Efficient self-consistent treatment of electron correlation within the random phase approximation

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Patrick Bleiziffer,[a)] Andreas Heßelmann, and Andreas Görling
Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3,
D-91058 Erlangen, Germany

A self-consistent Kohn-Sham (KS) method is presented that treats correlation on the basis of the adiabatic-connection dissipation-fluctuation theorem employing the direct random phase approximation (dRPA), i.e., taking into account only the Coulomb kernel while neglecting the exchange-correlation kernel in the calculation of the Kohn-Sham correlation energy and potential. The method, denoted self-consistent dRPA method, furthermore treats exactly the exchange energy and the local multiplicative KS exchange potential. It uses Gaussian basis sets, is reasonably efficient, exhibiting a scaling of the computational effort with the forth power of the system size, and thus is generally applicable to molecules. The resulting dRPA correlation potentials in contrast to common approximate correlation potentials are in good agreement with exact reference potentials. The negatives of the eigenvalues of the highest occupied molecular orbitals are found to be in good agreement with experimental ionization potentials. Total energies from self-consistent dRPA calculations, as expected, are even poorer than non-self-consistent dRPA total energies and dRPA reaction and non-covalent binding energies do not significantly benefit from self-consistency. On the other hand, energies obtained with a recently introduced adiabatic-connection dissipation-fluctuation approach (EXXRPA+, exact-exchange random phase approximation) that takes into account, besides the Coulomb kernel, also the exact frequency-dependent exchange kernel are significantly improved if evaluated with orbitals obtained from a self-consistent dRPA calculation instead of an exact exchange-only calculation. Total energies, reaction energies, and noncovalent binding energies obtained in this way are of the same quality as those of high-level quantum chemistry methods, like the coupled cluster singles doubles method which is computationally more demanding. © *2013 AIP Publishing LLC.*
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I. INTRODUCTION

Kohn-Sham (KS) methods that treat the correlation energy on the basis of the adiabatic-connection fluctuation-dissipation theorem (ACFD)[1,2] have raised considerable interest in recent years[3–46] and have proven to constitute a highly promising new type of density-functional methods that have the potential to overcome the shortcomings of conventional KS methods based on the generalized gradient approximation (GGA)[47–49] as well as of generalized KS methods[50] combining elements of the Hartree-Fock approach with the KS formalism.[50–53] The ACFD theorem yields an exact expression for the KS correlation energy in terms of frequency-dependent density-density (potential-density) response functions, more precisely in terms of the KS response function and response functions of interacting systems with an electron-electron interaction scaled by a coupling constant. While the KS response functions are known exactly and are easily accessible, the response functions of interacting systems have to be determined approximately via time-dependent density-functional theory (TDDFT), that is via density-functional response theory of first order.[54–56] The quantity to be approximated in TDDFT in the linear response regime is the exchange-correlation kernel, the frequency-

dependent functional derivative of the exchange-correlation potential.

In most KS methods based on the ACFD theorem the exchange-correlation kernel is neglected and only the known and frequency-independent Coulomb kernel, the functional derivative of the Hartree potential, is taken into account. This leads to a random phase approximation (RPA) within the framework of the KS formalism. Methods based on the ACFD theorem, therefore, commonly are denoted RPA methods, despite the fact that some of these methods go beyond the RPA. In order to distinguish the simple RPA methods from ACFD methods going beyond it, shall be denoted as direct RPA (dRPA) here. An advantage of dRPA methods is that they are able to describe Van-der-Waals interactions. Total energies from dRPA methods, however, are known to be poor, indeed much less accurate than total energies from GGA or hybrid methods, while dRPA reaction energies are of similar quality as those from conventional KS methods, see, e.g., Ref. 42 and results of this work. The poor dRPA total energies can be related to the fundamental flaw of the dRPA that it is not free of self-interaction. An obvious sign of this fundamental problem is the fact that the dRPA correlation energy of one-electron systems is not zero.

