dRPA correlation energy applied to Eq. (77) containing an approximate response function is surprisingly identical to the full coupling-strength integrated expression in Eq. (76). This holds true even though the coupling-strength integrated pair density is not in general identical to the amplitudes, i.e.

\[ \int_{0}^{1} d\alpha (X_{\alpha} - X_{0}) = \int_{0}^{1} d\alpha \left\{ X_{\alpha}X_{\alpha}^T X_{\alpha}Y_{\alpha}^T \right\} - 1 \neq YX^{-1} \]  

(79)

Since all RPA methods of this section that include exchange effects differ in third order of perturbation theory, it is instructive to derive explicit expressions for the correlation energy up to third order in terms of molecular integrals and orbital energies. For this we first expand the response function up to second order in the intermolecular interaction using Eq. (55):
\[ \chi^{(1+2)}_\alpha(i\omega) = \chi_0(i\omega) + \alpha \chi_0(i\omega) W \chi_0(i\omega) + \alpha^2 \chi_0(i\omega) W \chi_0(i\omega) W \chi_0(i\omega) \quad (80) \]

where it is employed that the interaction operator \( W \) linearly depends on the interaction strength \( \alpha \). The RPA correlation pair density can then generally be written as

\[
P^{(1+2)} = \int_0^1 d\alpha \frac{1}{2\pi} \int_0^\infty d\omega \left( \chi^{(2)}_\alpha(i\omega) - \chi_0(i\omega) \right)
= \int_0^1 d\alpha \frac{1}{2\pi} \int_0^\infty d\omega \left( \alpha \chi_0(i\omega) W \chi_0(i\omega) \right.
+ \alpha^2 \chi_0(i\omega) W \chi_0(i\omega) W \chi_0(i\omega) \left. \right) \quad (81) \]

Now note that, as discussed above, in the NRPA approaches the coupling strength integration in Eq. (81) is not performed, but the average of Eq. (57) is taken. Because of this the NRPA and AC-RPA methods will obtain different prefactors in second order in \( W \):

\[
P^{(1+2),NRPA} = \frac{1}{4\pi} \int_0^\infty d\omega \chi_0(i\omega) W \chi_0(i\omega)
+ \frac{1}{6\pi} \int_0^\infty d\omega \chi_0(i\omega) W \chi_0(i\omega) W \chi_0(i\omega) \quad (82) \]

\[
T^{(1+2),AC-RPA} = \frac{1}{4\pi} \int_0^\infty d\omega \chi_0(i\omega) W \chi_0(i\omega)
+ \frac{1}{6\pi} \int_0^\infty d\omega \chi_0(i\omega) W \chi_0(i\omega) W \chi_0(i\omega) \quad (83) \]

The full response function (at \( \alpha = 1 \)) is given by (compare Eqs. (51) and (53)):

\[
\chi_{\alpha=1}(i\omega) = \left\{ \begin{pmatrix} \epsilon - i\omega & 0 \\ 0 & \epsilon + i\omega \end{pmatrix} + \left( \begin{array}{cc} A & B \\ B & A \end{array} \right) \right\}^{-1}
= \chi_0^{-1} + W = \chi_0 - \chi_0 W \chi_0 + \chi_0 W \chi_0 W \chi_0 + \ldots \quad (84) \]

The corresponding response function for coupling strengths \( \alpha \) can be obtained with Eq. (84) by scaling the interaction matrix \( W \) with a factor of \( \alpha \). From Eq. (84) the uncoupled response function \( \chi_0 \) and the interaction operator \( W \) in Eqs. (82) and (83) can be identified as:

\[
\chi_0(i\omega) = \begin{pmatrix} \frac{\epsilon - i\omega}{\epsilon^2 + \omega^2} & 0 \\ 0 & \frac{\epsilon + i\omega}{\epsilon^2 + \omega^2} \end{pmatrix} = \begin{pmatrix} \chi_0^{-1} & 0 \\ 0 & \chi_0^{-1} \end{pmatrix} \quad (85) \]

\[
W = \begin{pmatrix} A & B \\ B & A \end{pmatrix} \quad (86) \]
where we use the short-hand notation \( \lambda^- = (\varepsilon - i\omega)^{-1} \) and \( \lambda^+ = (\varepsilon + i\omega)^{-1} \). Thus the correlated first-order RPA pair density is given by

\[
P^{(1)} = \frac{1}{4\pi} \int_0^\infty d\omega \chi_0(i\omega) W \chi_0(i\omega) = \frac{1}{4\pi} \text{Re} \int_0^\infty d\omega \left\{ \lambda^- A \lambda^- + \varepsilon \lambda^- B \lambda^- + \lambda^- A \lambda^- B + \lambda^- B \lambda^- A \right\} \]  

(87)

where it has been used that the imaginary terms of the response matrix cancel in each order of perturbation theory and thus only the real parts of the four submatrices in Eq. (87) need to be considered. Integration over \( \omega \) yields:

\[
P^{(1)} = \frac{1}{4} \left\{ 0 \ \tilde{B} \right\} \]  

(88)

where the definition \( \overline{M}_{ia,jb} = \frac{M_{ia,jb}}{\varepsilon_{ia} + \varepsilon_{jb}} \) for a matrix \( M \) has been used. With this result the second-order energy is given by (see Eqs. (56) and (59))

\[
E^{(2),\text{NRPA}}_c = \frac{1}{4} \text{Tr}(W P^{(1)}) = \frac{1}{8} \text{Tr} \left\{ \left( \begin{array}{cc} A & B \\ B & A \end{array} \right) \circ \left( \begin{array}{c} 0 \\ \tilde{B} \ 0 \end{array} \right) \right\} 
\]

\[
= \frac{1}{4} \sum_{ia,jb} \frac{\langle ij||ab\rangle \langle ab||ij \rangle}{\varepsilon_{ia} + \varepsilon_{jb}}
\]

(89)

where \( \varepsilon_{ia} = \varepsilon_i - \varepsilon_a \). The second order energy expression in Eq. (89) can readily be identified as the exact second order energy if a Hartree-Fock basis is used. Correspondingly the second-order energy of the AC-RPA method is given by

\[
E^{(2),\text{AC-RPA}}_c = \frac{1}{2} \text{Tr}(\widetilde{W} P^{(1)}) = \frac{1}{4} \text{Tr} \left\{ \left( \begin{array}{cc} C & C \\ C & C \end{array} \right) \circ \left( \begin{array}{c} 0 \\ \tilde{B} \ 0 \end{array} \right) \right\} 
\]

\[
= \frac{1}{4} \sum_{ia,jb} \frac{\langle ij||ab\rangle \langle ab||ij \rangle}{\varepsilon_{ia} + \varepsilon_{jb}}
\]

(90)

and thus, too, is exact to second order of perturbation theory.

For the (unscaled, i.e. without a prefactor due to the coupling strength integration) second-order pair density one gets

\[
P^{(2)} = \frac{1}{2\pi} \int_0^\infty d\omega \chi_0(i\omega) W \chi_0(i\omega) W \chi_0(i\omega) = \frac{1}{2\pi} \text{Re} \int_0^\infty d\omega \times \]

\[
\left\{ \lambda^- A \lambda^- + \varepsilon \lambda^- B \lambda^- + \lambda^- A \lambda^- B + \lambda^- B \lambda^- A \right\} \left\{ \lambda^+ B \lambda^- A \lambda^- + \varepsilon \lambda^+ A \lambda^- B \lambda^- + \lambda^+ B \lambda^- B \lambda^- + \lambda^+ A \lambda^- A \lambda^- \right\}
\]

\[
= \frac{1}{2} \left\{ \begin{array}{cc} \tilde{B} B & \tilde{A} B + \tilde{A} B \end{array} \right\}
\]

(91)

where in the last expression the contraction \( \overline{N}_{ia,jb} = \frac{M_{ia,kc} N_{kc,jb}}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} \) for two
matrices $M$ and $N$ has been used.

Now note that one can perform either a coupling-strength integration over each term in Eq. (91) which yields a prefactor of $\frac{1}{3}$ or, as is done in NRPA, one uses a coupling strength average using a prefactor of $\frac{1}{2}$ (see above) but disregards the diagonal blocks in $P^{(2)}$ since they correspond to the small component part $YY^T$ of the two-matrix (the $XX^T$ can be eliminated by using the normalisation relation). This may be done because, while the diagonal terms in each order may not be small, their sum to infinite order can expected to be small compared to the nondiagonal part of the total pair density. Interestingly it turns out that both options yield the same third-order (NRPA1 or rCCD) energy (see also [84, 114]):

$$E^{(3),\text{NRPA1}}_c = \frac{1}{2} \text{Tr}(WP^{(2)}) = \frac{1}{2} \text{Tr}[\overline{B}\overline{A}\overline{B}] = \frac{1}{2} \sum_{ia,jb,kc} \frac{(ij||ab)(kb||cj)(ac||ik)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})}$$  \hspace{1cm} (92)

In the AC-RPA method the pair density in Eq. (91) is integrated over the coupling-strength yielding a prefactor of $\frac{1}{3}$ (see Eq. (83)) and the result for the third order energy is (see also [114]):

$$E^{(3),\text{AC-RPA}}_c = \frac{1}{2} \text{Tr}([\hat{W}P^{(2)}]) = \frac{1}{3} \text{Tr}[\overline{B}\overline{A}\overline{C} + \overline{A}\overline{B}\overline{C} + \overline{B}\overline{B}\overline{C}]$$

$$= \frac{1}{3} \sum_{ia,jb,kc} \left( \frac{(ij||ab)(jc||bk)(ki||ca)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} + \frac{(ib||aj)(jc||bk)(ki||ca)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} + \frac{(ij||ab)(jk||bc)(kc||ia)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} \right)$$

$$\hspace{1cm} + \frac{(i\bar{j})||ab)(j\bar{k})||bc)(k\bar{i})||ca)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} + \frac{(i\bar{j})||ab)(j\bar{k})||bc)(k\bar{i})||ca)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} + \frac{(i\bar{j})||ab)(j\bar{k})||bc)(k\bar{i})||ca)}{(\varepsilon_{ia} + \varepsilon_{jb})(\varepsilon_{ia} + \varepsilon_{kc})} \right)$$  \hspace{1cm} (93)

A corresponding perturbation analysis can be made for the other RPA approaches discussed above. The result is comprised in table 2 which shows for various RPA correlation methods the prefactors of the perturbation theory terms up to third order as given in table 1.

4. Combining elements of HF and KS based RPA

Here we relate the EXX-RPA method of Section 2 [53, 55] to the AC-RPA method of Section 3, Eqs. (75) and (76), (termed as HF-RPA in Ref. [53]). To this end the coupling constant-dependent singlet-singlet TDHF eigenvalue equation of the AC-RPA method is written in the reduced generalised eigenvalue equation form

$$(\varepsilon_{HF} + \alpha A_{HF} + \alpha B_{HF})u_n = \Omega^2_n(\varepsilon_{HF} + \alpha A_{HF} - \alpha B_{HF})^{-1}u_n $$  \hspace{1cm} (94)

$$\left[ \varepsilon_{HF}^2 + \alpha \varepsilon_{HF}^{1/2}(A_{HF} + B_{HF})\varepsilon_{HF}^{1/2} \right]z_n = \Omega^2_n\left[ 1 + \alpha \varepsilon_{HF}^{1/2}(A_{HF} - B_{HF})\varepsilon_{HF}^{-1/2} \right]^{-1}z_n$$  \hspace{1cm} (95)
with \( U = X + Y \) and \( Z = \varepsilon_{HF}^{1/2} U \) or considering columns of the matrices \( U, X, Y, \) and \( Z \), see Eq. (51). \( u_n = x_n + y_n \) and \( z_n = \varepsilon_{HF}^{1/2} u_n \). In this Section like in Section 2 non-spin-polarized electron systems are considered. The elements of the matrices \( \varepsilon_{HF}, A_{HF}, \) and \( B_{HF} \) are defined as in the TDEXX equation (36), however, with respect to HF not EXX spatial orbitals and their eigenvalues. Because in this Section matrix elements defined with respect to HF or EXX orbitals occur we designate matrices with elements defined with respect to HF orbitals with a subscript 'HF'.

Eq. (94) can be expressed in EXX orbitals and eigenvalues if the approximation is made that the EXX orbitals and HF orbitals can be transformed into each other through an occupied-occupied virtual-virtual unitary transformation, see Refs. [70, 76, 115] for details. This approximation is equivalent to the approximation that the EXX and the HF determinant equal each other which is known to be a very good approximation [76]. As a result of the transformation of the orbitals the matrices \( A_{HF} \) and \( B_{HF} \) turn into the corresponding matrices \( A \) and \( B \) with respect to KS orbitals and the matrix \( \varepsilon_{HF} \) turns into \( \varepsilon + \Delta \) with \( \Delta \) defined as in the TDEXX equation (36) [69, 71]. From the transformed Eq. (94) a transformed Eq. (95) results that has the form

\[
\left[ \varepsilon^2 + \varepsilon^{1/2} [\Delta + \alpha (A + B)] \varepsilon^{-1/2} \right] z_n = \Omega_n^2 \left[ 1 + \varepsilon^{-1/2} [\Delta + \alpha (A - B)] \varepsilon^{-1/2} \right]^{-1} z_n
\]

(96)

Eq. (96) would be exactly equivalent to Eq. (94) and Eq. (95) if occupied and virtual EXX and HF orbitals could be exactly transformed into each other by an occupied-occupied and a virtual-virtual unitary transformation, respectively. For two-electron systems this is indeed exactly true, for other electronic systems this is an approximation, which, however, as mentioned above, is very good and, as shown in Section 5, has only negligible effects. We therefore can consider Eq. (96) as an alternative basis of the AC-RPA approach that enables a calculation of the AC-RPA correlation energy with EXX orbitals and eigenvalues and therefore lends itself to a straightforward comparison with the EXX-RPA correlation energy. The crucial difference of Eq. (96) and the TDEXX equation (36) is that the matrix \( \Delta \) in Eq. (96) is not scaled by the coupling constant because it arises there from the transformation from HF to EXX orbitals while it is scaled with the coupling constant \( \alpha \) in the TDEXX equation because it emerges from the exchange kernel in this case. A second difference between Eq. (96) and Eq. (36) are the matrices on the right hand side of the equations. In Ref. [71] it was shown that the differences in the matrices on the right hand side of the equations have little effect. The reason why the EXX-RPA method yields distinctively superior results as the AC-RPA approach [55] could be attributed to the different scaling of the matrix \( \Delta \) with the coupling constant \( \alpha \) [55].

