Random-phase-approximation-based correlation energy functionals: Benchmark results for atoms

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The random phase approximation (RPA) for the correlation energy functional of density functional theory has recently attracted renewed interest. Formulated in terms of the Kohn-Sham (KS) orbitals and eigenvalues, it promises to resolve some of the fundamental limitations of the local density and generalized gradient approximations, as for instance their inability to account for dispersion forces. First results for atoms, however, indicate that the RPA overestimates correlation effects as much as the orbital-dependent functional obtained by a second order perturbation expansion on the basis of the KS Hamiltonian. In this contribution, three simple extensions of the RPA are examined, (a) its augmentation by an LDA for short-range correlation, (b) its combination with the second order exchange term, and (c) its combination with a partial resummation of the perturbation series including the second order exchange. It is found that the ground state and correlation energies as well as the ionization potentials resulting from the extensions (a) and (c) for closed sub-shell atoms are clearly superior to those obtained with the unmodified RPA. Quite some effort is made to ensure highly converged RPA data, so that the results may serve as benchmark data. The numerical techniques developed in this context, in particular for the inherent frequency integration, should also be useful for applications of RPA-type functionals to more complex systems.

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I. INTRODUCTION

Recent years have seen a revival of interest in the random phase approximation (RPA) and its extensions, both in the framework of Kohn-Sham density functional theory (KS-DFT) and within Green’s function-based many-body theory for ground state properties. Within KS-DFT, the RPA for the energy and response function of the homogeneous electron gas played an important role in the development of the local-density approximation (LDA) as well as the generalized gradient approximation (GGA) for the exchange-correlation (XC) energy functional . Current interest in the RPA is stimulated by the concept of orbital-dependent (implicit) XC functionals, in which the XC energy is represented in terms of the KS orbitals and eigenenergies. Within this approach an RPA-type correlation energy functional is most easily formulated on the basis of the KS response function. Compared to LDA/GGA-type explicit XC functionals, implicit functionals have several attractive features: (1) the exchange can be treated exactly, leading to exchange energies and potentials which are free of self-interaction; (2) the long-range dispersion interaction can be correctly described; (3) static correlation effects can be incorporated even within a spin-unpolarized formalism.

A systematic formulation of orbital-dependent XC functionals is possible within KS-based many-body theory, i.e. using the KS Hamiltonian as non-interacting reference Hamiltonian in the framework of standard many-body theory (KS-MBT). In this approach the exact exchange of DFT emerges as first order contribution to a straightforward perturbation expansion in powers of . All higher order terms constitute the DFT correlation energy. The lowest order correlation contribution resulting from perturbation theory, , has been extensively studied for atoms and small molecules. Correctly accounts for the dispersion interaction and the corresponding correlation potential reproduces the shell-structure and asymptotic behavior of atomic correlation potentials. On the other hand, the magnitude of the energies and potentials resulting from overestimates the corresponding exact data significantly. Moreover, is found to be variationally unstable for systems with a very small energy gap between the highest occupied and the lowest unoccupied molecular orbital (HOMO-LUMO gap) (as, for instance, the beryllium atom) and fails to describe chemical bonding in such elementary molecules as the nitrogen dimer. The variational instability of can be resolved by resummation of suitable higher order contributions to infinite order (e.g. in the form of Feynman diagrams). The simplest functional of this type is obtained by resummation of selected ladder-type diagrams, i.e. the Epstein-Nesbet(EN)-diagrams. The resulting functional is not only found to be variationally stable for all neutral and singly-ionized atoms, but also gives more accurate correlation energies and potentials than . However, EN-type functionals still face fundamental problems in the case of degenerate or near-degenerate systems. A more suitable partial resummation scheme is needed to establish a universally applicable, implicit XC functional, the RPA and its extensions being the prime candidates.

In standard many-body theory, the RPA is obtained by resummation of the so-called ring diagrams. This concept can be directly transferred to the framework of KS-MBT. On the other hand, in the context of DFT, the RPA can also be derived from the adiabatic connection fluctuation-dissipation (ACFD) theorem. The ACFD formalism is, for instance, the conceptual starting point for the recent development of van-der-Waals DFT. It has also been applied directly to various systems, including jellium surfaces and slabs, atoms, small molecules, and solids. All these calculations have demonstrated promising features of RPA-based functionals.
On the other hand, the results for atoms\textsuperscript{21,44} for which rigorous benchmark data are available, indicate that the pure RPA overestimates correlation energies and potentials as much as $E_c^{(2)}$.

One is therefore led to consider extensions of the RPA. The most obvious starting point for extension is the inclusion of the second order exchange (SOX) contribution. However, in its pure form it neglects the screening of the Coulomb interaction, which is the core feature of the RPA. One would thus expect an imbalance between direct and exchange contributions, when combining the RPA with the pure SOX term. A fully screened form of the SOX is easily formulated, following the line of thought used for the derivation of GGAs.\textsuperscript{25} The resulting functional, however, is computationally much more demanding than the RPA. For that reason it is worthwhile to examine alternative modifications of the SOX term which reduce its net contribution. Given the success of the EN-resummation in the context of the complete $E_c^{(2)}$, an EN-extension of the SOX term suggests itself (this functional is denoted as RSOX in the following).

The SOX term, be it screened or not, is inherently a short-range contribution. This raises the question whether it is sufficient to account for the complete screened SOX in an approximate fashion, relying on the LDA. In fact, using this strategy, one can easily include all short-range correlation effects beyond the RPA.\textsuperscript{26} Clearly, the resulting LDA-type functional (here labelled as RPA+) is even more efficient than the RSOX.