Because of the shortcomings of the dRPA various approaches have been developed that introduce corrections and modifications to it, e.g., by invoking perturbation

a)patrick.bleiziffer@fau.de

theory,[14,20,57] augmentations by additional first-order singles terms,[39] or by devising methods employing range-separation techniques in order to treat only parts of the correlation energy via the dRPA while other parts are treated by approximate semilocal functionals.[21,22,29,30,58–60]

A fundamental step beyond the dRPA is to take into account not only the Coulomb kernel but also the exact frequency-dependent exchange-kernel[54,61–63] in the construction of the coupling-constant-dependent response functions. Such methods were denoted EXXRPA+ methods[46] and were implemented for atoms using numerical grid procedures[15,16,32] and for general molecular systems employing Gaussian basis sets.[36–38,46] EXXRPA+ methods are free of self-interactions, yield total as well as binding energies that are more accurate than GGA or hybrid methods, describe Van-der-Waals interactions with high accuracy and even are able to treat systems characterized by static correlation.[37]

So far, methods based on the ACFD theorem almost exclusively were applied in a post self-consistent-field (SCF) fashion, i.e., first, a self-consistent conventional or hybrid calculation is carried out and the orbitals and eigenvalues resulting from this calculation then are used to exactly evaluate the exchange energy and the ACFD correlation energy. Exceptions are self-consistent dRPA and EXXRPA+ calculations for atoms based on numerical grid techniques[15,32] and self-consistent dRPA calculations for a number of atoms and small molecules with Gaussian basis set implementations[44,45] that exhibit an unfavorable scaling of the computational effort with the system size and, therefore, are not suitable for most systems of interest. In this work, we introduce a self-consistent dRPA method using Gaussian basis sets that exhibits the same N^4 scaling with the system size N, e.g., the number of electrons, as methods evaluating in a post-SCF way only the dRPA correlation energy.

By employing the dRPA in a self-consistent manner the fundamental shortcomings of the dRPA discussed above cannot be overcome. Indeed total energies from a self-consistent dRPA approach have to be even worse than those from post-SCF dRPA methods. The reason is that the dRPA correlation energy is too large in magnitude leading to a too low total energy. Going from a post-SCF to a self-consistent dRPA evaluation of the correlation energy, however, has to lower the total energy further because self-consistent dRPA methods are variational with respect to the orbitals and their eigenvalues, or more specifically with respect to the effective KS potential determining the former. The motivation to develop a self-consistent dRPA, therefore, is not primarily to calculate self-consistent dRPA energies. The main motivations instead are: (i) to have a method that yields correlation potentials that are reasonable approximations to exact KS correlation potentials and (ii) to do a step towards a generally applicable fully self-consistent EXXRPA+ method. With respect to the first point note that approximate GGA exchange-correlation potentials are known to exhibit a completely wrong behavior compared to the exact KS correlation potentials.[64] Indeed in the test case of small atoms, in which a construction of exact correlation potentials was possible, it was shown that GGA correlation potentials have no resemblance to the exact ones.[64] This

highly disturbing point is well-known since long but mostly ignored. This may be justified to some degree in calculations aiming at total and particular reaction energies but it is certainly highly problematic whenever KS orbitals and eigenvalues, which are quite sensitive to the exchange-correlation potential, are used in subsequent calculations, e.g., in TDDFT calculations aiming at excitation energies or in the calculation of quasi-particle band structures by many-body perturbation approaches like the GW approximation.[65,66] Self-consistent dRPA calculations for atoms[15] showed that the resulting correlation potentials are in fair agreement with the true ones. Because the self-consistent dRPA method presented here also treats the exchange potential exactly, the method enables, in a routine way, the computationally efficient calculation of exchange-correlation KS potentials of molecules that can be assumed to be realistic.

Concerning the second motivation it has to be pointed out that EXXRPA+ total energies evaluated with exact-exchange-only (EXX) orbitals and eigenvalues are highly accurate but in almost all cases are slightly too small in magnitude compared to reference data and, therefore, lead to slightly too high total energies. A self-consistent EXXRPA+ method would yield lower and, therefore, most likely even better total energies. Because the dRPA correlation potential can be considered to be a reasonable approximation to the full EXXRPA+ correlation potential it can also be predicted that the EXXRPA+ total energies will be lowered and thus get even more accurate if the EXXRPA+ correlation energy is evaluated with self-consistent dRPA instead of EXX orbitals and eigenvalues.