We now consider a hybrid approach between the EXX-RPA and the AC-RPA method. To that end the matrix \( \Delta \) in Eq. (96) is scaled by the coupling constant \( \alpha \) like in the TDEXX equation (36) or conversely the form of the right hand side of the TDEXX equation (36) is changed into the form of Eq. (96) with the matrix \( \Delta \) scaled by \( \alpha \). This results in
In order to interpret the hybrid approach of Eq. (97) the matrix $1 + \alpha\varepsilon^{-1/2}(\Delta + A - B)\varepsilon^{-1/2}$ on the right hand side of Eq. (96) is expanded in a series with respect to $\alpha\varepsilon^{-1/2}(\Delta + A - B)\varepsilon^{-1/2}$

$$\left[1 + \alpha\varepsilon^{-1/2}(\Delta + A - B)\varepsilon^{-1/2}\right]^{-1} \approx 1 - \alpha\varepsilon^{-1/2}(\Delta + A - B)\varepsilon^{-1/2} + \alpha^2\varepsilon^{-1/2}(\Delta + A - B)\varepsilon^{-1}(\Delta + A - B)\varepsilon^{-1/2} - \ldots \quad (98)$$

If the expansion (98) is inserted into Eq. (97) and second and higher order terms are neglected then the TDEXX equation (36) results. That means the hybrid approach based on Eq. (97) differs from the EXX-RPA method only by the second and higher order contributions of the expansion (98). Inserting the expansion (98) in Eq. (97) and rearrangement suggests the eigenvalue equation

$$\left[\varepsilon^2 + \varepsilon^{1/2}\left[\alpha(\Delta + A + B) - \alpha\omega^2(\Delta + A - B) + \alpha^2\omega^2(\Delta + A - B)\varepsilon^{-1}(\Delta + A - B) + \ldots\right] \varepsilon^{1/2}\right] z_n(\alpha, \omega) = \Omega_n^2(\alpha, \omega) z_n(\alpha, \omega) \quad (99)$$

Eq. (99) is a an eigenvalue equation that is nonlinear in $\omega$. If the frequencies $\omega$ equal the square root $\Omega_n$ of an eigenvalue then this $\Omega_n$ is also an eigenvalue of Eq. (97) that can be interpreted as excitation energy. In this sense Eq. (99) is equivalent to Eq. (97) the basis of the considered hybrid method. Eq. (99) has exactly the form the basic equation (35) of TDDFT. The contributions $[\alpha(\Delta + A + B) - \alpha\omega^2(\Delta + A - B)]$ that are linear in $\alpha$ represent the Hartree and the exact frequency-dependent exchange kernel. The terms of higher order in $\alpha$ have to be interpreted as frequency-dependent contributions of the correlation kernel because only the correlation kernel contains contributions of quadratic and higher order in $\alpha$. Because terms up to infinite order in $\alpha$ are contained in Eq. (99) and thus taken into account in the EXX- and AC-RPA hybrid method based on Eq. (99) we call this method EXX-RPA[\infty] here.

The correlation energy both of the EXX-RPA and the EXX-RPA[\infty] method can be written in the general form

$$E_{c}^{\text{EXX-RPA}} = \frac{1}{2} \int_0^1 d\alpha \text{Tr}\left[C(U_\alpha U_\alpha^T - 1)\right] = \frac{1}{2} \int_0^1 d\alpha \text{Tr}\left[CP_\alpha\right] \quad (100)$$

with $U_\alpha$ containing in its columns the eigenvectors $u_n^\alpha = (\omega_n^\alpha)^{-1/2}\varepsilon^{1/2}z_n^\alpha$ for a given coupling strength $\alpha$, compare Eqns. (76) and (39) where the eigenvectors $z_n^\alpha$ in case of EXX-RPA are obtained from Eq. (36) and in case of EXX-RPA[\infty] from
Eq. (97) or (99), respectively. It has been shown in Ref. [53] that the EXX-RPA correlation energy according to Eq. (100) reproduces the correct second-order energy of perturbation theory along the adiabatic connection [116, 117] apart from the missing singles term due to the assumption that the EXX and Hartree-Fock orbitals are obtained by an occupied-occupied virtual-virtual unitary transformation only. While this can be shown to hold true also for the EXX-RPA[∞] method, the corresponding third-order correlation energies differ in both cases. More precisely, it can be shown that the third-order expansion of the EXX-RPA correlation energy can not be cast into the particle-hole terms of the form of those given in Eq. (93) or table 1. On the other hand, for the EXX-RPA[∞] approach one obtains the same third-order correlation energy terms as for the AC-RPA method (written in terms of EXX orbitals and eigenvalues, however), accompanied by the four additional contributions $(2b_{lx}^\alpha), (2b_{lx}^\alpha), (2g_{lx}^\alpha)$ and $(2h_{lx}^\alpha)$ stemming from $\Delta$ matrix elements, see table 1. As will be demonstrated in section 5, the additional terms in EXX-RPA and EXX-RPA[∞] approaches will yield significant contributions to the total correlation energy. Thus exchange RPA methods using a Kohn-Sham reference determinant should account for these non-standard contributions in practical calculations. Note, however, that this is not true for the SOSEX variant, since, by definition, here no exchange contributions are accounted for in the calculation of the response function, see section 3.2.

It has been shown [55] that the EXX-RPA correlation energies are distinctively different from those from the AC-RPA method. The reason for this is that, while the coupling-strength integrand $CP_\alpha$ in both cases is similar for $\alpha \to 0$ (where $CP_\alpha \to 0$) and $\alpha \to 1$, for coupling strengths between 0 and 1 the partitioning into an interacting and noninteracting response function leads to significant differences in both cases, especially in cases where the static correlation is dominating [55].

The analogue to the NRPA1 (rCCD) method using Kohn-Sham exchange will yield the same expression for the correlation energy

$$E_{c}^{EXX-NRPA1} = \frac{1}{4} \text{Tr}(B Y X^{-1})$$

but the eigenvector components $X$ and $Y$ are obtained from the supermatrix form of the TDHF eigenvalue equation written in terms of EXX orbitals and eigenvalues:

$$\begin{pmatrix} \varepsilon + \Delta + A & B \\ -B & -\varepsilon - \Delta - A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}$$

It has recently been shown by Jansen et al. [114] that the NRPA1 correlation energy is identical to following expression (see also section 3.2):

$$E_{c}^{NRPA1} = \frac{1}{4} \int_{0}^{1} d\alpha \text{Tr}[B P_\alpha] + \text{Tr}[ (A - B)(X_\alpha X_\alpha^T + Y_\alpha Y_\alpha^T - 1) \]$$

Since in the local exchange case the relation

$$\Delta + A - B \approx 0$$

holds true, which implies the closeness between the adiabatic and non-adiabatic
form of the eigenvalue Eq. (99), the EXX-RPA1 correlation energy from Eq. (101) then can also be approximated as

$$E_{c}^{\text{EXX-NRPA1}} \approx \frac{1}{4} \int_{0}^{1} d\alpha \text{Tr} \left[ BP_{\alpha} \right]$$

which directly links the NRPA1 (rCCD) correlation energy to an adiabatic connection formula that differs, however, from Eq. (100) due to the occurrence of antisymmetric integrals in Eq. (105). Performing the same transformation as between Eq. (46) and Eq. (74) one arrives at the expression

$$E_{c}^{\text{EXX-NRPA3}} \approx \frac{1}{2} \int_{0}^{1} d\alpha \text{Tr} \left[ CP_{\alpha} \right]$$

which is identical to the EXX-RPA correlation energy expression in Eq. (100) and which is termed EXX-NRPA3 as it is found that it gives practically the same correlation energy as the NRPA3 approach (Eq. (69)) in terms of local Kohn-Sham exchange

$$E_{c}^{\text{EXX-NRPA3}} = \frac{1}{2} \text{Tr} \left( \left[ 1B -3B \right] Y^{-1}X^{-1} \right) = \frac{1}{2} \text{Tr} \left( C^{1}YX^{-1} \right)$$

A reason for the similarity between Eqs. (100) and (107) can be deduced using the perturbation theory analysis from the last section. Considering the second-order response propagator of Eq. (91) and using $\Delta + A \approx B$ (note that $\Delta + A = B$ for two-electron systems) which follows from Eq. (104), then all terms in Eq. (91) are approximately identical (substitute $A$ by $\Delta + A$ in the equation). In case of the adiabatic connection method the number of terms contributing to $P^{(2)}$ is 6 (since two of the diagonal contributions are zero after frequency integration) while in case of EXX-NRPA3 one only accounts for the nondiagonal terms in Eq. (91), that is 4. Since in EXX-RPA the prefactor in third order is $\frac{1}{3}$ and in case of EXX-NRPA3 it is $\frac{1}{2}$ both methods have the same number of terms in that order and thus it holds true that the third-order contribution to the response propagator is approximately identical for EXX-RPA and EXX-NRPA3 (in case of two-electron systems it is exactly equal to each other).

Since the EXX-NRPA3 correlation energy of Eq. (106) should be identical to the NRPA3 correlation energy of Eq. (69) if the Hartree-Fock and EXX determinants can be transformed into each other through occupied-occupied unitary transformations, we can derive the following energy relationship:

$$E_{c}^{\text{NRPA3}} \approx E_{c}^{\text{EXX-NRPA3}} \approx E_{c}^{\text{EXX-RPA}}$$

Correspondingly, the AC-RPA correlation energy of Eq. (76) expressed in terms of the solutions of the TDHF Eq. (94) and the AC-RPA correlation energy of Eq. (76) evaluated with the solution vectors of Eq. (96), a TDHF equation expressed in terms of EXX orbitals, are similar to each other due to the similarity of the EXX and Hartree-Fock determinants. The latter approximation, i.e., the evaluation of the AC-RPA correlation energy expression (76) with vectors $x_{n} + y_{n} = z_{n}$ and excitation energies $\Omega_{n}$ obtained from the TDHF equation expressed in EXX orbitals, Eq. (96), shall be denoted AC-RPA(EXX). Differences between AC-RPA and AC-
RPA(Exx) correlation energies are caused exclusively by the small differences of
Exx and HF determinants. This will be further discussed considering numerical
results in the sections 5 and 6.

5. Total energies from RPA correlation functionals

Total energies have been calculated for a range of small molecules shown in fig-
ure 1 using the aug-cc-pVTZ basis set of Dunning et al. [118]. The geometries
for the molecules were optimised at the MP2 level using the aug-cc-pVTZ basis
set and are taken from Ref. [119]. The exact-exchange Kohn-Sham (Exx) calcula-
tions were done in two steps: firstly the local exchange potential was calculated
using the uncontracted triple-zeta auxiliary and orbital basis sets from Ref. [75]. In
the second step these exchange potentials were used in a subsequent Kohn-Sham
calculation with the smaller contracted aug-cc-pVTZ basis set in which only the
Coulomb potential was optimised self-consistently. Direct RPA calculations were
also performed using orbitals and eigenvalues from the Perdew-Burke-Ernzerhof
(Pbe) exchange-correlation functional [120]. Note that in this case the exchange
energy was calculated using the exact exchange energy functional in terms of Pbe
orbitals. Core electrons were correlated in the calculations. All calculations were
done using the developers version of the molpro quantum chemistry program [121].

A comparison of total energies for RPA methods based on Hartree-Fock with
total energies from other correlation methods can be found elsewhere [112]. Here
we will focus mainly on the RPA methods based on Kohn-Sham reference determi-
nants. Figure 1 displays the energy differences of several RPA methods to CCSD(T)
reference values. Note that the methods Exx-Rpa and Exx-Rpa\[\infty\] are excluded
in the diagram, since they yield energy differences that are indistinguishable from
the Exx-NRPA3 values on the scale of figure 1, see below. It can be seen that
with exception of Exx-NRPA3 and Exx-SoSEX all other methods overestimate
the CCSD(T) correlation energy. (Note that the correlation energy for Kohn-Sham
based RPA approaches includes also a small contribution due to the differences of
the Exx/Pbe and Hartree-Fock determinants.) For Pbe-dRpa and Exx-dRpa
one can observe the strongest deviations to the CCSD(T) values, which is due to
the large self-correlation errors in both methods. One can see that the Exx-dRpa
and Pbe-dRpa results are very similar to each other and thus it can be stated that
the dRpa functional is relatively insensitive with respect to the choice of the KS
reference determinant. Note that in case of Pbe-dRpa the exchange energy is calculated
in the same way as in Exx based methods, that is, by evaluating the exact
exchange energy expression with Pbe orbitals. While the dRpa self-correlation
error is corrected to some extend by all other RPA methods including exchange
effects (beyond first order) displayed in figure 1, the Exx-NRPA1, Exx-NRPA2
and Exx-NRPA4 methods still strongly underestimate the CCSD(T) energies,i.e.,
strongly overestimate the magnitude of the correlation energy. An analysis of the
third-order contribution of the correlation energy shows that this is due to the
strong negative third-order correlation terms (2b) and (2h) that more than quench
the positive direct term (2a), see tables 2 and 1 (see also Ref. [112]). In case of
Exx-SoSEX these third-order terms are absent, see table 2, but the only third-
order exchange term (2e) in the SoSEX method is generally much smaller than
the (2a) term, so that the CCSD(T) energies are underestimated by Exx-SoSEX
for the molecules shown in figure 1. The best agreement of the considered RPA
methods with the CCSD(T) energies is obtained with the Exx-NRPA3 method
and thus also with the Exx-Rpa and Exx-Rpa\[\infty\] methods that yield almost
identical results, as already mentioned above. The third-order analysis from table
2 shows that the NRPA3 method contains the (2b) term but misses the (2h) contribution and therefore its third-order correlation contribution is generally much smaller than with the EXX-NRPA1, EXX-NRPA2 and EXX-NRPA4 methods.

In figure 2 the differences of the total energies of the methods EXX-NRPA3, EXX-RPA, EXX-RPA[∞], AC-RPA, and AC-RPA(Exx) to the NRPA3 energies are shown for the range of molecules. As already anticipated in section 4, the total energies of the EXX-NRPA3, EXX-RPA, EXX-RPA[∞], and NRPA3 methods do not differ by more than 1–4 millihartree on average. Interestingly the diagram in figure 2 shows that the EXX-RPA[∞] energies are even closer to the NRPA3 energies than the EXX-NRPA3 energies although the methods are not directly related to each other by unitary orbital transformations. The largest deviations to the NRPA3 energies is found for EXX-RPA. Figure 2 also contains the energy differences for the AC-RPA and AC-RPA(Exx) methods to NRPA3. Going from the AC-RPA over the AC-RPA(Exx) and the EXX-RPA[∞] method the importance of various changes between the methods can be considered step by step. Differences between the AC-RPA and the AC-RPA(Exx) method are small and due to the only small differences between EXX and HF determinants, differences between the AC-RPA(Exx) and the EXX-RPA[∞] correlation energies are more substantial and are due to the fact whether or not the matrix Δ in Eq. (96) and Eq. (97) are scaled with the coupling constant or not. This scaling obviously has an important influence. Finally the difference between the EXX-RPA[∞] and the EXX-RPA correlation energies is small again. This difference is due to the difference between the right hand sides of Eq. (97) and the TDEXX equation (36) which are only of second order in $\varepsilon^{-1/2}|A - B + \Delta|\varepsilon^{-1/2}$. In the next section it will be investigated whether these energy differences affect energy differences for a set of chemical reactions.