In this work, we study the RPA and these simple extensions for a series of prototype atoms and ions, for which highly accurate reference data are available for comparison. In order to provide benchmark results a numerically exact, i.e. basis-set-accurate reference data are available for comparison. In order to mention a series of prototype atoms and ions (we will no longer distinguish between neutral atoms and atomic ions in the following) are presented and compared to the corresponding exact data. Section V provides a summary. Atomic units are used throughout this paper.

II. THEORY

A. RPA correlation energy on basis of the ACFD formalism

Based on the adiabatic connection and the zero-temperature fluctuation-dissipation theorem,\textsuperscript{42,52} the exact KS correlation energy can be written as

$$E_c = - \frac{1}{2\pi} \int_0^\infty du \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}’ v_{\text{ee}}(\mathbf{r} - \mathbf{r}’) \times [\chi_\lambda(\mathbf{r}, \mathbf{r}’; iu) - \chi_0(\mathbf{r}, \mathbf{r}’; iu)] ,$$  \hspace{1cm} (1)

where $v_{\text{ee}}(\mathbf{r}, \mathbf{r}’) = 1/|\mathbf{r} - \mathbf{r}’|$ is the bare Coulomb interaction, $\chi_0$ is the KS response function,

$$\chi_0(\mathbf{r}, \mathbf{r}’; iu) = \sum_{ia} \phi_a^\dagger(\mathbf{r}) \phi_a(\mathbf{r}’) \phi_a^\dagger(\mathbf{r}) \phi_a(\mathbf{r}’) / iu + \varepsilon_i - \varepsilon_a + c.c. ,$$  \hspace{1cm} (2)

and $\chi_\lambda$, with $\lambda \in [0, 1]$, is the density-density response function of a fictitious system in which electrons interact with a scaled Coulomb potential $\lambda v_{\text{ee}}(\mathbf{r}, \mathbf{r}’)$, and simultaneously move in a modified external potential, chosen such that the electron density remains identical to that of the fully interacting system with $\lambda = 1$. Throughout this paper we use the convention that $i, j, \ldots$ denote occupied (hole) KS states, while $a, b, \ldots$ are used for unoccupied (particle) states and $p, q, \ldots$ for the general case. $\chi_\lambda$ is related to $\chi_0$ by a Dyson-like integral equation,\textsuperscript{25}

$$\chi_\lambda(\mathbf{r}, \mathbf{r}’, iu) = \chi_0(\mathbf{r}, \mathbf{r}’, iu) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_0(\mathbf{r}, \mathbf{r}_1, iu) K_\lambda(\mathbf{r}_1, \mathbf{r}_2, iu) \chi_\lambda(\mathbf{r}_2, \mathbf{r}’, iu) ,$$  \hspace{1cm} (3)
where
\[ K_{\lambda}(r_1, r_2, iu) = \lambda v_{ee}(r_1, r_2) + f_{xc}^{\lambda}(r_1, r_2, iu) \] (4)
is the Coulomb and XC kernel.

The RPA correlation energy is obtained from Eq. 1 if one neglects the XC contribution to the right-hand side of Eq. 3. Integrating over \( \lambda \) one ends up with
\[
E_c^{\text{RPA}} = \int_0^\infty \frac{du}{2\pi} \text{Tr} \{ \ln(1 - \chi_0(iu)v_{ee}) + \chi_0(iu)v_{ee} \},
\]
where the trace indicates integration over all spatial coordinates. It is often more instructive to rewrite the integrand in Eq. 5, denoted as \( E_c(iu) \), as a power series in the Coulomb interaction,
\[
E_c(iu) = -\sum_{n=2}^\infty \text{Tr} \{ (\chi_0(iu)v_{ee})^n \}. \quad (6)
\]

**B. Correlation energy beyond RPA**

The ACFD theorem provides a natural starting point for the development of correlation functionals beyond the RPA: Inclusion of some approximation for \( f_{xc} \) in the Dyson equation (3) automatically yields an extension of the RPA. Several approximate XC kernels have been introduced in the context of (3) automatically yields an extension of the RPA. Several approximations have been suggested in the context of the second order functional \( E_c^{(2)} \). The inclusion of the direct hole-hole contribution to the Epstein-Nesbet-type ladder diagrams into the SOX term substantially improves second order energies and potentials, without introducing any additional computational effort. Although the physical background of these ladder diagrams is quite different from dynamical screening, it seems worthwhile to analyze this “effective” screening. The resulting correction will be denoted as RSOX,
\[
E_c^{\text{RSOX}} = -\frac{1}{2} \sum_{i,j,a,b} (ij \parallel ab) (ab \parallel ji) \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b - (ij \parallel ji), \quad (11)
\]

This approach is supported by the fact that the gradient correction to the short-range correlation is much smaller than that to the complete correlation energy. Though the RPA+ functional has been used recently to describe the inter-layer dispersion interaction in boron nitride \( ^{22,24} \), a direct comparison of the RPA+ with exact results is still missing even for closed-shell atoms. Using numerically exact RPA correlation energy available for atoms, we are able to give a unambiguous assessment of the quality of the RPA+ correlation functional.