The paper is organized as follows. In Sec. II, the underlying formalism is explained and derived. First in Subsection II A the evaluation of the dRPA correlation energy is reviewed, then in Subsection II B the method to construct the dRPA correlation potential is derived, next in Subsection II C the processing of the required auxiliary basis sets and procedures to increase the numerical stability of the new method are discussed, and the computational steps of the presented method are summarized. Section III provides computational details, in Sec. IV dRPA correlation potentials are discussed, and in Sec. V dRPA and EXXRPA+ energies (total and reaction energies as well as energies of noncovalent bonds) based on EXX and dRPA orbitals and eigenvalues are analyzed. Furthermore, we consider ionization potentials and KS eigenvalue gaps between the highest occupied and the lowest unoccupied KS orbital in this section. Finally in Sec. VI concluding remarks are made.

II. FORMALISM

A. Correlation energy in the random phase approximation

Functionals for the KS correlation energy E_c within the RPA are based on the adiabatic-connection fluctuation-dissipation theorem[1,2]

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$
$$[\chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega)], \quad (1)$$

which represents an exact expression for E_c in terms of the frequency-dependent or dynamic KS response function χ_0 and the corresponding coupling-constant-dependent response functions χ_α. The dynamic KS response function for a frequency ν is given by

$$\chi_0(\nu, \mathbf{r}, \mathbf{r}') = \sum_i \sum_a \varphi_i(\mathbf{r})\,\varphi_a(\mathbf{r})\,\lambda_{ia}(\nu)\,\varphi_a(\mathbf{r}')\,\varphi_i(\mathbf{r}'), \quad (2)$$

in terms of the occupied and unoccupied KS orbitals φ_i and φ_a, respectively, and in terms of the corresponding KS eigenvalues ε_i and ε_a via

$$\lambda_{ia}(\nu) = -4\varepsilon_{ia}/\left(\varepsilon_{ia}^2 - \nu^2\right), \quad (3)$$

with $\varepsilon_{ia} = \varepsilon_a - \varepsilon_i$. Throughout this paper we consider non-spin-polarized electronic systems with real-valued KS orbitals. Spin is taken into account via appropriate prefactors. The response functions χ_α are frequency-dependent density-density (potential-density) response functions of interacting electronic systems along the adiabatic connection for a coupling constant α, i.e., of hypothetical electronic systems that have the same ground state electron density as the real fully interacting electron system but contain electrons that interact with an electron-electron interaction scaled by the coupling constant $0 \le \alpha \le 1$. For $\alpha = 0$ the response function χ_α turns into the KS response function χ_0, for $\alpha = 1$ into the response function of the fully interacting real electron system.

In contrast to the KS response function χ_0 the coupling-constant-dependent response functions χ_α are not exactly known for $\alpha \ne 0$. Methods based on the RPA within the KS framework determine the response functions χ_α by TDDFT more precisely by density-functional response theory of first order.[54–56] Within TDDFT the response functions χ_α are given by

$$\chi_\alpha(\nu, \mathbf{r}, \mathbf{r}')$$
$$= \chi_0(\nu, \mathbf{r}, \mathbf{r}')$$
$$+ \int d\mathbf{r}'' d\mathbf{r}''' \chi_0(\nu, \mathbf{r}, \mathbf{r}'')\, f_{\mathrm{Hxc}}^\alpha(\nu, \mathbf{r}'', \mathbf{r}''')\, \chi_\alpha(\nu, \mathbf{r}''', \mathbf{r}').$$
$$(4)$$

In Eq. (4) f_{Hxc}^α is the sum of the Coulomb or Hartree kernel $f_{\mathrm{H}}^\alpha(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ and the exchange-correlation kernel f_{xc}^α the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density. The approximation chosen for the exchange-correlation kernel determines the quality of the resulting approach. With the exact exchange-correlation kernel the exact correlation energy would be obtained. The RPA is defined by neglecting completely the exchange-correlation kernel and keeping only the Coulomb kernel. If only the correlation contribution to the exchange-correlation kernel is neglected and the exchange contribution is treated exactly together with the Coulomb kernel the EXXRPA+ (exact-exchange RPA) method of Refs. 16, 32, 36–38, and 46 is obtained. The name EXXRPA+ is somewhat misleading because the EXXRPA+ method actually goes beyond the simple RPA. In order to distinguish the RPA method considered here which is based on the original RPA from methods like the EXXRPA+ method we will denote it dRPA method here. With the dRPA, i.e., the

neglect of the exchange-correlation kernel, Eq. (4) for the response function χ_α simplifies to

$$\chi_\alpha(\nu, \mathbf{r}, \mathbf{r}') = \chi_0(\nu, \mathbf{r}, \mathbf{r}')$$
$$+ \int d\mathbf{r}'' d\mathbf{r}''' \chi_0(\nu, \mathbf{r}, \mathbf{r}'')\, \frac{\alpha}{|\mathbf{r}'' - \mathbf{r}'''|}\, \chi_\alpha(\nu, \mathbf{r}''', \mathbf{r}')$$
$$(5)$$

and contains only accessible quantities.