Figure 3 displays the correlation energies for Hartree-Fock based and EXX-based RPA methods for the molecules CH$_4$ (top) and HCOOH (bottom) together with the corresponding sum of the second- and third-order contributions in each case. It can be observed that the NRPA1, NRPA3 and NRPA4 correlation energies are very close to the corresponding EXX-NRPA1, EXX-NRPA3 and EXX-NRPA4 correlation energies. This, again, can be explained by the closeness of the RPA amplitudes due to the similarity between the time-dependent Hartree-Fock and time-dependent EXX equations. In contrast to this, the NRPA2 and EXX-NRPA2 correlation energies differ strongly from each other, because the second-order correlation energy contained in the energy expression for EXX-NRPA2 (see Eq. (66)) differs strongly if evaluated with EXX or Hartree-Fock orbitals due to the different orbital energies in both cases. The differences of the orbital eigenvalue spectrum are also the reason why one can observe huge differences of the correlation energies for the dRPA and SOSEX methods in the diagrams in figure 3. Since the single particle transition energies in EXX are generally lower than in Hartree-Fock theory due to the self-interaction correction for the virtual states, the EXX-dRPA and EXX-SOSEX correlation energies are considerably larger in magnitude than the corresponding dRPA and SOSEX correlation energies, respectively. In case of adiabatic connection RPA methods a significant difference between the AC-RPA and EXX-RPA[∞] can be seen in figure 3 which is due to the differences between the TDHF and TDEXX response functions at coupling strengths between 0 and 1, compare with Ref. [55] where the differences between AC-RPA and EXX-RPA is discussed. A comparison of the total correlation energies with the corresponding sum of the second- and third-order correlation terms shows that in case of the Hartree-Fock based RPA methods the higher order correlation contributions, given by the difference $E_c - E_c^{(2)} - E_c^{(3)}$, are, with exception of the NRPA2 values, rather small, while in
case of the EXX based methods larger higher order correlation contributions can be observed. Thus the perturbation expansion of the RPA correlation energy is not that well converged in low orders if calculated with KS orbitals.

6. Reaction energies from RPA correlation functionals

The total energies for the set of molecules shown in figure 1 were used to calculate the reaction energies for a set of 16 chemical reactions listed in the first column in table 3.

Table 3 shows a comparison between the NRPA3, EXX-NRPA3, EXX-RPA and EXX-RPA\[∞\] methods as well as for the AC-RPA and AC-RPA(EXX) methods for the set of chemical reactions. The last column in table 3 contains the CCSD(T) reference data from Ref. [53]. It can be seen that in spite of slight deviations in the total energies between the different RPA methods, see table 2, their reaction energies for the given chemical reactions are basically identical among the NRPA3, EXX-NRPA3, EXX-RPA and EXX-RPA(EXX) on the one hand and among AC-RPA and AC-RPA(EXX) on the other hand. The root-mean squared (rms) errors and mean-absolute (mae) errors to the CCSD(T) reaction energies all differ by no more than 0.3 millihartree, see last two lines in table 3. Therefore one can conclude that one can practically expect the same accuracy from the NRPA3, EXX-NRPA3, EXX-RPA and EXX-RPA\[∞\] methods and correspondingly for AC-RPA and AC-RPA(EXX) in quantum chemistry applications.

In figure 4 the rms errors (top diagram) and relative percentual deviations (bottom diagram) of various Kohn-Sham orbital based RPA methods to the CCSD(T) reference reaction energies are shown. Along with the errors for the RPA methods, the diagrams in figure 4 also contain the corresponding error bars for Hartree-Fock, MP2 (second-order Møller-Plesset) and CCSD for comparison. Note that the errors for some RPA methods (EXX-NRPA1, EXX-NRPA2 and EXX-NRPA4) are not shown due to their strong differences to the CCSD(T) values which are even worse than Hartree-Fock errors. For the RPA methods shown in figure 4 one can observe rms errors that are consistently smaller than with MP2, but all methods have larger average errors than CCSD. Interestingly, the PBE-dRPA, EXX-dRPA and EXX-SOSEX methods yield, for the chemical reactions considered, about the same accuracy as the EXX-RPA method in spite of strongly differing total energies, see section 5: for EXX-dRPA the rms error is only about 0.2 kcal/mol larger than with EXX-RPA and the percentual deviation, which more emphasises reactions with small reaction energies, is even about 1% smaller compared to EXX-RPA. The SOSEX approach, which corrects the dRPA correlation method in second (and higher) order, does not lead to an improvement of the dRPA values for the set of chemical reactions.

7. Summary

Starting from a relation between the two-particle density matrix and the response function of the many-body system, expressions for the correlation energy of electronic systems have been given in terms of the interacting and noninteracting response functions. This relation, called fluctuation-dissipation theorem, represents a general way to obtain correlated ground-state properties of an interacting many-body system and solely depends on approximations of the response function. By combining this ansatz with a coupling-constant integration along the adiabatic connection the adiabatic-connection fluctuation-dissipation theorem is obtained which
provides an exact expression for the correlation energy as defined in the Kohn-Sham formalism of density-functional theory.

A first approximation to the interacting response function is obtained by taking Coulomb interactions between the particles into account. This approximation is termed as direct random-phase approximation (dRPA) and has most often been used for the description of solid states in the past. It turns out that, at least if a Hartree-Fock (HF) reference state is used, total dRPA correlation energies are not very accurate due to a large self-correlation error. An advantage of RPA based on a Kohn-Sham (KS) reference determinant is that errors may be somewhat reduced since a KS description of the reference state can mimic the effect of missing singly excited determinants in RPA methods.

In order to correct the self-correlation error of dRPA, exchange interactions have to be accounted for in second and higher orders, that is, the electron interaction operator has to be complemented by an additional exchange kernel. It has been shown that several RPA methods can be derived that include exchange interactions. While all of them yield, in a perturbation series expansion, the correct second-order expression known from many-body perturbation theory, they differ in third-order of perturbation theory. An analysis of the different RPA methods based both, on HF and exact Kohn-Sham exchange (EXX) determinants reveals that the differences of the correlation energies in third order lead also to strong differences in the total correlation energies of these methods. A comparison with coupled-cluster singles doubles with perturbative triples (CCSD(T)) energies shows, that with exception of the (in this work termed) NRPA3 and adiabatic connection RPA method the other RPA variants considered in this work yield large errors for the correlation energies for a set of small molecules. It has been shown that for RPA based on the EXX determinant, the corresponding EXX-NRPA3 and EXX-RPA (the adiabatic connection RPA method in an EXX KS formalism) are closely related to each other and yield similar total energies. Since the (HF based) NRPA3 and the EXX-NRPA3 method too give similar results due to the closeness between the HF and EXX determinants, also a relation between the HF based NRPA3 method and the EXX based EXX-RPA method can be derived.

The accuracy of the different RPA methods considered in this work has also been tested for the description of reaction energies for a set of 16 chemical reactions for some small organic molecules. By comparing the results with accurate CCSD(T) reference values, it was found that the methods that have the smallest errors for the total energies, namely NRPA3 and EXX-RPA, also give the best agreement for reaction energies. The, historically, older RPA methods termed as NRPA1 (identical to the ring coupled-cluster doubles method), NRPA2 and NRPA4 here, yield large errors also for the description of reaction energies. In contrast to this, the KS orbital based dRPA and SOSEX approach produce reaction energies that are not much worse than reaction energies energies from NRPA3 or EXX-RPA methods and even slightly better than with second-order Møller-Plesset perturbation theory. This result may be interesting from a practical point of view, since dRPA and SOSEX methods can be implemented in a more efficient way than NRPA3 and EXX-RPA methods.

Generally it can be concluded that the use of Kohn-Sham orbitals in RPA methods instead of Hartree-Fock orbitals offers new possibilities to make RPA methods both, more accurate and also more efficient for the description of correlated molecular ground states. The first point may be true, since the Kohn-Sham orbitals can be expected to be closer to variationally optimised orbitals within RPA methods, since it has been shown that, depending on the underlying exchange-correlation potentials, KS orbitals are closer to Brueckner orbitals from a coupled-cluster doubles...
wave function than HF ones [88]. The second argument regarding the efficiency to date holds true especially for solids for which direct RPA methods have been implemented with a low computational cost [40]. In case of RPA methods for molecules the development of efficient computer programs is a field of active research and a number of different methods were already presented in recent years [39, 45].

Acknowledgments

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References

13. Orbital-dependent correlation functionals

13. Orbital-dependent correlation functionals

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Table 1. Second- and third-order correlation energy terms. The definition \( M_{ia,jb} = \frac{M_{ia,jb}}{\varepsilon_i - \varepsilon_j} \) for a matrix \( M \) has been used. The matrix elements are defined as \( C_{ia,jb} = \langle i|a|b \rangle \), \( K_{ia,jb} = P_{ab} C_{ia,jb} \) (the permutation operator \( P_{ab} \) exchanges indices \( a \) and \( b \)), \( \Delta_{ia,jb} = \delta_{ab} (\varepsilon_i^{NL} - \varepsilon_j^{NL}) - \delta_{ij} (\varepsilon_i - \varepsilon_j) \) (\( \varepsilon_i^{NL} \): nonlocal exchange potential, \( \varepsilon_i \): local exchange potential) and \( \varepsilon_{ia} = \varepsilon_i - \varepsilon_a \). In the terms (2i)-(2l) the matrix elements are defined according to \( E_{cd}^{ad} = \langle a|d|c \rangle \) and \( S_{kl}^{ij} = \langle ij|kl \rangle \). The terms (1a) and (1b) correspond to the direct and exchange part of the second-order correlation energy, terms (2a)-(2h) are particle-hole terms and terms (2i)-(2l) are particle-particle—hole-hole terms. Note that only particle-hole terms are contained in conventional RPA correlation methods, see table 2. The additional terms (2b\( ^{lx} \)), (2d\( ^{lx} \)), (2g\( ^{lx} \)) and (2h\( ^{lx} \)) originate from local exchange and occur only in RPA methods based on EXX. Note that the terms (2d) and (2g) as well as (2e) and (2f) are identical if real-valued orbitals are used.

<table>
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<tr>
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<tbody>
<tr>
<td>(1a)</td>
<td>( \frac{1}{2} \text{Tr} [\bar{C}C] )</td>
</tr>
<tr>
<td>(1b)</td>
<td>( \frac{1}{2} \text{Tr} [\bar{C}K] )</td>
</tr>
<tr>
<td>(2a)</td>
<td>( \text{Tr} [\bar{C}C\bar{C}] )</td>
</tr>
<tr>
<td>(2b)</td>
<td>(- \text{Tr} [\bar{C}J\bar{C}] )</td>
</tr>
<tr>
<td>(2c)</td>
<td>( \text{Tr} [\bar{K}C\bar{K}] )</td>
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<tr>
<td>(2d)</td>
<td>( \text{Tr} [\bar{K}J\bar{C}] )</td>
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<tr>
<td>(2e)</td>
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<tr>
<td>(2g)</td>
<td>( \text{Tr} [\bar{C}J\bar{K}] )</td>
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<td>(2h)</td>
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<td>(2p)</td>
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Table 2. Comparison of the third order expansions of various RPA correlation methods. The diagram labels correspond to the ones given in table 1. The column values correspond to the respective prefactor for each perturbation diagram.

<table>
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<td>(2b)</td>
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<td>(2c)</td>
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<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
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</tr>
<tr>
<td>(2d)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(2e)</td>
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<td>0.5</td>
<td>1</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(2f)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(2g)</td>
<td>1</td>
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<td>1</td>
<td>0</td>
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<tr>
<td>(2h)</td>
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<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
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<td>0</td>
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<tr>
<td>(2i)</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>(2j)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
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<td>(2k)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>(2l)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Note that higher order RPA approaches using the wave function ansatz from Eq. (67) are exact through third order.

b The EXX-RPA[∞] method contains the same perturbation diagrams as AC-RPA in the Hartree-Fock basis, but differs from it due to a different separation of the response function into an uncoupled and correlation part of the response function, see text. This leads to additional diagrams for the third-order contributions (2b), (2d), (2g) and (2h) which are given in table 1.

c These contributions are accompanied by additional terms in case of RPA with exact local exchange, see table 1.
Table 3. Reaction energies for several RPA methods in a.u. (aug-cc-pVTZ basis set). Geometries taken from H.-J. Werner, T.B. Adler, and F.R. Manby, *J. Chem. Phys.* 126 (2007) 164102. The last two lines show the root-mean squared (rms) and mean-absolute errors (mae) to the CCSD(T) reaction energies in $10^{-3}$ a.u.