In the language of Feynman diagrams, the RPA correlation energy is obtained from the second order direct diagram by replacing the bare Coulomb interaction by the dynamically screened Coulomb interaction. The dominant contribution that is missing in the RPA is the second order exchange diagram (SOX),
\[
E_c^{\text{SOX}} = -\frac{1}{2} \sum_{i,j,a,b} (ij \parallel ab) (ab \parallel ji) \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b - (ij \parallel ji), \quad (9)
\]
where the notation
\[
(pq \parallel rs) = \int d^3r \int d^3r' \frac{\phi^\dagger_p(r)\phi_q(r)\phi^\dagger_j(r')\phi_s(r')}{|r-r'|} \quad (10)
\]
has been used for the KS Slater integral. Combining the RPA with the SOX term, one obtains a new functional, denoted as RPA+SOX. However, one would expect the SOX to overcorrect the error in the RPA, since the Coulomb interaction enters the SOX term in its bare, i.e. un-screened, form. Screening can be introduced into the SOX term in a systematic way by use of the same, dynamically screened interaction as in the direct term. Unfortunately, the resulting functional is computationally much more demanding than the RPA expression. A technically much simpler way to reduce the SOX contribution has been suggested in the context of the second order functional \( E_c^{(2)} \). The inclusion of the direct hole-hole contribution to the Epstein-Nesbet-type ladder diagrams into the SOX term substantially improves second order energies and potentials, without introducing any additional computational effort. Although the physical background of these ladder diagrams is quite different from dynamical screening, it seems worthwhile to analyze this “effective” screening. The resulting correction will be denoted as RSOX,
\[
E_c^{\text{RPA}} = -\frac{1}{2} \sum_{i,j,a,b} (ij \parallel ab) (ab \parallel ji) \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b - (ij \parallel ji), \quad (11)
\]

**C. RPA correlation functional for spherical systems**

In the case of spherical systems, the KS potential only depends on the radial coordinate \( r \), \( v_s(r) = v_s(r') \), and each KS orbital can be written as the product of a radial orbital and a spherical harmonic \( Y_{lm}(\theta, \varphi) \),
\[
\phi_l(r) \to \phi_{nlm}(r) = \frac{P_{nl}(r)}{r} Y_{lm}(\theta, \varphi), \quad (12)
\]
where \( n, l \), and \( m \) are the principle, angular and magnetic quantum numbers, respectively. The \( P_{nl} \) are solutions of the radial KS equation,
\[
\left[ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right] v_s(r) + v_s(r) P_{nl}(r) = \varepsilon_{nl} P_{nl}(r). \quad (13)
\]
Two-body functions like the Coulomb interaction and \( \chi_0 \) can also be decomposed according to the spherical symmetry. To simplify notations, we use the following decomposi-
tion convention. The Coulomb interaction is expanded as

\begin{equation}
\nu_{ee}(r,r') = \sum_{L=0}^{\infty} \frac{4\pi}{2L+1} v_L(r,r') \times \sum_{M=-L}^{L} Y_{LM}(\theta, \varphi) Y_{LM}^*(\theta', \varphi') ,
\end{equation}

where

\begin{equation}
v_L(r,r') := \frac{r_<^L}{r_>^{L+1}} \quad (15)
\end{equation}

with \( r_< = \operatorname{Min}(r,r') \) and \( r_> = \operatorname{Max}(r,r') \). The response function \( \chi_0 \) can be written as

\begin{equation}
\chi_0(r,r',iu) = \sum_{L=0}^{\infty} \frac{2L+1}{4\pi} \chi_0 L(r,r',iu) \times \sum_{M=-L}^{L} Y_{LM}(\theta, \varphi) Y_{LM}^*(\theta', \varphi') .
\end{equation}

The \( L \)-dependent radial response function \( \chi_{0L}(r,r',iu) \) can be calculated utilizing the radial orbitals

\begin{equation}
\chi_{0L}(r,r',iu) = -\sum_{ia\sigma} C_{L;ia\sigma} D_{ia\sigma}(u) \Phi_{ia\sigma}(r) \Phi_{ia\sigma}(r') ,
\end{equation}

where

\begin{equation}
C_{L;ia\sigma} := \left( \frac{2l+1}{2L+1} \right) \left( \begin{array}{ccc} l_i & l_a & L \\ 0 & 0 & 0 \end{array} \right)^2
\end{equation}

\begin{equation}
D_{ia\sigma}(u) := \frac{2(\varepsilon_{ia\sigma} - \varepsilon_{ia})}{u^2 + (\varepsilon_{ia\sigma} - \varepsilon_{ia})^2}
\end{equation}

\begin{equation}
\Phi_{ia\sigma}(r) := P_{\sigma}(r) P_{a\sigma}(r) .
\end{equation}

Using the multipole expansion of both \( \nu_{ee} \) and \( \chi_0 \), the building block of the RPA correlation energy, \( \text{Tr}\{\chi_0 v\} \), is be obtained as

\begin{equation}
\text{Tr}\{\chi_0 v\} = \sum_{L} (2L+1) \int_0^{\infty} dr dr' \chi_0 L(r,r',iu) v_L(r',r) .
\end{equation}