In order to evaluate the response function χ_α via Eq. (5) we introduce an auxiliary basis set, the resolution-of-the-identity (RI) basis set,[67–71] by the unsymmetric resolutions of the identity

$$\delta(\mathbf{r} - \mathbf{r}') = \sum_{pq} \tilde{f}_p(\mathbf{r})\, \left[\widetilde{\mathbf{S}}^{-1}\right]_{pq} \int d\mathbf{r}''\, \frac{\tilde{f}_q(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|}, \quad (6)$$

$$= \sum_{pq} \int d\mathbf{r}''\, \frac{\tilde{f}_p(\mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|}\, [\widetilde{\mathbf{S}}^{-1}]_{pq}\, \tilde{f}_q(\mathbf{r}'), \quad (7)$$

with the RI Gaussian basis functions $\tilde{f}_p$ and the overlap matrix $\widetilde{\mathbf{S}}$ with respect to the Coulomb norm defined by its matrix elements

$$\widetilde{S}_{pq} = \int d\mathbf{r} d\mathbf{r}'\, \frac{\tilde{f}_p(\mathbf{r})\, \tilde{f}_q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (8)$$

The tilde on $\tilde{f}_p$ and $\widetilde{\mathbf{S}}$ indicates that the original RI basis functions, e.g., from basis sets libraries like those of Refs. 72 and 73, and their overlap matrix are preliminary quantities that, later on, will be modified to the auxiliary basis functions and overlap matrix actually used, see Subsection II C.

By acting with the resolution of the identity (6) from the left and with the resolution of the identity (7) from the right in Eq. (5) and by inserting the resolution of the identity (6) into the right hand side of Eq. (5) after the Coulomb kernel, Eq. (5) turns into the matrix equation

$$\widetilde{\mathbf{S}}^{-1}\, \widetilde{\mathbf{X}}_\alpha(\nu)\, \widetilde{\mathbf{S}}^{-1} = \widetilde{\mathbf{S}}^{-1}\, \widetilde{\mathbf{X}}_0(\nu)\, \widetilde{\mathbf{S}}^{-1}$$
$$+ \alpha\, \widetilde{\mathbf{S}}^{-1}\, \widetilde{\mathbf{X}}_0(\nu)\, \widetilde{\mathbf{S}}^{-1}\, \widetilde{\mathbf{X}}_\alpha(\nu)\, \widetilde{\mathbf{S}}^{-1}, \quad (9)$$

which can be rearranged into the expression

$$\widetilde{\mathbf{X}}_\alpha(\nu) = [\mathbf{1} - \alpha\, \widetilde{\mathbf{X}}_0(\nu)\, \widetilde{\mathbf{S}}^{-1}]^{-1}\, \widetilde{\mathbf{X}}_0(\nu) \quad (10)$$

for the matrix representation $\widetilde{\mathbf{X}}_\alpha(\nu)$ of the coupling-constant-dependent response function χ_α. The matrix elements of the uncoupled KS response matrix $\widetilde{\mathbf{X}}_0(\nu)$ are given by

$$\widetilde{X}_{0,pq}(\nu) = \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''\, \frac{\tilde{f}_p(\mathbf{r}''')\, \chi_0(\nu, \mathbf{r}'', \mathbf{r}')\, \tilde{f}_q(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'||\mathbf{r}'' - \mathbf{r}'''|}. \quad (11)$$

In order to calculate $\widetilde{\mathbf{X}}_0(\nu)$ we define the integrals

$$(\varphi_i\, \varphi_a \mid \tilde{f}_p) = \int d\mathbf{r} d\mathbf{r}'\, \frac{\varphi_i(\mathbf{r})\, \varphi_a(\mathbf{r})\, \tilde{f}_p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (12)$$

The matrix elements $\widetilde{X}_{0,pq}(\nu)$ of the uncoupled KS response function $\widetilde{\mathbf{X}}_0(\nu)$ are given by

$$\widetilde{X}_{0,pq}(\nu) = \sum_{ia} (\varphi_i\, \varphi_a \mid \tilde{f}_p)\, \lambda_{ia}(\nu)\, (\varphi_i\, \varphi_a \mid \tilde{f}_q), \quad (13)$$

with $\lambda_{ia}(\nu)$ defined in Eq. (3).