<table>
<thead>
<tr>
<th>reaction</th>
<th>NRPA3</th>
<th>EXX-NRPA3</th>
<th>EXX-RPA</th>
<th>EXX-RPA[$\infty$]</th>
<th>AC-RPA</th>
<th>AC-RPA(EXX)</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_2+\text{H}_2\rightarrow\text{C}_2\text{H}_4$</td>
<td>-0.084</td>
<td>-0.083</td>
<td>-0.083</td>
<td>-0.084</td>
<td>-0.086</td>
<td>-0.085</td>
<td>-0.081</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4+\text{H}_2\rightarrow\text{C}_2\text{H}_6$</td>
<td>-0.068</td>
<td>-0.068</td>
<td>-0.067</td>
<td>-0.068</td>
<td>-0.070</td>
<td>-0.069</td>
<td>-0.066</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6+\text{H}_2\rightarrow\text{2CH}_4$</td>
<td>-0.029</td>
<td>-0.030</td>
<td>-0.030</td>
<td>-0.030</td>
<td>-0.030</td>
<td>-0.030</td>
<td>-0.029</td>
</tr>
<tr>
<td>$\text{CO}+\text{H}_2\rightarrow\text{HCHO}$</td>
<td>-0.011</td>
<td>-0.010</td>
<td>-0.010</td>
<td>-0.010</td>
<td>-0.012</td>
<td>-0.011</td>
<td>-0.011</td>
</tr>
<tr>
<td>$\text{HCHO}+\text{H}_2\rightarrow\text{CH}_3\text{OH}$</td>
<td>-0.052</td>
<td>-0.052</td>
<td>-0.051</td>
<td>-0.051</td>
<td>-0.053</td>
<td>-0.053</td>
<td>-0.049</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2+\text{H}_2\rightarrow\text{2H}_2\text{O}$</td>
<td>-0.144</td>
<td>-0.145</td>
<td>-0.145</td>
<td>-0.144</td>
<td>-0.146</td>
<td>-0.147</td>
<td>-0.139</td>
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<tr>
<td>$\text{C}_2\text{H}_2+\text{H}_2\text{O}\rightarrow\text{CH}_3\text{CHO}$</td>
<td>-0.067</td>
<td>-0.065</td>
<td>-0.064</td>
<td>-0.066</td>
<td>-0.069</td>
<td>-0.067</td>
<td>-0.064</td>
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<tr>
<td>$\text{C}_2\text{H}_4+\text{H}_2\text{O}\rightarrow\text{C}_2\text{H}_5\text{OH}$</td>
<td>-0.028</td>
<td>-0.027</td>
<td>-0.026</td>
<td>-0.026</td>
<td>-0.029</td>
<td>-0.027</td>
<td>-0.026</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CHO}+\text{H}_2\rightarrow\text{C}_2\text{H}_5\text{OH}$</td>
<td>-0.045</td>
<td>-0.045</td>
<td>-0.045</td>
<td>-0.044</td>
<td>-0.046</td>
<td>-0.046</td>
<td>-0.042</td>
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<tr>
<td>$\text{CO}+\text{NH}_3\rightarrow\text{HCONH}_2$</td>
<td>-0.018</td>
<td>-0.017</td>
<td>-0.016</td>
<td>-0.017</td>
<td>-0.020</td>
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<td>-0.018</td>
</tr>
<tr>
<td>$\text{CO}+\text{H}_2\text{O}\rightarrow\text{CO}_2+\text{H}_2$</td>
<td>-0.008</td>
<td>-0.008</td>
<td>-0.007</td>
<td>-0.008</td>
<td>-0.010</td>
<td>-0.009</td>
<td>-0.012</td>
</tr>
<tr>
<td>$\text{HNCO}+\text{NH}_3\rightarrow\text{NH}_2\text{CONH}_2$</td>
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<td>-0.036</td>
<td>-0.035</td>
<td>-0.036</td>
<td>-0.039</td>
<td>-0.038</td>
<td>-0.033</td>
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<tr>
<td>$\text{CO}+\text{CH}_3\text{OH}\rightarrow\text{HCOOCH}_3$</td>
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<td>-0.022</td>
<td>-0.021</td>
<td>-0.022</td>
<td>-0.025</td>
<td>-0.024</td>
<td>-0.025</td>
</tr>
<tr>
<td>$\text{HCOOH}+\text{H}_3\rightarrow\text{HCONH}_2+\text{H}_2\text{O}$</td>
<td>-0.002</td>
<td>-0.002</td>
<td>-0.002</td>
<td>-0.002</td>
<td>-0.002</td>
<td>-0.002</td>
<td>-0.001</td>
</tr>
<tr>
<td>$\text{CO}+\text{H}_2\text{O}_2\rightarrow\text{CO}_2+\text{H}_2\text{O}$</td>
<td>-0.152</td>
<td>-0.153</td>
<td>-0.152</td>
<td>-0.152</td>
<td>-0.156</td>
<td>-0.156</td>
<td>-0.151</td>
</tr>
<tr>
<td>$\text{H}_2\text{CCO}+\text{CH}_2\text{O}\rightarrow\text{C}_2\text{H}_4\text{O}+\text{CO}$</td>
<td>-0.008</td>
<td>-0.008</td>
<td>-0.008</td>
<td>-0.008</td>
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<td>-0.007</td>
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<td>rms [$10^{-3}$ a.u.]</td>
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<td>2.9</td>
<td>2.9</td>
<td>2.6</td>
<td>3.9</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>mae [$10^{-3}$ a.u.]</td>
<td>2.5</td>
<td>2.5</td>
<td>2.4</td>
<td>2.3</td>
<td>3.3</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>
13. Orbital-dependent correlation functionals

Molecular Physics

Figure 1. Energy differences to CCSD(T) reference energies for various Kohn-Sham orbital based RPA methods.

Figure 2. Energy differences to NRPA3 energies (Eq. (69)) for the methods EXX-NRPA3 (Eq. (107)), EXX-RPA, EXX-RPA[∞] (Eq. (100)), AC-RPA (Eq. (76)) and AC-RPA(EXX).
Figure 3. Correlation energies for various RPA methods of the CH$_4$ (top diagram) and HCOOH molecule (bottom diagram). The first and third bars show the sum of the second- and third-order energy for the HF-based and EXX-based RPA methods and the second and fourth bars show the total correlation energies for the HF-based and EXX-based RPA methods, respectively.
Figure 4. Root mean squared errors (rms) and relative percentual deviations for Hartree-Fock and various correlation methods to CCSD(T) reaction energies shown in table 3.
14. Other scientific publications

14.1. A self-contained and portable density functional theory library for use in Ab Initio quantum chemistry programs

**journal:** Journal of Computational Chemistry

**author(s):** P. Salek, A. Heßelmann

**year:** 2007

**volume:** 28

**pages:** 2569

**Key words:**

- functional differentiation
- automatic code generation
- numerically unstable functionals
- Coulomb attenuated functionals
A Self-Contained and Portable Density Functional Theory Library for Use in Ab Initio Quantum Chemistry Programs

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Abstract: A major unresolved problem of density functional theory is the yet unknown exchange-correlation functional, which leads to a proliferation of its less or more successful approximations. A practical implementation of these numerous functionals can present a substantial challenge particularly if the higher order functional derivatives are required. We present a systematic method of functional implementation. The method allows a clean handling of a large number of functionals in a mutually independent way. We developed an extensive set of automatic test routines to facilitate functional and derivative testing with respect to the implementation correctness and numerical stability. An integral part of the presented solution is a program for automatic code generation from analytical formulas that uses only freely available tools. Code for evaluation of functionals and their first, second, third, and fourth derivatives can be generated, which accelerates the development, implementation, and testing of new functionals.


Key words: Density Functional Theory; LDA; automatic code generation

Introduction

When Hohenberg and Kohn presented their theorems and founded the density functional theory (DFT), they left one major problem unresolved: determination of the energy functional. While the energy functional remains unknown until today, theorists came up over the years with various approximations to it. One difficult problem—the kinetic energy functional that the generalization of the Thomas-Fermi method as suggested by Lewis1 fails to describe, was nicely solved by Kohn and Sham (KS) by introducing orbitals and computing the kinetic energy in a way similar to Hartree–Fock theory.2 The method they proposed is nowadays probably the most common way of estimating that part of the energy functional. The only unknown quantity in the KS model is the exchange-correlation (xc) functional, the determination of which remains a challenge. The Dirac–Slater formula is the one that is commonly used to estimate the dominant share of the exchange part of the interaction.2–4 The first closed formulas to approximate the correlation interaction of the electron gas as a function of its density, which were usable in chemistry, were presented by Perdew and Zunger5 and later improved by Vosko et al.6 The Dirac–Slater and VWN functionals are used until now and are possibly the most commonly used functionals of the local density approximation (LDA), i.e., that assume that the exchange-interaction energy is an integral of local energy contributions

\[ E_{xc} = \int F_{xc}(\rho(\vec{r})) \, d\vec{r} \]  

However, LDA was shown to be not an impressively good approximation for molecules that have electron densities spanning over several orders of magnitude. It has become clear that some additional nonlocal correction is needed to make the DFT work better for molecular applications. Additional density-gradient dependent corrections were introduced to improve the quality of the results generated by DFT, transforming LDA into a Generalized Gradient Approximation (GGA). Becke proposed in 1988 a gradient-dependent correction to the Dirac–Slater exchange functional.7 In the same year a novel form of the correlation energy functional was proposed by Lee et al.8 They were soon followed by many other approximations.9–16 Such gradient-dependent functionals, however, while nonlocal, cannot account for global slow density changes. Therefore various hybrid functionals including a fraction of non-local Hartree-Fock exchange were proposed17–19 as an attempt to mitigate this deficiency. This class of functionals

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proved to be very successful and is possibly the most commonly used one in quantum chemistry nowadays. Another way of including non-locality is to include the density current \( j(\vec{r}, t) \) dependency, which for a system described by a wave function \( \phi(\vec{r}, t) \) is given as

\[
\dot{j}(\vec{r}, t) = -i\frac{1}{2}(\phi^*(\vec{r}, t)\nabla\phi(\vec{r}, t) - \phi(\vec{r}, t)\nabla\phi^*(\vec{r}, t)).
\]  

(2)

It has been argued that the inclusion of the current may improve the prediction of linear response properties, like polarizabilities of long conjugate chains.20,21 We note that current density is also needed to treat magnetic field perturbations explicitly.

A self-contained density functional code has to be able to evaluate all these numerous density functionals. The vast amount of raw formulas needed for each of them makes it difficult to cleanly separate different modules of the code, scaring young adepts by its steep learning curve. Additionally, many different conventions are used throughout the literature: some functionals are expressed in terms of the total density and spin density, others in terms of \( \alpha \) - and \( \beta \)-spin densities. The expressions are often complicated, making it time consuming to derive, implement, and test high order functional derivatives required, for example for second, third, and fourth order time dependent DFT applications.22, 23 This formula complexity may lead to the fact that a direct comparison of apparently the same functionals between different programs is sometimes impossible. The authors are aware of at least two different variants of the B3LYP and PBE functionals, respectively. These difficulties also caused that in some cases second and higher order derivatives have been computed by numerical differentiation.18

The aim of this study is to present a unified DFT functional framework that is meant to achieve the following goals: (1) Functionals are to be implemented in a uniform way so that simple finite-difference methods can be used to verify the correctness of functional derivative implementation. (2) The entire functional module has to be hermetic so that other parts of the program are independent of the functional currently used for the respective calculation. (3) The framework should allow for automatic code generation to the maximum possible extent.

Similar attempts have been made before.24 This one differs in a few points: (a) it delivers higher functional derivatives up to the fourth order, (b) it does not require external commercial software to run, (c) the expressions get simplified extensively and common terms are factored out, and, finally, (d) it delivers higher functional derivatives up to the fourth order. Our methodology provides also an uniform way to process the functional configuration and set its parameters if needed. This makes adding a new functional as simple as registering it in the array of available functionals by adding just one entry. The framework is able to find the functional when requested from the program input and locates also functions computing the functional or its first, second, or third derivatives.

Automatic singularity localization or numerical stability checking is not attempted at this stage. It is known that reliable automatic detection of numerical stability is difficult and probably the only method that is reasonably reliable is interval arithmetic.25 To contain this deficiency, we developed an extensive testing framework for both the functional values themselves as well as all their derivatives. Such tests are vital: We show in Numerically Unstable Functionals section an example of a functional that has numerical instabilities over a wide range of density values. The code described in this article is available under the terms of the GNU General Public License.26

### The Framework

The DFT assumes the existence of a density functional \( E[\rho] \). The ground state density is determined by minimizing this functional. For practical reasons the local form of the density functional is commonly used, possibly with additional gradient dependence, which is omitted here for clarity reasons. The Kohn–Sham formulation of DFT requires the construction of the Kohn–Sham exchange-correlation (xc) potential matrix \( V_{xc} \) expanded into the basis set \( \{\phi_p(\vec{r})\} \)

\[
V_{xc}^{\rho_\alpha} = \int \phi_p(\vec{r})\phi_q(\vec{r}) \left( \frac{\partial F_{xc}}{\partial \rho} \right)_{\rho = \rho(\vec{r})} d\vec{r}
\]  

(3)

where \( \partial F_{xc}/\partial \rho \) is the functional derivative of the xc-energy given in Eq. (1). Time-dependent DFT may require even higher derivatives of \( F_{xc}(\rho) \).22, 23 This number of needed derivatives is multiplied additionally by the fact that in many practical applications an unrestricted formalism has to be used and \( \alpha \) and \( \beta \) electron densities and gradients have to be treated as independent. Specifically, the derivatives need to be evaluated separately with respect to \( \rho_\alpha \), \( \rho_\beta \) and corresponding density gradient components \( \nabla \rho_\alpha, \nabla \rho_\beta, \nabla \rho_\alpha \cdot \nabla \rho_\beta \) . However, many functionals are expressed in terms of the norm of density gradient to the first power. Therefore we introduce \( g_e := |\nabla \rho_e| \), \( w := \nabla \rho_e \cdot \nabla \rho_e \) and for convenience choose to implement the functionals in terms of the following parameters \( \{\rho_\alpha, \rho_\beta, g_e, g_\alpha \cdot g_\beta\} \). Utilizing the Gelfand–Fomin formula and integration by parts leads to the following expression for the exchange-correlation contribution to the Kohn–Sham matrix for GGA functionals:

\[
V_{xc}^{\rho_\alpha} = \sum_\sigma \int \left[ \phi_p(\vec{r})\phi_q(\vec{r}) \left( \frac{\partial F_{xc}}{\partial \rho_\alpha} \right)_{\rho = \rho(\vec{r})} 
\right.
\]

\[
+ \nabla(\phi_p(\vec{r})\phi_q(\vec{r})) \left( \frac{\partial F_{xc}}{\partial g_\alpha} + \frac{\partial F_{xc}}{\partial g_\beta} \right) \]  

\]  

(4)

which has the advantage that no second derivatives of the basis functions are required.

One of our goals was to take advantage of the “implement once, use everywhere” strategy. This principle is used to share the functional code between the DIRAC, DALTON and ERGO quantum chemistry programs.28–30 The “One file per functional” principle makes it easier to introduce changes and automatically generate ready to compile functional modules. All the functional routines accept arguments and return values in the same way, allowing for modification of the input structures so that the same code can handle LDA, GGA, and possibly current-dependent density functionals.

The functional source code needs to export only one symbol: a structure containing pointers to the functional name (used in input
14. Other scientific publications

DFT Library for Use in Ab Initio Quantum Chemistry Programs

parsing and calculation reports) and a number of functions internal to the module that actually perform the evaluation of the functional and its various derivatives. Few dependencies make it easy to port the source code between different programs. Only two modifications are necessary to drop a new functional in to the library: the list of available functionals needs to be modified, and the name of the file containing the functional source has to be added to the make file.