There are two options for the calculation of the radial integral in Eq. (21):

\begin{enumerate}
\item **Real space approach:** In this approach, \( \chi_{0L}(r,r') \) is calculated on a discrete radial mesh, which allows to evaluate (21) by direct numerical integration,

\begin{equation}
\text{Tr}\{\chi_0 v\} = \sum_{L} (2L+1) \sum_{i,j} w_{ij}(r_i) w(r_j) \chi_0 L(r_i,r_j) v_L(r_j,r_i)
\end{equation}

\begin{equation}
= \sum_{L} (2L+1) \sum_{i,j} \chi_{0L},_{ij} [v_L]_{ij} ,
\end{equation}

\begin{equation}
= \sum_{L} (2L+1) \text{Tr}\{\chi_0 v_L\} ,
\end{equation}

where \( w_i \) denotes the radial integral weight at mesh point \( i \). In case of powers of \( \text{Tr}\{\chi_0 v\} \) one has

\begin{equation}
\text{Tr}\{(\chi_0 v)^n\} = \sum_{L} (2L+1) \text{Tr}\{(\chi_0 v_L)^n\} . \quad (23)
\end{equation}

The sum over \( n \) in Eq. (6) then leads to

\begin{equation}
E_{c}(iu) = \sum_{L} (2L+1) \text{Tr}\{\ln(1 - \chi_0 v_L) + \chi_0 v_L\} . \quad (24)
\end{equation}

\item **Orbital-product space approach:** In this second approach one inserts (16) and (17) into Eq. (21). Using the radial Slater integrals

\begin{equation}
R_{L;ia\sigma,jb\sigma} := \int_0^{\infty} dr \int_0^{\infty} dr' \Phi_{ia\sigma}(r) v_L(r,r') \Phi_{jb\sigma}(r') ,
\end{equation}

one finds

\begin{equation}
\text{Tr}\{\chi_0 v\} = \sum_{L} (2L+1) \sum_{ia\sigma} C_{L;ia\sigma} D_{ia\sigma}(u) \times \int dr \int dr' \Phi_{ia\sigma}(r) v_L(r,r') \Phi_{ia\sigma}(r')
\end{equation}

\begin{equation}
= \sum_{L} (2L+1) \sum_{ia\sigma} C_{L;ia\sigma} D_{ia\sigma}(u) R_{L;ia\sigma,ia\sigma} .
\end{equation}

With the definitions

\begin{equation}
V_{L;ia\sigma,jb\sigma} := \sqrt{C_{L;ia\sigma}} R_{L;ia\sigma,jb\sigma} \sqrt{C_{L;jb\sigma}} \quad (27)
\end{equation}

\begin{equation}
S_{L;ia\sigma,jb\sigma} := -\sqrt{D_{ia\sigma}(u)} V_{L;ia\sigma,jb\sigma} \sqrt{D_{jb\sigma}(u)} \quad (28)
\end{equation}

one ends up with

\begin{equation}
\text{Tr}\{\chi_0 v\} = \sum_{L} (2L+1) \sum_{ia\sigma} S_{L;ia\sigma,ia\sigma} \quad (29)
\end{equation}

One can furthermore show that

\begin{equation}
\text{Tr}\{(\chi_0 v)^n\} = \sum_{L} (2L+1) \text{Tr}\{(S_L)^n\} \quad (30)
\end{equation}

so that

\begin{equation}
E_{c}(iu) = -\sum_{L} (2L+1) \text{Tr}\left\{ \frac{1}{n} \sum_{n=2}^{\infty} (S_L)^n \right\}
\end{equation}

\begin{equation}
= \sum_{L} (2L+1) \text{Tr}\{\ln(1 - S_L) + S_L\}
\end{equation}

\begin{equation}
= \sum_{L} (2L+1)[\ln \text{Det}(1 - S_L) + \text{Tr}\{S_L\}] .
\end{equation}

The final expressions for \( E_{c}^{\text{RPA}} \) are quite similar in the real-space and orbital-product-space approaches, but their numerical efficiency can be very different, depending on the size of the system. In the real-space approach, the dimension of the
matrix involved is determined by the number of mesh points used for radial integration, $I_{\text{max}}$. As $I_{\text{max}}$ is never larger than a few thousand even for heavy atoms, the resulting memory requirement is quite low. On the other hand, $\chi_{0L}$ needs to be constructed on the radial mesh for each frequency, which can be very cpu-time-intensive. The situation is quite different in the case of the orbital-product space approach. Here the dimension of the matrix involved is given by $N_{\text{occ}} \times N_{\text{vir}}$, where $N_{\text{occ}}$ denotes the number of occupied orbitals and $N_{\text{vir}}$ is the number of unoccupied orbitals taken into account. $N_{\text{occ}} \times N_{\text{vir}}$ can be easily as high as tens of thousands. However, the matrix $V_L$, Eq. (27), is independent of frequency and can be calculated in advance and stored in the memory. Limitations of the available memory can be circumvented by taking advantage of the fact that, for given $L$, $V_L$ and $S_L$ are quite sparse (usually the ratio of non-zero elements is less than 1%). One can therefore use standard sparse matrix techniques to reduce the storage requirement and accelerate the computation of the determinant.

### III. NUMERICAL DETAILS

#### A. Hard-wall cavity approach

The RPA correlation energy depends on the occupied as well as on the unoccupied KS states. For free atoms, the spectrum of the unoccupied states includes both discrete Rydberg states and continuum states. However, the handling of continuum states in the evaluation of the correlation energy is nontrivial. Moreover, the presence of continuum states causes additional problems in the context of orbital-dependent functionals: One does no longer find a solution of the corresponding OPM equation which satisfies the standard boundary conditions for the correlation potential. To resolve this problem, we developed a hard-wall cavity approach in which the KS equation is solved on a discrete radial mesh with hard-wall boundary conditions imposed at a finite, but large radius $R_{\text{max}}$. The same approach is used in the present work.