The routines that constitute the implementation compute the functional or its derivatives for a single point in space. The implementation may have additional functions for setting up the functional if necessary: changing the default values of the parameters of the functional is one example. We have considered to process several grid points in one call but such an approach complicates the code without noticeable performance gains. This can be understood by noticing that the call overhead of a routine with only few arguments is often negligible compared with the usually large number of floating point operations needed to evaluate the functional or particularly all its derivatives to a given order.

The implementation of a functional has to set the following fields in the exported Functional structure:

```c
struct Functional_ {
    const char* name;
    IsGGAFunc is_gga;
    ReadInputFunc read;
    ReportFunc report;
    EnergyFunc func;
    FirstOrderFun first;
    SecondOrderFun second;
    ThirdOrderFun third;
    FourthOrderFun fourth;
};
```

where all the fields apart from name are function pointers. Field name defines the name of the functional. This field can be used to report the currently selected functional as well as for input processing. Field is_gga is a pointer to a function that determines whether the functional is density gradient dependent or not. This field is deliberately not a variable but a function to allow for dynamic type determination for functionals consisting of several contributions. Field read points to a function that configures the functionals from a configuration string. This is useful for functionals that depend on frequently changed coefficients—these coefficients can be passed from the calculation input. This pointer can be NULL if the given functional is not configurable. Another field, report, points to a function that reports more information about the selected functional. It can be set to NULL—in such a case only the functional name will be printed. Providing an own reporting function is recommended for configurable functionals that depend on variable parameters. Remaining fields point to routines computing the functional and its derivatives. Function energy computes the value of the functional \( F \) for given density. Function first computes first derivatives of the functional: \( \frac{\partial F}{\partial \rho}, \frac{\partial F}{\partial \rho_x}, \frac{\partial F}{\partial \rho_y}, \frac{\partial F}{\partial \rho_z} \). Only fields that are nonzero are to be altered—derivatives that always vanish need not to be set. The derivatives computed by this routine are used for example for the evaluation of Kohn–Sham matrix elements. Next field second points to a function that computes all first derivatives as well and additionally all second order derivatives: \( \frac{\partial^2 F}{\partial \rho^2}, \frac{\partial^2 F}{\partial \rho_x \partial \rho_y}, \frac{\partial^2 F}{\partial \rho_y \partial \rho_z}, \frac{\partial^2 F}{\partial \rho_z \partial \rho_x} \).

Remaining fields are function pointers to routines computing the second, third and fourth derivatives as well. In general, we observe that the first derivatives are the most important quantities, but computing also all third and fourth order derivatives, respectively. We designed the code structure so it can be extended to higher orders if required.

**Implemented Functionals**

### DFT Functionals

The functionals we programmed can be divided into two groups: generic and combined functionals. Combined functionals are linear combinations of generic ones. We provided a facility to create own combined functionals by using a separate keyword.

**Generic Functionals**

**BECKE**

Becke exchange correction presented in Ref. 7. Observe that the full Becke88 exchange functional is given by the sum Slater + Becke.

- **B97**
  - hybrid Becke exchange-correlation functional.
  - **B97-1**
  - Hamprecht et al. hybrid exchange-correlation functional.
  - **B97-2**
  - Wilson et al. hybrid exchange-correlation functional.

**HCTH93**

Hamprecht, Cohen, Tozer and Handy exchange-correlation functional.

**KT**

Keal and Tozer GGA exchange functional.

**LB94**

Asymptotically correct xc-potential of Leeuw and Baerends. This functional improves the description of the asymptotic density on the expense of core and inner valence.

**LYP**

correlation functional by Lee, Yang and Parr.

**OPTx**

exchange functional of Handy and Coworkers.

**P86**

correlation functional of Perdew.

**PBEc**

correlation functional by Perdew et al.

**PBEex**

exchange functional by Perdew et al.

**PW86x**

Perdew and Wang exchange functional.

**PW91**

correlation functional of Perdew et al.

**Slater**

Dirac–Slater exchange functional.

**VWN3**

correlation functional by Vosko et al. (number III).

**VWN5**

correlation functional by Vosko et al. (number V—the recommended parametrization).

### Combined Functionals

A number of useful exchange-correlation functionals are linear combinations of those mentioned above. Several commonly occurring combinations are preprogrammed but we allow for creating arbitrary user-specified mixes with a separate keyword **Combine**.

**BLYP**

is a sum of the Slater functional, Becke correction, and the LYP correlation functional. It is equivalent to Combine slater=1 becke=1 lyp=1

**B3LYP**

the Becke three-parameter hybrid functional equivalent to:

Combine hf=0.2 slater=0.8 becke=0.72 lyp=0.81 vwn5=0.19
B3LYP-G hybrid functional with VWN3 form used for correlation—this is the form used by the Gaussian quantum chemistry program. This functional can be explicitly set up by

\[
\text{Combine hf}=0.2 \text{ slater}=0.8 \text{ becke}=0.72 \text{ lyp}=0.81 \text{ vwn3}=0.19
\]

BP86 Becke exchange functional and Perdew86 correlation functional. The explicit form is:

\[
\text{Combine slater}=1 \text{ becke}=1 \text{ p86}=1
\]

B3P86 variant of B3LYP with P86 functional used instead of LYP for correlation.

\[
\text{Combine hf}=0.2 \text{ slater}=0.8 \text{ becke}=0.72 \text{ p86}=0.81 \text{ vwn3}=0.19
\]

CAMB3LYP Coulomb Attenuated Method Functional of Yanai et al.19 This functional accepts additional arguments \( \alpha, \beta, \) and \( \mu \) to modify the fraction of HF exchange for short-range interactions, additional fraction of HF exchange for long-range interaction and the interaction switching factor \( \mu \). This input can be specified as follows:

\[
\text{CAMB3LYP alpha}=0.190 \text{ beta}=0.460 \text{ mu}=0.330
\]

KT1 Slater-VWN5 functional with the KT GGA correction.12,37

\[
\text{Combine slater}=1 \text{ vwn5}=1 \text{ kt}=-0.006
\]

KT2 differs from KT1 only in that the weights of the Slater and VWN5 functionals are from an empirical fit.12,37

\[
\text{Combine slater}=1.07173 \text{ vwn5}=0.576727 \text{ kt}=-0.006
\]

KT3 a hybrid functional of Slater, OPTX and KT exchange with the LYP correlation functional.13 The explicit form is

\[
\text{Combine slater}=1.092 \text{ kt}=-0.004 \text{ lyp}=0.864409 \text{ optx}=-0.925452
\]

OLYP is the sum of the OPTX exchange functional with the LYP correlation functional.15

\[
\text{Combine slater}=1.05151 \text{ optx}=-1.43169 \text{ lyp}=1
\]

Mixed functionals such as OP86 and OPW91 may be constructed with Combine by trivial modification of the line above.

PBE0 a hybrid functional of Perdew, Burke and Ernzerhof with 0.25 weight of exact exchange, 0.75 of PBEx functional and PBEc correlation functional.18,38

\[
\text{Combine hf}=0.25 \text{ pbeex}=0.75 \text{ pbec}=1
\]

PBE same as above but with exchange estimated exclusively by the PBEx functional.11 This is the form used by e.g. CADPAC and NWChem quantum chemistry programs.

\[
\text{Combine pbeex}=1 \text{ pbec}=1
\]

It is worth mentioning that the quantum chemistry program Molpro uses the PW91c correlation functional instead of PBEc which is equivalent to the following:

\[
\text{Combine pbeex}=1 \text{ pw91c}=1
\]

Testing Framework

The way from providing an analytical formula to a code that can be used to evaluate third-order derivatives of the functional is not straightforward. The functional expressions are often lengthy, may use auxiliary functions and most often depend non-linearly on their parameters which causes that the derivative expression become even more lengthy. The task is not made simpler by the fact that there are forty third order functional derivatives to be evaluated and the number of fourth order derivatives is even higher. We have therefore developed test programs that can be used to test the functional routines. First program (fun-tester) uses a finite difference method for error detection in functional derivatives as well as numerical instabilities. This program scans a wide range of density and density gradient values and checks whether the derivatives computed analytically by the automatically generated code match those evaluated numerically. For example, the first derivatives \( \frac{\partial F}{\partial a} \), where \( a \) is one of the density or density gradient components are tested as follows:

\[
\frac{\partial F}{\partial a} = \frac{F(a + \Delta a) - F(a - \Delta a)}{2\Delta a}.
\]

Above, \( \Delta a \) is a small displacement of the variable \( a \). This method allows to test all the derivatives, from the first to the fourth but does not validate the computed exchange-correlation energies. For this purpose, a second program (inttest) is provided. It computes the exchange-correlation energy for a spherically symmetric charge distribution described by either gaussians or slater functions. The computed value can be compared with one obtained by other means, for example with other programs. A set of reference values for commonly used functionals is provided with the library.

Automatic Code Generation

The increasing complexity of quantum chemistry methods and thereby the difficulties which arise when algebraic formulas have to be translated into a computer programming language makes the development of automatic code generators particularly useful in this field. Setting up suitable translators from the abstract mathematical formulas to computer languages like FORTRAN or C not only accelerates the implementation of new quantum chemistry methods but also limits the amount of errors which often occur in large self-written computer programs. Since nowadays quantum chemistry programs are more and more used by "nonexperts" in the field of theoretical chemistry as a black-box tool to make predictions about chemical structures or reactivities, it is of crucial importance that one can rely on the results produced by these programs.

Automatic code generators in different fields of computational chemistry have been developed by several groups before, e.g., for the calculation of atomic integrals,39 in the field of Coupled-Cluster or Configuration-Interaction60 via the general “Tensor Contraction Engine” framework,41 or, as in this work, for the production of Density Functional code.24 In the latter case the main purpose is to
produce a framework in which the user can derive a complete working computer code for the calculation of the exchange-correlation energy kernel and its derivatives just by defining the underlying xc-energy kernel in a most convenient manner. In this work this is done by creating an input file which can be interpreted by the MAXIMA computer algebra system.\cite{42} For example in case of the Becke88 gradient-corrected exchange functional the input file is given as:

\begin{verbatim}
cx: -2 * (1/3) * (3/4) * (3/8*PI) * (1);
b: 0.0042;
K(xhoa,grada, rhob, gradb, gradab):=
cx*(xhoa^4/3) + rhob*(4/3)) - (xhoa^4/3)*(b*xoa(xhoa,grada)^2)
- (rhob)*(4/3)*(b*xoa(xrhob,gradb)^2)
+ (1+6*b*xoa(xrhob,gradb)*asin(xa(xao,grada)))));
\end{verbatim}

where $K$ is the xc-energy kernel and $xhoa$ and $grada$ are the alpha-spin density and its gradient, respectively (accordingly $xrhob$ and $gradb$ denote the beta-spin quantities). Note that very often GGA functionals are expressed in terms of the dimensionless gradient $\rho_d = |\nabla \rho_d|/\rho_d$. This quantity is automatically detected as variables $x_a$ and $x_b$ in the above example, i.e., the code generator program will automatically substitute these variables before it performs the differentiations. The expressions for the various derivatives which are needed (see The Framework section) are then simplified by the OPTIMIZE facility of MAXIMA. This is particularly important for rather long functional expressions to reduce the number of floating-point operations by extracting common sub-expressions and if non-optimized compilers are evoked afterwards.

Through the use of the FLOAT and STRING functions of MAXIMA the expressions are then converted into a form which is read by a Perl program. This program then translates the expressions finally into C conformable routines by also adding the proper skeleton shared to the program. This program then translates the expressions finally into C

exchange interactions—the long-range interactions are estimated by the ordinary Hartree-Fock expression. To achieve this, the exchange part of the functional includes an additional factor that attenuates the long-range contribution in the exchange energy functional $K_\sigma$ where

$$E_{xc}(\rho, \ldots) = \int K_\sigma(\rho, \ldots) d\vec{r}. \quad (6)$$

The switching is determined by three parameters: $\alpha$, $\beta$ and $\mu$. The error function erf$(\mu r)$ switches between $\alpha$ fraction of exact HF exchange at short distance to $\alpha + \beta$ at long interelectronic distances. By altering the switching one can recover the B3LYP form of the functional by setting $\alpha = 0.2$ and $\beta = 0$ (no additional HF exchange for long distances) or $\mu = 0$ (infinitesimally slow increase of the HF exchange with distance), with the only difference being the weight of the nonlocal Becke88 exchange functional. This weight is set to 0.72 in case of B3LYP and 0.8 in case of CAM-B3LYP. Similarly, setting $\mu = \infty$ will give a functional with $\alpha + \beta$ fraction of HF exchange for all the distances but 0. The expression we use is:

$$E_{xc} = \int K_\sigma B_\sigma d\vec{r} \quad (7)$$

The parameters depend on a scaled exchange energy functional:

$$B_\sigma = 1 - \alpha - \frac{8}{3} \beta a_\sigma \left[ \sqrt{\pi} \text{erf} \left( \frac{1}{2a_\sigma} \right) + 2a_\sigma (b_\sigma - c_\sigma) \right] \quad (8)$$

$$a_\sigma = \frac{\mu \sqrt{-2K_\sigma}}{6\sqrt{\pi} \rho_d}, \quad (9)$$

$$b_\sigma = \exp \left( -\frac{1}{4d_\sigma^2} \right) - 1, \quad (10)$$

$$c_\sigma = 2a_\sigma^2 b_\sigma + \frac{1}{2} \quad (11)$$

The functional does not depend on the explicit form of $K_\sigma$ and in principle, one can use any exchange functional in this place. This is the improved form presented in\cite{19, 43} and not the one presented originally in Ref. 44. However, this form has also stability issues for both small and large values of the scaled exchange $a_\sigma$. We analyze first the stability of the multiplicative factor $B_\sigma$ and its first derivative. Later, we describe issues with higher derivatives of this factor with respect to $a_\sigma$. Let us first look at the definition of $B_\sigma$ for large parameters $a_\sigma$. In such a case, factor $b_\sigma$ becomes a difference of almost equal numbers and its value will be strongly influenced by numerical precision. For $a_\sigma > 4.25$, we choose to replace Eq. (8) by its Taylor expansion:

$$B_\sigma \approx 1 - \alpha - \beta \left[ 1 - \frac{1}{9(2a)^2} + \frac{1}{60(2a)^4} - \frac{1}{420(2a)^6} + \frac{1}{3240(2a)^8} - \frac{1}{27720(2a)^{10}} \right] \quad (12)$$

Numerically Unstable Functionals

We devote some attention to a class of functionals that cannot be treated with the above described automatic code generation. One such a functional is the CAM-B3LYP functional.\cite{19} The exchange part of this functional was designed to treat only short-range

DFT Library for Use in Ab Initio Quantum Chemistry Programs

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The first derivative of the $B_\sigma$ factor in this case becomes just a derivative of the series

$$B_\sigma' \overset{a \to \infty}{\approx} \beta \left[ -\frac{4}{9(2a)^2} + \frac{2}{15(2a)^3} - \frac{2}{70(2a)^4} + \frac{2}{405(2a)^5} \right]$$  (13)

Higher order derivatives of $B_\sigma$ are instable for large $a_\sigma$ as well. We use the following expansions for $a_\sigma > 4.25$ which follow just from the analytical differentiation of the series expansion (13)

$$B_\sigma'(3) = \beta \left[ -\frac{2}{3a_\sigma^3} + \frac{1}{8a_\sigma^4} - \frac{1}{80a_\sigma^5} + \frac{1}{1152a_\sigma^6} \right]$$  (15)

$$B_\sigma'(4) = \beta \left[ -\frac{10}{3a_\sigma^4} - \frac{7}{8a_\sigma^5} + \frac{9}{80a_\sigma^6} - \frac{11}{1152a_\sigma^7} \right]$$  (16)

Similarly we need to expand $B_\sigma$ around $a_\sigma = 0$ in order to stabilize its behavior for small values of $a_\sigma$. We obtain the following equation for $B_\sigma$ itself:

$$B_\sigma \overset{a \to 0}{\approx} 1 - \alpha - \beta \left( \frac{8}{3} \sqrt{\pi} a_\sigma + 8a_\sigma^2 - \frac{32}{3} a_\sigma^4 \right)$$  (17)

and for its first derivative:

$$B_\sigma' \overset{a \to 0}{\approx} \frac{8}{3} \beta \left[ -\sqrt{\pi} + 6a_\sigma + 16 \left[ \exp \left( -\frac{4}{a_\sigma^2} \right) - 1 \right] a_\sigma^3 \right]$$  (18)

For the range $a_\sigma \in (0.14, 4.25)$ the energy and first derivatives of the $B$ factor are computed from the explicit expression in Eq. (8).

Higher order derivatives of $B_\sigma$ behave in a more controlled manner for small values of $a_\sigma$. The following limits are useful to avoid division by 0:

$$\lim_{a_\sigma \to 0} B_\sigma' = 16$$  (19)

$$\lim_{a_\sigma \to 0} B_\sigma'(3) = 0$$  (20)

$$\lim_{a_\sigma \to 0} B_\sigma'(4) = -256$$  (21)

**Summary**

We have developed a modern density functional library to be included in many quantum chemistry programs. The functionals are programmed in a uniform way and treated on an equal footing. Their correctness can be verified by simple finite-difference methods at any time, allowing to detect not only bugs in the code but also in the compiler or run-time libraries. The entire functional module is hermetic so that other parts of the program are independent of the functional currently used for the calculation. Our framework allows for automatic code generation with the help of freely available tools.

The C code generated from a set of analytical formulas is included in the library and is ready for compilation. The library has already successfully been embedded in the DIRAC, DALTON and ERGO quantum chemistry programs, proving its portability. The vastly growing number of density functionals present in different quantum chemistry programs will augment the usefulness of this library as a reference tool in the future.

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Hyperfine coupling constants of the nitrogen and phosphorus atoms: A challenge for exact-exchange density-functional and post-Hartree–Fock methods

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I. INTRODUCTION

The accurate theoretical description of hyperfine coupling constants (HFCCs) by quantum-chemical methods is crucial for the adequate interpretation of electron paramagnetic resonance (EPR) spectra.1 The computation of HFCCs is often still a challenge for existing methods due to the need to describe very subtle effects of spin polarization in the valence and core shells of the relevant atoms. Therefore, HFCCs are also very useful and interesting quantities for evaluating and developing new methodologies, e.g., in density-functional theory (DFT). A large sensitivity of the results to the DFT exchange-correlation functional or to details in post-Hartree–Fock methodology [e.g., regarding certain higher excitations in multireference configuration interaction (CI) calculations2] is known for atoms, for certain organic π-radicals,3 and also for transition-metal nuclei.4,5

Here we will use the seemingly simple but in fact very challenging HFCCs of the isolated nitrogen and (particularly) phosphorus atoms in their quartet ground state to evaluate the performance and methodological aspects of a number of exact-exchange (EXX) methods in DFT. These two HFCCs have recently stimulated substantial interest in the context of EPR and electron-nuclear double resonance measurements of their endohedral fullerene complexes, e.g., N @ C60, P @ C60, N @ C70, etc.6 The HFCC of the N(4S) atom and of related atomic and molecular systems has furthermore already been studied by a large range of ab initio methods7 (the corresponding literature is too vast to be covered here in detail; it documents the need for large basis sets and CI expansions) in contrast to P(4S). It was found that for phosphorus, DFT methods with semilocal or standard hybrid functionals did not even give the correct sign of the HFCC for these endohedral complexes nor for the isolated atoms.8 The ground quartet state (4S) for these two atoms arises from the electronic configuration ns2np3 (n=2,3) and thus should be well described by a single Slater determinant at the Hartree–Fock (HF) or Kohn–Sham DFT (KS DFT) levels. However, the spin polarization of the doubly occupied core and valence-shell s-orbitals by the singly occupied valence p-orbitals is entirely responsible for the spin density at the nucleus and thus for the dominant Fermi-contact (FC) contribution to the HFCC in these two atoms. This spin polarization is apparently very difficult to reproduce reliably by formally single-determinant methods.9 As will be shown below, agreement with experiment for the spin densities of the isolated N atom and, particularly, of the P atom can only be attained with highly correlated post-HF methods such as fourth-order Möller–Plesset (MP4) perturbation theory or coupled-cluster levels [CCSD(T)] using very large basis sets. Currently available standard DFT methods provide reasonable results only for N(4S) but not for P(4S).

14. Other scientific publications

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From experience for the abovementioned π-radicals and transition-metal complexes, it is clear that EXX is a necessary ingredient of any functional that shall be successful for these subtle HFCCs and their associated spin-polarization effects. We will therefore use the two HFCCs in particular to evaluate the way in which modern exchange-correlation potentials deal with the EXX admixture in a self-consistent DFT calculation. Standard programs tend to use the nonlocal HF potential to implement hybrid functionals. This leads us outside the regular KS DFT framework, which would require a local and multiplicative KS potential. To obtain the latter, the so-called optimized effective potential [OEP (Ref. 10)] is needed. This is not generally straightforward in finite-basis-set molecular calculations, and a variety of approximate OEP methods has been developed over the past 10–15 years. Their differences will be evaluated here by HFCC calculations.

First the methodological differences between various approximations to the OEP method will be described (Sec. II). The computational details of a series of benchmark post-HF calculations from perturbation theory to CCSD(T), of standard DFT calculations, and of various OEP-based calculations will be summarized in Sec. III. Results and discussion will be reported in the same order of methods (Sec. IV), which also includes detailed analyses, followed by a brief summary (Sec. V).

II. THEORY: THE OEP METHOD AND ITS APPROXIMATIONS

The determination of the spin density for open-shell atoms or molecules using EXX-only DFT (EXX, correlation is neglected) requires the solution to the unrestricted KS equations

\[ -\frac{1}{2}\nabla^2 + v^\sigma_{KS}(\mathbf{r}) \phi^\sigma_i(\mathbf{r}) = \varepsilon^\sigma_i \phi^\sigma_i(\mathbf{r}), \quad \sigma = \alpha, \beta, \]  

with \( \phi^\sigma_i \) and \( \varepsilon^\sigma_i \) being the KS spin orbitals and corresponding eigenvalues. The KS potentials \( v^\sigma_{KS} \) and \( v^\sigma_{KS} \) contain the external potential, i.e., the electrostatic potential of the nuclei, the Coulomb potential, and, if only exchange interactions are considered, the spin-dependent local EXX potentials \( v^\sigma_{x}(\mathbf{r}) \) and \( v^\sigma_{x}(\mathbf{r}) \). Note that Eqs. (1) and (2) are coupled as the Coulomb potential depends on both \( \alpha \)- and \( \beta \)-spin orbitals. In contrast to the nonlocal and nonmultiplicative HF exchange potentials (operators),

\[ [v^{NL,\sigma}_{x} \psi^\sigma](\mathbf{r}) = - \sum_i \psi^\sigma_i(\mathbf{r}) \int \frac{\phi^\sigma_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi^\sigma_i(\mathbf{r}') d\mathbf{r}' , \quad (2) \]

where \( \psi \) is an arbitrary \( \sigma \)-spin one-electron function (real-valued functions are considered throughout the paper), the local and multiplicative exchange potentials, \( v^\sigma_{x}(\mathbf{r}) \) and \( v^\sigma_{x}(\mathbf{r}) \), can be obtained from the solutions of the OEP equations,

\[
\int d\mathbf{r}' \chi_{i}^{\sigma}(\mathbf{r}, \mathbf{r}') v^\sigma_{x}(\mathbf{r}) \\
= 2 \sum_i \sum_{\alpha} \phi^\sigma_i(\mathbf{r}) \phi^\sigma_i(\mathbf{r}) \left( \frac{\psi^\sigma_i(\mathbf{r}^{NL,\alpha}) \psi^\sigma_i(\mathbf{r}^{NL,\beta})}{\varepsilon^\sigma_i - \varepsilon^\sigma_i} \right), \quad \sigma = \alpha, \beta, \]  

where \( \chi_{i}^{\sigma} \) and \( \chi_{i}^{\sigma} \) are the KS response matrices and the indices \( i \) and \( \sigma \) refer to occupied and virtual KS orbitals, respectively. Note that the nonlocal exchange operator \( \psi^{NL,\alpha} \) in Eq. (3) has the form of the HF operator, Eq. (2), but it is constructed from KS orbitals, i.e., EXX orbitals in the present context.

A number of serious complications may arise when attempting to solve the OEP integral equation (3) in a straightforward way for molecules within basis-set methods. Therefore, various approximations have been introduced. One of the most successful is the localized HF (LHF) approach, which is equivalent to the common energy denominator approximation (CEDA). The starting point of the LHF method is the approximative assumption of the identity between the HF and EXX KS determinantal wave functions. After a series of transformations, such a supposition leads to the following expressions for the local and multiplicative exchange potentials:

\[ v^\sigma_{x}(\mathbf{r}) = v^{S,\sigma}_{x}(\mathbf{r}) + v^{corr,\sigma}_{x}(\mathbf{r}), \]  

where \( v^{S,\sigma}_{x} \) is the so-called Slater potential (orbital-averaged nonlocal exchange potential [Eq. (2)]),

\[ v^{S,\sigma}_{x}(\mathbf{r}) = \frac{\sum_i (\phi^\sigma_i(\mathbf{r}) v^{NL,\sigma}_{\psi^\sigma_i}(\mathbf{r}) \phi^\sigma_i(\mathbf{r}))}{\rho^\sigma(\mathbf{r})} , \]

and \( v^{corr,\sigma}_{x} \) is the \( \sigma \)-spin correction (or response) potential,

\[ v^{corr,\sigma}_{x}(\mathbf{r}) = \frac{\sum_i (\phi^\sigma_i(\mathbf{r}) v^{NS,\sigma}_{\psi^\sigma_i}(\mathbf{r}) \phi^\sigma_i(\mathbf{r}) - v^{NL,\sigma}_{\psi^\sigma_i}(\mathbf{r}) \phi^\sigma_i(\mathbf{r}))}{\rho^\sigma(\mathbf{r})} , \]

where the prime at the sum indicates that the term with \( i = j = N_{xc} \) is excluded. All the technical details of handling Eqs. (5) and (6) can be found in the original Ref. 12. Neglecting all the “off-diagonal” terms in Eq. (6) (i.e., those with \( i \neq j \)) reduces the LHF method to the Krieger–Li–Irafte approximation (KLI), which historically has been proposed first. In the series of approximations to the OEP method, KLI approximation is actually the crudest one and (unlike LHF) suffers from being noninvariant with respect to unitary transformations of occupied orbitals. We note also that the CEDA formalism starts from different assumptions but turns out to be equivalent to the LHF approach (see above).

The other family of methods to solve the OEP integral equation (3) is associated with the expansion of the OEP in various auxiliary basis sets. The most advanced representatives of these approaches are able to yield many molecular properties that are hardly distinguishable from those provided by numerical solution of the OEP integral equation. Thus, in the current work the OEP equations (3) were solved with the method described in Ref. 18 using exchange-change and highest occupied molecular orbital (HOMO) conditions for both the \( \alpha \)- and \( \beta \)-spin OEP poten-
tial (see Ref. 18 for details; note that in contrast the LHF implementation accounts only approximately for the HOMO condition).

The results will be presented in the form of (a) spin densities at the nucleus $\rho^{\alpha\beta}(R_k)$ and (b) nonrelativistic isotropic FC HFCCs, $A_{\text{FC}}$, that are known to be directly proportional to the former (in the nonrelativistic case),

$$A_{\text{FC}}(K) = \frac{4\pi}{3} \beta_e \beta_N g_e g_k (S_\phi)^{-1} \rho^{\alpha\beta}(R_k).$$

Here $\beta_e$ is the Bohr magneton, $\beta_N$ is the nuclear magneton, $g_e$ is the free-electron $g$ factor, and $g_k$ is the $g$-value of nucleus $K$. $(S_\phi)$ is the expectation value of the $z$-component of the total electronic spin. For the most abundant $^{14}$N and $^{31}$P nuclei, both nuclear $g$ values are positive, thus giving positive $A_{\text{FC}}$ for positive $\rho^{\alpha\beta}(R_k)$ and simplifying the discussion of the results.

III. COMPUTATIONAL DETAILS

A. Post-HF benchmark calculations

As the HFCCs for the two title atoms present such a challenge for DFT methods and as the highest level used so far in $ab$initio computations of the phosphorus HFCC has been MP2, benchmark post-HF calculations at the highest available levels appear in order. These were done at second- and fourth-order many-body (Møller–Plesset) perturbation theory (MP2 and MP4) at the CCSD level and augmented by perturbative triple corrections [CCSD(T)].