Its crucial parameters are the cavity radius $R_{\text{max}}$ as well as the energetically highest state (characterized by its principle quantum number $n_{\text{max}}$) and the highest angular momentum $l_{\text{max}}$ included in sums over virtual states. In the following, neutral Ar is used for a systematic convergence study with respect to $R_{\text{max}}$, $n_{\text{max}}$ and $l_{\text{max}}$.

We first consider $R_{\text{max}}$. $R_{\text{max}}$ has to be chosen so large, that all ground state properties, and, in particular, the correlation energy, do no longer change when $R_{\text{max}}$ is increased further. However, any increase of $R_{\text{max}}$ directly affects the spectrum of the positive energy states, i.e. the density of states. In order to keep the space available for virtual excitations constant, when increasing $R_{\text{max}}$, one therefore has to fix the energy $\varepsilon_{\text{max}}$ of the highest unoccupied state $n_{\text{max}}$ taken into account. In the case of very high-lying virtual states one has a simple relation between $R_{\text{max}}$ and $\varepsilon_{\text{max}}$, resulting from the fact that high-lying states are no longer sensitive to the detailed structure of $v_0$:

$$\varepsilon_{\text{max}} \propto \left( \frac{n_{\text{max}}}{R_{\text{max}}} \right)^2.$$  \hfill (32)

The space available for virtual excitations is therefore kept constant, as soon as the ratio $n_{\text{max}}/R_{\text{max}}$ is fixed. Table I shows the values of $E_c^{\text{RPA}}$ for Ar obtained with different

| $n_{\text{max}}$ | $\varepsilon_{\text{max}}$ | $E_{c}^{\text{RPA}} - E_{c}^{\text{RPA}}(\text{FC})$ |
|------------------|------------------|------------------|
| 25               | 25.1             | 0.6840           |
| 50               | 111.9            | 0.9097           |
| 100              | 471.2            | 1.0028           |
| 150              | 1077.6           | 1.0273           |
| 200              | 1930.8           | 1.0354           |
| 250              | 3030.9           | 1.0384           |
| 300              | 4377.6           | 1.0398           |
| 350              | 5951.9           | 1.0399           |
| 400              | 7754.8           | 1.0400           |

TABLE I: Convergence of $E_c^{\text{RPA}}$, the exact exchange energy and the eigenvalue of the highest occupied KS orbital ($\varepsilon_{\text{HOMO}}$) obtained by self-consistent exchange-only calculations for Ar for different cavity radii $R_{\text{max}}$ (with $n_{\text{max}}/R_{\text{max}} = 10$ Bohr$^{-1}$ and $l_{\text{max}} = 4$, all energies in Hartree).

| $l_{\text{max}}$ | $E_{c}^{\text{RPA}} - E_{c}^{\text{RPA}}(\text{FC})$ |
|------------------|------------------|
| 2                | 0.7661           |
| 4                | 1.0028           |
| 6                | 1.0431           |
| 8                | 1.0529           |
| 10               | 1.0562           |
| 12               | 1.0574           |
| 14               | 1.0580           |
| 16               | 1.0582           |

TABLE II: Convergence of full $E_c^{\text{RPA}}$ (Column 3) and $E_c^{\text{RPA}}$ within the frozen core approximation excluding virtual excitations of the $1s$, $2s$ and $2p$ electrons (Column 4) of Ar with respect to $n_{\text{max}}$ (with $R_{\text{max}} = 10$ Bohr and $l_{\text{max}} = 4$, all energies in Hartree).

| $l_{\text{max}}$ | $E_{c}^{\text{RPA}} - E_{c}^{\text{RPA}}(\text{FC})$ |
|------------------|------------------|
| 2                | 0.7661           |
| 4                | 1.0028           |
| 6                | 1.0431           |
| 8                | 1.0529           |
| 10               | 1.0562           |
| 12               | 1.0574           |
| 14               | 1.0580           |
| 16               | 1.0582           |

TABLE III: Convergence of full $E_c^{\text{RPA}}$ (Column 3) and $E_c^{\text{RPA}}$ within the frozen core approximation excluding virtual excitations of the $1s$, $2s$ and $2p$ electrons (Column 4) of Ar with respect to $l_{\text{max}}$ (with $R_{\text{max}} = 10$ Bohr and $n_{\text{max}} = 100$, all energies in Hartree).
$R_{\text{max}}$, but fixed $n_{\text{max}}/R_{\text{max}} = 10 \text{ Bohr}^{-1}$, which corresponds to an energy cut-off of about 500 Hartree. For comparison, the corresponding exchange energy and the eigenvalue of the highest occupied orbital, $\epsilon_{\text{HOMO}}$, resulting from exchange-only calculations are also listed. One observes that $E_{c}^{\text{RPA}}$ is less sensitive to $R_{\text{max}}$ than the exchange energy, which is consistent with the fact that the length scale related to the RPA correlation energy is smaller compared to that of the exchange.

Argon is the heaviest atom considered in this work. We have also made systematic convergence tests for other, less compact atoms like Na and Mg. For all atoms considered in this work, the choice $R_{\text{max}} = 10 \text{ Bohr}$ leads to errors less than 1 mHartree.