Higher angular momentum basis functions than those for DFT are needed here to describe the Coulomb correlation cusp, and it is expected that correlation has to be treated accurately for these subtle properties. While Dunning’s family of “correlation-consistent” basis sets is very popular for energy properties, their convergence properties are in our experience not as favorable for more delicate properties such as magnetic-resonance parameters (where also the contraction in the outer core space is important; see, for example, Ref. 21). Here the recently developed “polarization-consistent” basis sets of Jensen are more suitable. For the present purpose, this holds in particular for the pcJ-$n$ (aug-pcJ-$n$, $n=1,\ldots,4$) family, designed for the description of NMR spin-spin coupling constants, a quantity that is also dominated by FC-type hyperfine interactions. For comparison, we have also performed calculations using IGLO-IV (Ref. 25) basis sets, as well as Huzinaga basis sets ([73/7] for N and [533/53] for P). Fully uncontracted and augmented according to the prescriptions of Ref. 8 [these basis sets are denoted below as “uc-Huzinaga+ (2df)”). All the relaxed-density MP2, MP4, CCSD, and CCSD(T) calculations have been performed using the ACES-II code.

For HFCCs, both scalar relativistic (SR) and spin-orbit (SO) effects may be non-negligible, particularly for the P atom. SR effects may be estimated by scaling the nonrelativistic values with an $a$ posteriori Breit-type factor. SO effects have been computed with our DFT-based second-order perturbation approach using atomic-meanfield SO operators (the method dependence of the SO effects is much lower than that of the FC term). Depending on the functional employed [local spin-density approximation (LSDA), Perdew–Burke–Ernzerhof (PBE), or B3LYP], our calculations (aug-pcJ-4 basis set) give SO corrections to the HFCCs from $-0.222$ to $-0.227$ MHz for $N(4S)$ and from $-7.09$ to $-7.55$ MHz for $P(4S)$. SR corrections have the opposite sign and amount to 0.04 MHz for $N(4S)$ and 1.2 MHz for $P(4S)$. We thus estimate total relativistic corrections (SR+SO) as $-0.18$ MHz for $N(4S)$ and $-6$ MHz for phosphorus. These have to be added to the computed values for a comparison with experiment. We thus arrive at nonrelativistic reference values of approximately 10.63 MHz for $N(4S)$ and of approximately 61 MHz for $P(4S)$.

B. DFT/OEP-based methods

Very large uncontracted Gaussian basis sets including very tight functions have to be used to obtain converged spin densities at the nuclear position of the $N(4S)$ and $P(4S)$ atoms. For both atoms we have used an uncontracted even-tempered [38s32p] basis set with maximum exponents of 10$^6$ (s-type functions) and 5$\times$10$^5$ (p-type functions) and a progression factor of 1.75 (s- and p-type functions) in both cases.

The OEP method in Ref. 18 uses a finite auxiliary basis set to expand the KS response matrix and the local exchange potential. The auxiliary basis set needs to be balanced with the orbital basis set in order to obtain physically meaningful KS orbitals and eigenvalues. In this work auxiliary basis sets used for the solution of the OEP equations (3) and (4) were taken that have the same progression of 1.75 as the orbital basis set (note that of course only s-type functions are required to represent the local exchange potential for atoms). According to the rather dense progression of the corresponding orbital basis set, this choice is unproblematic concerning the stability of the solutions of the OEP equation. However, it has been observed that in contrast to, e.g., the total energy, the spin densities at the origin were rather sensitive with respect to the exact values of the exponents used in the auxiliary basis. In order to obtain stable OEP results, the auxiliary basis sets have to be smaller than the corresponding orbital basis sets, and the exponents should span only a smaller range compared with the exponents in the orbital basis. For the N and P atom we have taken auxiliary basis sets with maximum exponents of 200 and 400 respectively, and 18 Gaussian functions altogether and then started to incrementally increase these basis sets by one additional tight function in order to investigate the saturation of the auxiliary basis with respect to large exponents based on the convergence of the spin density. It was found in both cases that the spin density at the origin oscillated upon adding one additional tight function, by about 0.05 atomic units (a.u.) for $N(4S)$ and by about 0.1 a.u. for $P(4S)$. The magnitude of these oscillations was found to depend on the exact values of the exponents used in the auxiliary basis. That is, the oscillations depend on the starting point of the geometric series defining an auxiliary basis set. A solution to this problem turned out to be given by an optimization of each basis set with given size with respect to the total energy. That is, the exponents were determined such that the total OEP energy
TABLE I. Spin density at the nucleus (in a.u.) and FC HFCC (in megahertz) for the N(4S) atom from post-HF calculations. The experimental value is 10.45 MHz (Ref. 46). From this a relativistic correction of −0.18 MHz (see text) should be subtracted to give a nonrelativistic reference value of 10.63 MHz to which the calculations should be compared. The a.u. of the spin density is Bohr−3.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Composition</th>
<th>MP2 Spin density</th>
<th>MP4 Spin density</th>
<th>CCSD Spin density</th>
<th>CCSD(T) Spin density</th>
</tr>
</thead>
<tbody>
<tr>
<td>pcl-2</td>
<td>(127p3d2f,[75p5d3f2]g)</td>
<td>0.0632 6.81</td>
<td>0.0627 6.75</td>
<td>0.0691 7.44</td>
<td>0.0685 7.38</td>
</tr>
<tr>
<td>pcl-3</td>
<td>(161p5d3f1g,[105p5d3f1g])</td>
<td>0.0807 6.69</td>
<td>0.0869 9.36</td>
<td>0.0937 10.09</td>
<td>0.0954 10.27</td>
</tr>
<tr>
<td>pcl-4</td>
<td>(191s12p7d4f2g1h)</td>
<td>0.0821 8.84</td>
<td>0.0880 9.48</td>
<td>0.0946 10.18</td>
<td>0.0967 10.41</td>
</tr>
<tr>
<td>aug-pcl-2</td>
<td>(13s8p4d3f,[85p4d3f])</td>
<td>0.0759 8.18</td>
<td>0.0775 8.34</td>
<td>0.0842 9.07</td>
<td>0.0856 9.22</td>
</tr>
<tr>
<td>aug-pcl-3</td>
<td>(17s11p6d4f2g,[115p6d4f2g])</td>
<td>0.0822 8.85</td>
<td>0.0878 9.46</td>
<td>0.0945 10.18</td>
<td>0.0964 10.39</td>
</tr>
<tr>
<td>aug-pcl-4</td>
<td>(20s13p6d3f2g,[161s10d3f5g2h])</td>
<td>0.0824 8.87</td>
<td>0.0879 9.47</td>
<td>0.0945 10.19</td>
<td>0.0966 10.40</td>
</tr>
<tr>
<td>uc-aug-pcl-3</td>
<td>(17s11p6d4f2g)</td>
<td>0.0823 8.87</td>
<td>0.0879 9.47</td>
<td>0.0945 10.19</td>
<td>0.0966 10.40</td>
</tr>
<tr>
<td>uc-aug-pcl-4</td>
<td>(19s12p7d4f2g1h)</td>
<td>0.0824 8.87</td>
<td>0.0881 9.49</td>
<td>0.0946 10.19</td>
<td>0.0968 10.42</td>
</tr>
<tr>
<td>IGLO-IV</td>
<td>(11s7p3d3f,[87p3d3f])</td>
<td>0.0826 8.90</td>
<td>0.0856 9.22</td>
<td>0.0926 9.97</td>
<td>0.0942 10.14</td>
</tr>
<tr>
<td>uc-Huzinaga+ (2df)</td>
<td>11s8g2d1f</td>
<td>0.0774 8.33</td>
<td>0.0803 8.65</td>
<td>0.0868 9.34</td>
<td>0.0875 9.43</td>
</tr>
<tr>
<td>uc-Huzinaga “plus”</td>
<td>15s12p6d5f1g</td>
<td>0.0883 9.51</td>
<td>0.0942 10.15</td>
<td>0.1007 10.84</td>
<td>0.1023 11.02</td>
</tr>
</tbody>
</table>

was minimized. This has been achieved by scaling for each basis set all basis functions with a common optimization parameter such that the progression of 1.75 within each basis set was conserved. It has been found that different basis sets constructed in this way lead to OEP solutions that give practically identical spin densities at the nucleus, almost independent of the precise number of s-type functions and the precise range spanned by the exponents. This indicated convergence of the spin densities, which agreed then excellently (see below) with the accurate numerical OEP/EXX results by Krieger et al.30 in those cases where a comparison was possible (i.e., in the pure EXX case without the use of approximate correlation potentials). The results presented in this work were obtained by such optimized auxiliary basis sets. For both N and P auxiliary basis sets of 18 s-type Gaussian functions with maximum exponents of 205 in case of N and 420 in case of P were used. The basis-expansion OEP calculations were done using the developers’ version of the MOLPRO quantum chemistry program.45

For comparison purposes we provide also results with some standard (semi)local and hybrid exchange-correlation functionals: (i) with the LSDA in form of Slater–Dirac exchange,32 (S) combined with local correlation parameterized within two somewhat different schemes according to Vosko, Wilk and Nussair33 (VWN3 and VWN5); (ii) the PBE (Ref. 34) generalized gradient approximation (GGA); (iii) the currently most popular hybrid functional B3LYP,35–37 with 20% EXX, as well as PBE0 (Ref. 38) (25% EXX) and TPSSh (Ref. 39) (10% EXX). We also augmented 100% localized EXX by various correlation functionals, such as VWN, VWN5,33 Perdew–Wang–92 (PW92),30 Becke–88 (B88),41 and Becke–95 (B95).42 Unrestricted HF (UHF) calculations augmented by various dynamical correlation functionals [PBE,43 LYP,42 Perdew–86 (P86),42 31 and TPSS (Ref. 44)] were also used to estimate the effect of the correlation functional. All standard DFT and UHF+correlation, as well as LHF/CEDA and KLI calculations, have been performed using a locally modified version of the TURBOMOLE package.45

IV. RESULTS AND DISCUSSION

A. Post-HF benchmark calculations

The extremely high demands on the post-HF level and on the one-particle basis set to reproduce correctly the spin density at the nucleus in these two systems is apparent from the data given in Tables I and II. This holds in particular for the phosphorus atom (Table II). An accurate treatment of Coulomb correlation is crucial, and UHF calculations give qualitatively incorrect results [even the wrong sign for P(4S); see discussion and Table III further below]. For N(4S) (Table I), already MP2 gives qualitatively correct but too low HFCCs, with further successive quantitative improvement at MP4, CCSD, and CCSD(T) levels. Compared to the largest aug-pcJ-4 basis, the pcJ-2 basis is obviously insufficient, errors at pcJ-3 level are already much smaller, and pcJ-4 is essentially converged (with the relativistic correction of −0.18 MHz (see above); at this level the remaining error compared to the experimental HFCC of 10.45 MHz (Ref. 46) is about −0.2 MHz). Augmentation of the Jensen basis sets provides significant improvement up to aug-pcJ-3. The Huzinaga basis sets are somewhat less successful. Note again the extensive literature related to CI calculations of HFCCs for first-row atoms and radicals.7

Results for the P(4S) HFCC vary over a much larger range (Table II). After relativistic correction of −6 MHz, even the highest level CCSD(T)/aug-pcJ-4 understimates the experimental value of 55 MHz by about 3 MHz. For this extremely sensitive HFCC, the accuracy of MP2 is clearly unacceptable, and previous agreement7 with experiment was due to error compensation with too small basis sets. For example, augmentation of the uc-Huzinaga+ (2df) basis, which was claimed to be “sufficiently large” in ref. 8, by three sets of tight functions, one set of diffuse s-, p-, d-, and f-functions, and a g-function (exponent taken from the pcJ-3.
basis) moves the computed HFCC to dramatically lower values (entry uc-Huzinaga “plus” in Table II) and thus away from experiment. It is now close to the “best” MP2 value of 3.41 MHz obtained with the largest aug-pc-4 basis [note also the improvement at CCSD(T) level for the same basis augmentation]. The IGLO and other Huzinaga basis sets are also clearly insufficient here. Augmentation of the Jensen basis sets also proves to be even more important than for nitrogen. MP4 with the largest basis sets gives already much improved agreement with the experiment. CCSD is now significantly too low (cf. aug-pc-3 basis in Table II), and the triples correction in CCSD(T) is crucial for optimal agreement (note that MP4 also introduces triples corrections).

### B. DFT calculations with standard LSDA, GGA, and hybrid functionals

The DFT-based results for these two atomic HFCCs are summarized in Table III. We note first that the basis-set requirements in the DFT calculations are very different from those of the post-HF methods above. While tight s-functions are still crucial for the HFCCs, higher angular momentum basis functions are not important. The large primitive basis sets used are in part due to the requirements of the basis-set expansion of the OEP (see Sec. III above and OEP results below). We consider the HF and KS basis-set limits reached with the large uncontracted even-tempered [38s33p] basis sets. This is also evident from the virtually identical results obtained with the aug-pc-4 basis set (values in parentheses for UHF and LSDA).

Starting with the N(4S) case, we see that the LSDA and the PBE GGA fail to reproduce the correct sign and give a small negative HFCC. Interestingly, the B3LYP hybrid provides very good agreement with experiment [in contrast to P(4S); see below]. This agreement is probably in part fortuitous, as it has been analyzed for the related case of \( \pi \)-radicals. Much more severe problems become apparent for the P(4S) case: now none of the standard functionals reproduce the correct sign. While LSDA and B3LYP give a reasonable magnitude with the wrong sign, PBE provides even a three times larger negative HFCC. The B3LYP results are similar to those obtained with the largest uncontracted basis sets in Ref. 8. We have evaluated a larger number of standard functionals, but all of them give negative HFCCs between \(-2 \) and \(-140\) MHz for the P(4S) HFCC. It is clear that the subtle interplay between the spin-polarization contributions of the phosphorus 1s, 2s, and 3s atomic orbitals (AOs) to the spin density at the nucleus is extremely challenging for standard functionals. In case of second-period atoms such as N(4S), only the spin polarization of the 1s and 2s AOs has to be balanced, which is somewhat less demanding \(^{40}\) [see Ref. 5 for a detailed analysis of the spin-polarization effects, illustrated in detail for N(4S), for some first-row transition ions, and for a series of 3d metal complexes]. The prediction of spin-polarization-induced spin densities at nuclei thus remains one of the greatest challenges for modern DFT methods and may be used to validate new functionals. As we place hope in novel EXX-based functionals such as local hybrids, \(^{40}\) the self-consistent treatment of the EXX contributions is of particular interest.