With $R_{\text{max}}$ fixed, one can now examine the convergence of $E_{c}^{\text{RPA}}$ with respect to $n_{\text{max}}$ and $l_{\text{max}}$. Tables II and III show $E_{c}^{\text{RPA}}$ for Ar obtained with different $n_{\text{max}}$ and $l_{\text{max}}$. In general, the absolute value of $E_{c}^{\text{RPA}}$ converges quite slowly with respect to both parameters. The slow convergence with respect to $n_{\text{max}}$ mainly originates from the innermost shell — unoccupied states with high energies are only important for the description of virtual excitations of the highly localized, low-lying core states. In practice, fortunately only energy differences related to the valence electrons are really relevant. One would thus expect to achieve high accuracy for these energy differences with much more moderate values for $n_{\text{max}}$. This suggests to rely on the frozen core (FC) approximation, in which excitations from core levels are excluded. Tables II and III demonstrate that the FC approximation for $E_{c}^{\text{RPA}}$ converges much faster with increasing $n_{\text{max}}$. Even for a quite moderate $n_{\text{max}}$ of 25, corresponding to $\epsilon_{\text{max}} \sim 25 \text{ Hartree}$, $E_{c}^{\text{RPA}}$ is already converged to an accuracy of 2 mHartree. On the other hand, the convergence behavior of $E_{c}^{\text{RPA}}$ with respect to $l_{\text{max}}$ is not improved by the FC approximation. As one of the main aims of this work is to provide benchmark results for a set of prototype atoms, most results reported in this work are obtained without evoking the FC approximation. The results reported in the next section are obtained for $n_{\text{max}} = 300$ and $l_{\text{max}} = 14$, which ensures an accuracy of 1 mHartree for Ar and better for all lighter atoms.

B. Frequency integration

Any calculation of RPA energies involves two time-consuming steps: The first is the evaluation of all Slater integrals involved, i.e. of the matrix $R_{L}$, Eq. (25). In the present work the Slater integrals are calculated by numerical integration on the radial grid, using standard finite differences methods. Once $R_{L}$ is available, the second step is performing the frequency integration in Eq. (5). In order to understand the most appropriate way to do this frequency integration let us consider the integrand for some prototype atoms. Figure 1 shows $u^{4}E_{c}(iu)$ for He, demonstrating the fact that $E_{c}(iu)$ falls off as $u^{-4}$ for extremely large $u$. This behavior can be easily understood on the basis of Eq. (19): For frequencies beyond the maximum excitation energy $\delta \epsilon = \epsilon_{\text{max}}^{\text{m}-\epsilon_{\sigma}}$ included in the calculation (or provided by the basis set) $D_{i\sigma}(u)$ and thus $S_{L}(u)$ decay as $u^{-2}$ which allows a perturbative evaluation of (31) in powers of $S_{L}(u)$, with the second order term dominating the resulting $E_{c}(iu)$.

On the other hand, for the more important range of large frequencies less than $\delta \epsilon$ a decay close to $u^{-3}$ is found, as shown in Figure 2. The same behavior is observed for each individual shell, as illustrated by the $E_{c}(iu)$ obtained by excitation of only the M-shell of neutral Ar, also included in Figure 2.

This power law decay suggests a transformation of the frequency interval $0 \leq u < \infty$ to some finite interval via a power law transformation, as for instance

$$x = \frac{1}{1 + (u/s)} \quad 0 \leq x \leq 1,$$

FIG. 1: (Color online) $u^{4}E_{c}(iu)$ vs $u$ for He (maximum excitation energy $\delta \epsilon \approx 4000 \text{ Hartree}$).

FIG. 2: (Color online) $u^{2}E_{c}(iu)$ and $u^{3}E_{c}(iu)$ vs $u$ for moderately large $u$ for the case of He.
giving more weight to large $u$ than an exponential transformation. The scale factor $s$ is intrinsically related to the minimum energy required for a virtual excitation, which is roughly given by the eigenvalue difference $\epsilon_{LU/MO} - \langle \epsilon \rangle \approx |\langle \epsilon \rangle|$ for a shell with average eigenvalue $\langle \epsilon \rangle$. The most appropriate $s$ can only be determined empirically. For all atoms considered in detail the choice $s = 2|\langle \epsilon \rangle|$ seemed to work reasonably well (see also below). The result of the transformation (33) is shown in Figure 3 for He, Ar$^{16+}$ as well as the $M$-shell of neutral Ar. One obtains a smooth function of $x$, with values remaining on the same order of magnitude for all $x$. This ensures a rapid convergence of the numerical integration over $x$ with the number of grid points.

However, the frequency integration in (5) suffers from the fact that each shell in an atom (or molecule) introduces a new energy scale. Let us call the boundaries of the integration from 0 to $\epsilon_i$ in Hartree). It is therefore necessary to split the frequency into intervals associated with these individual energy scales. Let us call the boundaries of the intervals $b_i$,

$$0 = b_0 < b_1 < \ldots < b_n = \infty$$

with $n$ denoting the number of shells. The intervals are chosen such that the characteristic energy scale $s_n$ of shell $n$ is bracketed,

$$b_{i-1} < s_i < b_i.$$  

In practice, $s_1 = 2|\langle \epsilon_i \rangle|$ and $b_1 = 4|\langle \epsilon_i \rangle|$ seemed to provide a reasonable partitioning of the complete frequency range. Eq (5) may then be decomposed as

$$\int_0^\infty E_c(iu)\,du = \sum_{i=1}^n \int_{b_{i-1}}^{b_i} E_c(iu)\,du.$$  

In order to account for the piecewise decay of $E_c(iu)$ the transformation

$$x_i = \frac{1 + s_i/(b_i - b_{i-1})}{1 + (u - b_{i-1})/s_i} \frac{u - b_{i-1}}{s_i}$$

$$\frac{du}{dx_i} = s_i \frac{1 + s_i/(b_i - b_{i-1})}{1 + s_i/(b_i - b_{i-1}) - x_i^2}$$