### C. DFT/OEP calculations

We examine this in Table III for the EXX-only case and for EXX augmented by a correlation functional. Using the nonlocal UHF case as a starting point, we see that the neglect of Coulomb correlation gives a too large positive HFCC for N(4S) and a very large negative HFCC for P(4S), in dramatic disagreement with experiment. Our Gaussian basis-set-limit UHF data agree well with the numerical calculations in Ref. 14. As EXX-only OEP calculations give very similar energies as HF, one would expect the spin densities and HFCCs to be also very close to each other. This is indeed the case with N(4S) for the numerical OEP calculations in Ref. 14.
and for the present Gaussian basis-set expansion EXX calculations. In the latter case, this holds only when the careful energy-optimized construction of the orbital and auxiliary basis sets discussed in Sec. III is adhered to. Otherwise, the abovementioned oscillations of the spin density at the nucleus are observed even if the total energies are already well converged. For $P(4S)$, differences between the UHF and EXX data are more pronounced, with the latter being about 11 MHz more negative. This indicates that for this extremely sensitive HFCC, even the question of a local and multiplicative versus nonlocal and nonmultiplicative EXX potential may influence the result non-negligibly.

Turning to the LHF and KLI approximations to the EXX-only OEP (Table III), we find large discrepancies relative to both the UHF and exact OEP results, now even for nitrogen. In contrast to UHF or EXX, LHF gives a negative HFCC for $N(4S)$, and KLI provides an even more negative value. For $P(4S)$, LHF and KLI give a still appreciably more negative HFCC than the already much too negative UHF and EXX results.

Going beyond the EXX-only case, the addition of a correlation functional to EXX gives a moderate increase in the (already too positive) spin density and HFCC for $N(4S)$ (Table III). In contrast, for $P(4S)$ a striking dependence on $\nu_c$ is found. All five correlation functionals evaluated for EXX + $\nu_c$ move the results from a negative HFCC for pure EXX to positive yet too low values. The largest (and thus best) HFCC is found with B88C, the lowest with VWN3. Note that even the two LSDA variants for the correlation functional, VWN5 and VWN3, give notably different results. This underlines the extreme sensitivity of the $P(4S)$ HFCC to small changes in the electronic-structure method, which is also apparent from the post-HF results (see above). The redistribution of the $\alpha$- and $\beta$-densities by electron correlation

**TABLE III.** Spin densities at the nucleus (in a.u.) and HFCCs (in megahertz) evaluated at the DFT/OEP levels of theory. Unless stated otherwise, uncontracted [36s32p] basis sets were used (see text). [NL] and [L] indicate nonlocal and localized OEP treatments of the EXX contribution, respectively.

<table>
<thead>
<tr>
<th>Standard density functionals</th>
<th>Spin density</th>
<th>HFCC constant</th>
<th>Spin density</th>
<th>HFCC constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSDA (S + VWN5)</td>
<td>$-0.0167(-0.0166)^a$</td>
<td>$1.79(-1.79)^a$</td>
<td>$-0.0951(-0.0945)^a$</td>
<td>$-57.39(-57.08)^a$</td>
</tr>
<tr>
<td>B88-P86 (BP)</td>
<td>$-0.00887$</td>
<td>$-0.956$</td>
<td>$-0.0958$</td>
<td>$-91.07$</td>
</tr>
<tr>
<td>B88-LYP (BLYP)</td>
<td>0.0734</td>
<td>7.90</td>
<td>0.0927</td>
<td>55.96</td>
</tr>
<tr>
<td>PBE</td>
<td>$-0.0115$</td>
<td>$-1.24$</td>
<td>0.2540</td>
<td>153.4</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.0745</td>
<td>8.02</td>
<td>0.00432</td>
<td>2.61</td>
</tr>
<tr>
<td>B3LYP [NL]</td>
<td>0.0932</td>
<td>10.03</td>
<td>0.0752</td>
<td>45.42</td>
</tr>
<tr>
<td>B3LYP [L]</td>
<td>0.0906</td>
<td>9.76</td>
<td>0.0733</td>
<td>44.26</td>
</tr>
<tr>
<td>BHLYP [NL]</td>
<td>0.1446</td>
<td>15.57</td>
<td>0.0496</td>
<td>29.97</td>
</tr>
<tr>
<td>PB0 [NL]</td>
<td>0.0132</td>
<td>1.43</td>
<td>0.2302</td>
<td>138.98</td>
</tr>
<tr>
<td>PB0 [L]</td>
<td>0.0114</td>
<td>1.23</td>
<td>0.2290</td>
<td>138.26</td>
</tr>
<tr>
<td>TPSSb [NL]</td>
<td>0.0791</td>
<td>8.52</td>
<td>0.00905</td>
<td>-5.46</td>
</tr>
</tbody>
</table>

EXX only methods

Combinations of 100% EXX with various dynamical correlation functionals

<table>
<thead>
<tr>
<th>Spin density</th>
<th>HFCC constant</th>
<th>Spin density</th>
<th>HFCC constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF [NL]</td>
<td>0.1868(0.1873)$^a$</td>
<td>20.11(20.17)$^a$</td>
<td>$-0.1383(-0.1390)^a$</td>
</tr>
<tr>
<td>UHF [NL]$^b$</td>
<td>0.1875</td>
<td>20.19</td>
<td>-0.1394</td>
</tr>
<tr>
<td>LHF [L] $^c$</td>
<td>-0.2162</td>
<td>-23.28</td>
<td>-0.2090</td>
</tr>
<tr>
<td>KLI [L]$^d$</td>
<td>-0.3338</td>
<td>-35.95</td>
<td>-0.2128</td>
</tr>
<tr>
<td>EXX [L]$^e$</td>
<td>0.1901</td>
<td>20.48</td>
<td>-0.1561</td>
</tr>
<tr>
<td>EXX [L]$^f$</td>
<td>0.1897</td>
<td>20.43</td>
<td>-0.1576</td>
</tr>
</tbody>
</table>

$^a$Data in parentheses correspond to the aug-pcJ-4 basis set without higher angular momentum basis functions ($d$, $f$, $g$, and $h$ harmonics are not needed for the HF and KS calculations).

$^b$UHF and numerical EXX-only OEP and KLI data from Ref. 30.

$^c$Reference 46. Nonrelativistic reference value in parentheses.

$^d$Reference 55. Nonrelativistic reference value in parentheses.

4S, we find large discrepancies related to both the UHF and exact OEP results, now even for nitrogen. In contrast to UHF or EXX, LHF gives a negative HFCC for $N(4S)$, and KLI provides an even more negative value. For $P(4S)$, LHF and KLI give a still appreciably more negative HFCC than the already much too negative UHF and EXX results.
is crucial for the spin density at the nucleus, and here obviously none of the correlation functionals provide a fully satisfactory description. We note in passing that for atoms, we do not expect a large influence of nondynamical correlation. An EXX treatment with a correlation functional on top is thus in principle an adequate approach, but obviously dynamical correlation is not accounted for with sufficient accuracy for a more quantitative agreement. Yet, on a relative scale, the net contribution to the HFCC from the correlation functional varies only within 20%, i.e., it amounts to 107.7, 97.4, 108.4, 117.6, and 104.1 (values in MHz) for VWN5, VWN3, PW92, B88, and B95, respectively.

With the differences between EXX-OEP and UHF in mind, we have also explored a wider range of correlation functionals by combining the latter with nonlocal EXX (UHF). Again, none of the currently popular correlation functionals is able to provide an adequate description of the \( \text{P}(4S) \) FC HFCC. The difference of approximately 11 MHz between EXX-OEP and UHF is retained upon addition of a correlation functional. Interestingly, even the combination UHF+TPSS, which should satisfy most exact constraints \( \text{P}(4S) \). This is understandable from the fact that only 20% or 25% EXX, respectively, are included in these functionals. This suggests that for computation of hyperfine couplings with standard hybrid functionals, a nonlocal and an EXX-OEP treatment should give closely similar results, whereas we expect larger deviations with approximate OEP methods such as LHF or KLI (see above).

D. Analysis of differences between EXX and LHF

To rationalize the differences between LHF and exact OEP results, Figs. 1 and 2 compare the corresponding spin-exchange potentials for \( N(4S) \) and \( P(4S) \), respectively (black lines). Differences between LHF and exact OEP may be seen clearly for both atoms. We start with \( N(4S) \): Compared to the EXX-OEP curve, the LHF curve (i) is smoother and more featureless, and it fails to reproduce a small maximum at \( r \approx 0.35 \) Bohr; (ii) the global minimum near \( r \approx 0.6 \) Bohr is approximately 1.5 times deeper for LHF than that for EXX; (iii) as \( r \to 0 \), the LHF curve has the correct sign but tends to approximately 4–5 times larger value than exact EXX OEP. These differences give rise to noticeable differences in the spin-density distributions (green lines in Fig. 1). Thus, as \( r \to 0 \), the EXX curve tends to its limiting positive value from below, while the LHF curve approaches its limiting negative value from above while completely missing a shallow minimum at about 0.6 Bohr. For \( P(4S) \), neither the nonlocal UHF nor the local and multiplicative EXX potentials are able to reproduce even the sign of the HFCC. The differences between UHF and EXX values are more pronounced. Again, the LHF approximation makes the spin density more negative close to the nucleus (Fig. 2). Differences between the LHF and EXX exchange potentials are qualitatively analogous to those described above for \( N(4S) \).

Closer analysis by a decomposition of the spin-density curves into orbital contributions (Figs. 3 and 4) provides further insight. For the nitrogen atom (Fig. 3), the (ii) positive spin density at the nucleus at the EXX-only level arises from a slightly more positive 2s than negative 1s contribution. At the LHF level, the 2s contribution is changed comparatively little, whereas the 1s contribution is notably more negative, giving rise to an (incorrectly) negative spin density. For the phosphorus atom (Fig. 4), the more negative spin density at the origin for LHF (cf. Table III) arises almost equally from a reduced positive 2s contribution and from a more negative 1s contribution, while the 3s contribution is affected only weakly.

Occupied-unoccupied orbital products occurring in the response matrix of the OEP [Eq. (3)] will give strong contri-
butions close to the nucleus for high-lying unoccupied orbitals (since the latter will have large amplitudes). In the LHF/CEDA approximation this is probably smoothed out to some extent because the final expression for the EXX potential does not contain a summation over unoccupied orbitals to represent the continuum but is written solely in terms of occupied orbitals. This may be the origin of the deviations of the LHF (and even more so KLI) results from the exact OEP data. Note that Li et al.\textsuperscript{30} observed that the spin density at the nucleus obtained from the KLI method generally deviates more strongly from UHF and OEP if the atom has unpaired p or d electrons.

A closely related systematic comparison of different EXX-only methods for nuclear shieldings and HOMO–LUMO energy differences by Teale and Tozer\textsuperscript{54} should be mentioned here. Significant deviations of LHF and KLI results from exact OEP data were found for these properties. Notably, in graphical analyses of the deviations of LHF and KLI exchange potentials and (total) electron densities from the exact OEP results for the N\textsubscript{2} molecule, the former provided lower densities near the nuclei. Based on near-exact KS results, it was suggested that the EXX-only LHF and KLI potentials incorporate fortuitously some electron correlation effects.\textsuperscript{54}

**E. Analysis of differences between EXX and EXX + B88C for P\textsuperscript{(4S)}**

As addition of a suitable correlation functional to an EXX treatment may at least provide the correct sign of the P\textsuperscript{(4S)} HFCC (cf. Table III), it is also of interest to analyze the origin of the influence of the correlation functional. This is done in Fig. 5 for EXX+B88C. Differences in the exchange-correlation potential [Fig. 5(a)] relative to the EXX-only case [Fig. 4(a)] are minor on the scale of the plot but obviously sufficient to change the spin-density curve near the nucleus to a positive value. Therefore, Fig. 5(b)}
shows the curve of the B88C correlation potential on its own. It is zero near the nucleus but shows a first wiggle near a radius of approximately 0.2 bohr, with further structure near and above 1 bohr. Interestingly, the orbital analysis of the spin-density curve shows that the change from a negative spin density at the nucleus for the EXX-only case [Fig. 4(a)] to a positive one at EXX+B88C level [Fig. 5(c)] is almost exclusively due to the 3s-orbital contribution, which changes from negative (EXX-only) to positive (EXX+B88C) near the nucleus. As the precise way of spin polarization of the 3s valence orbital in the phosphorus atom is controlled mainly by its need to stay orthogonal to the corresponding spin-up and spin-down components of the 1s and 2s core shells, it seems likely that the notable effect of the correlation potential on the spin density at the nucleus arises from the subtle shifts of the nodes and maxima of these orbitals caused by Coulomb correlation.

V. SUMMARY AND OUTLOOK

While the free nitrogen and phosphorus atoms in their $^4S$ ground state exhibit a deceptively simple electronic structure, the quantum-chemical computation of their spin density at the nuclear position and of the closely associated HFCCs is a formidable challenge. This holds in particular for the third-period phosphorus atom, where a subtle balance between the core-shell spin-polarization contributions from the 1s-, 2s-, and 3s-shells to the HFCC is obviously very difficult to reproduce accurately. This renders this sensitive quantity useful for the evaluation of different quantum-chemical methods both post-HF ab initio and DFT.

For the former, the present results show clearly that MP2 with large basis sets does not adequately represent the HFCC for the P($^4S$) atom, in contrast to the N($^2S$) case (and in contrast to the results of a recent study which suffered from too small basis sets). CCSD also gives a too low value for P($^4S$), and triple excitations in CCSD(T) are mandatory to get within approximately 3 MHz of the nonrelativistic reference value of 61 MHz (MP4 gets to within approximately 7 MHz). Further improved accuracy might be achieved with a nonperturbative treatment of the triple excitations (or even quadruple excitations).

Matters are more severe for DFT, as no standard functional reproduces even the correct sign of the P($^4S$) HFCC. We have evaluated different variants of treating EXX within the framework of the OEP. Numerical EXX-only OEP results are about 11 MHz more negative than UHF data for the P($^4S$) HFCC. This is also reproduced with basis-set expansion OEP methods, provided that great care is taken in constructing orbital basis sets and auxiliary basis sets for the expansion of the potential. Approximate OEP variants such as the LHF/CEDA and KLI approaches deviate significantly from the exact OEP data both for the N($^2S$) and P($^4S$) HFCCs. This provides further evidence for the extreme sensitivity of these quantities to small changes in the electronic-structure method employed.

EXX OEP augmented by a dynamical correlation functional is the only DFT approach evaluated that provides the correct sign for the P($^4S$) HFCC. Differences between different correlation functionals are notable however, and none of the functionals tested so far gives truly satisfactory agreement with experiment. This provides valuable guidelines for the construction of accurate hyper-GGA-type functionals for such properties: (a) an adequate, relatively high amount of EXX will be mandatory in the core and semicore regions, (b) high demands have to be placed on the quality of the dy-
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14. Other scientific publications

namical correlation functional, 共c兲 to be applicable to molecules, such a functional also needs to deal accurately with
the balance between optimization of nondynamical correlation and reduction of self-interaction errors in the valence
space to avoid, among other problems, spurious spin contamination.
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