$(i = 1, \ldots n)$ is most suitable. Eq (36) can then be written as

$$\int_0^\infty E_c(iu)\,du = \sum_{i=1}^n \int_{-1}^1 dx_i \frac{du}{dx_i} E_c(iu(x_i)).$$

The success of this frequency partitioning plus power law transformation scheme is demonstrated in Figure 5 in which the final integrands $du/dx_i E_c(iu(x_i))$ are plotted for neutral Ar. In all three energy regimes a rather smooth integrand is obtained, which allows the application of Gauss-Legendre quadrature to each interval. As a result, the error obtained for a given total number of grid points $N_u$ used for the Gauss-Legendre quadrature is rather small already for very low $N_u$, as illustrated in Figure 6. The most critical interval in Eq (39) is the highest energy range, covering in particular excitations of the $1s$-state. For that reason the error is even lower if only excitations of the valence shell are included (i.e. in the FC approximation), as is obvious from the error found for He or the $M$-shell of neutral Ar.
IV. RESULTS

A. Sensitivity to form of KS orbitals

Standard KS-DFT calculations are based on the self-consistent solution of the KS equations, which requires the evaluation of the XC potential \( v_{xc}(r) = \frac{\delta E_{xc}(n)}{\delta n(r)} \). In the case of LDA and GGA functionals the calculation of \( v_{xc}(r) \) is straightforward. On the other hand, a self-consistent implementation represents a much more serious problem for RPA-type functionals. First of all, in the case of orbital-dependent functionals \( v_{xc} \) has to be determined via the OPM, i.e. by solution of an integral equation. The solution of the OPM integral equation is well-established for the exact exchange and manageable, though rather intricate, for the second order correlation functional \( E^{(2)}_{c} \). Its implementation for RPA-type functionals, however, is much more challenging, so that a full solution has only been reported very recently. On the other hand, a self-consistent implementation is only then advantageous if the resulting correlation potential leads to an improved total KS potential. It has been demonstrated that this is not the case for some standard GGAs and for \( E^{(2)}_{c} \), which by far overestimates correlation effects. The situation is not yet completely clear in the case of the RPA. The first RPA potentials available seem to improve over \( v^{(2)}_{c} = \frac{\delta E^{(2)}_{c}}{\delta n(r)} \) in the asymptotic regime, but otherwise often follow \( v^{(2)}_{c} \).

Independently of this more fundamental aspect, one might ask whether a self-consistent implementation is really necessary to obtain accurate RPA correlation and thus ground state energies. Clearly, a purely perturbative treatment of RPA-type functionals on the basis of a self-consistent calculation with the exact exchange would allow their application to much more complex systems, for which the solution of the corresponding OPM integral equation is beyond current computer resources. In fact, experience with conventional density functionals suggests that, at least for atomic systems, the RPA correlation energy is not sensitive to the detailed structure of \( v_{xc}(r) \).

In order to verify this expectation, the RPA ground state energy (i.e. the sum of the KS kinetic energy, the Hartree term, the exact exchange and \( E_{RPA}^{c} \)) has been calculated by insertion of KS orbitals resulting from different XC functionals: Orbitals obtained from self-consistent calculations with only the exact exchange (EXX-only), but neglecting \( v_{c} \) completely, are compared with self-consistent LDA and GGA orbitals. The results for a number of atoms are collected in Table [IV] which also includes recent self-consistent RPA energies whenever available. Table [IV] confirms the expectation: Even though the KS potentials obtained by EXX-only calculations differ substantially from their LDA and GGA
TABLE IV: Absolute RPA total energies (in Hartree) resulting from insertion of different KS orbitals. The last row lists the self-consistent RPA total energies given in Ref.43.

| KS orbitals | He  | Be  | Ne  | Mg  | Ar  | N   | Na  |
|-------------|-----|-----|-----|-----|-----|-----|-----|
| LDA         | 2.945 | 14.751 | 129.140 | 200.293 | 527.905 | 54.735 | 162.475 |
| BLYP        | 2.944 | 14.752 | 129.142 | 200.296 | 527.910 | 54.737 | 162.478 |
| EXX-only    | 2.945 | 14.752 | 129.143 | 200.298 | 527.913 | 54.738 | 162.480 |
| RPA         | 2.945 | 14.754 | 129.143 | 200.296 | 527.908 | —     | —     |

...correlates, the differences between the resulting RPA energies are quite small. The same is true for the deviations between the perturbative RPA energies on EXX-only basis and the self-consistent RPA results. This result is expected to hold quite generally, as long as one does not examine a quantity which is particularly sensitive to the correlation potential (as, for instance, the quantum defect of high Rydberg states). In fact, Table IV indicates that even a perturbative treatment of both the exact exchange and the RPA may be legitimate for very complex systems, in which even self-consistent calculations with the exact exchange are too expensive. In the following sections, self-consistent EXX-only orbitals are always used for the evaluation of the RPA correlation energy.

**B. RPA correlation energies of spherical atoms**

In this work, we focus on atoms with closed or half-filled shells, for which the ground state KS potentials for the two spin-channels are both spherically symmetric. Table IV lists the correlation energies obtained from all four RPA-based functionals for a series of atoms. To see trends more clearly, the relative errors resulting from the various functionals with respect to the exact correlation energies are plotted in Figure 7. Not surprisingly, the pure RPA always overestimates the true correlation energy. Adding the short-range correction within the LDA (RPA+) improves the results remarkably, reducing the mean absolute error by more than an order of magnitude. As expected, the unscreened SOX contribution by far overcorrects the error of the RPA. On the other hand, the inclusion of EN-corrections into the SOX term (RPA+SOX) reduces the overcorrection significantly. In general, both the RPA+ and the RPA+SOX produce more accurate correlation energies than the LYP-GGA, at least for the set of atoms considered in this work. Moreover, for light atoms one observes a tendency of the RPA+SOX to be superior to the RPA+.

**C. Ionization potentials**

Even more important than the accuracy of total (correlation) energies is the accuracy of energy differences. In the case of atoms the ionization potential (IP) serves as the prototype energy difference for assessing the quality of any approximation. Much more than the total atomic $E_c$, the IP probes the description of the correlation of the valence states. We have therefore calculated the IPs resulting from the four RPA-based correlation functionals for a number of atoms. In order to avoid any uncertainty associated with spherical averaging, the comparison is restricted to atoms for which both the KS potential of the neutral ground state and that corresponding to the ionic state are spherical. The results are collected in Table V. The most noteworthy features of these data are: (1) The pure RPA,
TABLE VI: First ionization potentials (in Hartree) of spherical atoms calculated from total energy differences (IP = \( E_{\text{tot}(N-1)} - E_{\text{tot}(N)} \)), using different XC functionals. The last row provides the mean absolute error (MAE) with respect to the exact results. Self-consistent EXX-only KS orbitals are used as input orbitals.

| atom | exact | EXX | RPA | RPA+ | RPA+SOX | RPA+RSOX | BLYP |
|------|-------|-----|-----|------|---------|----------|------|
| Li   | 0.198 | 0.195 | 0.220 | 0.205 | 0.185 | 0.203 | 0.201 |
| Be\(^+\) | 0.669 | 0.666 | 0.700 | 0.683 | 0.656 | 0.677 | 0.681 |
| Be | 0.343 | 0.295 | 0.352 | 0.338 | 0.323 | 0.336 | 0.329 |
| B\(^+\) | 0.924 | 0.861 | 0.935 | 0.919 | 0.897 | 0.912 | 0.904 |
| Na | 0.189 | 0.179 | 0.206 | 0.191 | 0.178 | 0.191 | 0.194 |
| Mg\(^+\) | 0.552 | 0.540 | 0.573 | 0.557 | 0.543 | 0.555 | 0.566 |
| Mg | 0.281 | 0.242 | 0.294 | 0.279 | 0.268 | 0.279 | 0.279 |
| Al\(^+\) | 0.691 | 0.643 | 0.706 | 0.691 | 0.677 | 0.688 | 0.691 |

MAE | 0.028 | 0.017 | 0.005 | 0.015 | 0.005 | 0.009 |

though showing significant improvement over the EXX-only approximation, generally overestimates the true IPs; (2) Correspondingly, the RPA+SOX underestimates IPs (consistent with the unscreened nature of the pure SOX term); (3) Both the RPA+ and the RPA+RSOX significantly improve over the pure RPA results, and are even more accurate than BLYP, the “most accurate” standard GGA.

V. SUMMARY AND CONCLUSIONS

In this work, we provide benchmark results for the RPA and three simple extensions, allowing for an unambiguous assessment of the functionals by comparison with exact data. Our results confirm earlier observations of the limited applicability of the pure RPA: The RPA substantially overestimates correlation energies, which then results in an overestimation of energy differences like ionization potentials. On the other hand, our results also demonstrate that already quite simple extensions of the RPA can be superior to standard GGAs: Adding either short-range corrections within the LDA (RPA+) or a suitably ‘screened’ second order exchange contribution (RPA+RSOX) significantly improves both absolute energies and energy differences. This success is consistent with the expectation that the dominant source of error in the RPA functional is the missing short-range SOX contribution.

It seems worthwhile emphasizing that the first of these extensions, the RPA+, essentially comes at no cost: Compared to the computational demands of an RPA-calculation, the cost of the LDA for the non-RPA correlation is irrelevant. Moreover, a systematic improvement of the RPA+ by inclusion of
gradient corrections for the non-RPA correlation contributions suggests itself. The RPA+RSOX involves an evaluation of the orbital-dependent SOX term, which is computationally almost as demanding as the calculation of the RPA energy itself, but still much less expensive than that of the fully screened SOX term.

In this work also several technical aspects of RPA-calcations have been studied systematically, of which two should be relevant beyond the regime of atoms considered here. The first of these aspects is the sensitivity of the RPA-expression to the orbitals and eigenvalues used for its evaluation. It turned out that the character of the KS spectrum inserted into the RPA has little impact on the resulting energy. Even if KS states obtained by LDA calculations are used the deviations from more accurate data remain small. In order to cover systems with more than one occupied shell, we have developed a partitioning scheme for the frequency integration inherent in all RPA-type functionals, which, together with a suitable transformation of the integration variable, allows to perform the frequency integration with a minimum number of mesh points. Both these numerical techniques should be particularly helpful for applications to more complex systems.

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