With Eqs. (5)–(7) and (10) the response function χ_α assumes the form

$$
\begin{aligned}
\chi_\alpha(\nu, \mathbf{r}, \mathbf{r}') \\
= \sum_p \sum_q \tilde{f}_p(\mathbf{r}) [\widetilde{\mathbf{S}}^{-1} \widetilde{\mathbf{X}}_\alpha(\nu) \widetilde{\mathbf{S}}^{-1}]_{pq}\, \tilde{f}_q(\mathbf{r}') \\
= \sum_p \sum_q \tilde{f}_p(\mathbf{r}) [\widetilde{\mathbf{S}}^{-1} [\mathbf{1} - \alpha \widetilde{\mathbf{X}}_0(\nu)\widetilde{\mathbf{S}}^{-1}]^{-1} \widetilde{\mathbf{X}}_0(\nu)\widetilde{\mathbf{S}}^{-1}]_{pq} \tilde{f}_q(\mathbf{r}') \\
= \sum_p \sum_q \tilde{f}_p(\mathbf{r}) [[\widetilde{\mathbf{S}} - \alpha \widetilde{\mathbf{X}}_0(\nu)]^{-1} \widetilde{\mathbf{X}}_0(\nu)\widetilde{\mathbf{S}}^{-1}]_{pq}\, \tilde{f}_q(\mathbf{r}').
\end{aligned}
\tag{14}
$$

In the ACFD theorem (1) the integral

$$
\begin{aligned}
\int d\mathbf{r} d\mathbf{r}'\, \frac{\chi_\alpha(\nu, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
= \sum_{pq} [[\widetilde{\mathbf{S}} - \alpha \widetilde{\mathbf{X}}_0(\nu)]^{-1} \widetilde{\mathbf{X}}_0(\nu)\widetilde{\mathbf{S}}^{-1}]_{pq}\, \widetilde{S}_{pq} \\
= \mathrm{Tr}\,[[\widetilde{\mathbf{S}} - \alpha \widetilde{\mathbf{X}}_0(\nu)]^{-1} \widetilde{\mathbf{X}}_0(\nu)]
\end{aligned}
\tag{15}
$$

occurs. For $\alpha = 0$, Eq. (14) gives the uncoupled KS response function $\chi_0(\nu, \mathbf{r}, \mathbf{r}')$ and Eq. (15) turns into the integral

$$
\int d\mathbf{r} d\mathbf{r}'\, \frac{\chi_0(\nu, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \mathrm{Tr}[\widetilde{\mathbf{S}}^{-1} \widetilde{\mathbf{X}}_0(\nu)].
\tag{16}
$$

Setting $\nu = i\omega$ and inserting Eqs. (15) and (16) into the ACFD theorem (1) leads to the expression

$$
\begin{aligned}
E_c^{\mathrm{dRPA}} = \frac{-1}{2\pi} \int_0^\infty d\omega \\
\times \int_0^1 d\alpha \mathrm{Tr}\,[[\widetilde{\mathbf{S}} - \alpha \widetilde{\mathbf{X}}_0(i\omega)]^{-1}\widetilde{\mathbf{X}}_0(i\omega) - \widetilde{\mathbf{S}}^{-1}\widetilde{\mathbf{X}}_0(i\omega)]
\end{aligned}
\tag{17}
$$

for the dRPA correlation energy E_c^{dRPA}. Equation (17) could be used to calculate the dRPA correlation energy. However, this would require to carry out numerically both the frequency and the coupling-strength integration. In order to perform the coupling-strength integration analytically and thus more efficiently we switch from the original RI basis functions $\tilde{f}_p$ to new auxiliary basis functions f_p which are linear combinations of the original ones. The linear combinations are determined such that the corresponding overlap matrix $\mathbf{S}$ with respect to the Coulomb norm, i.e., the analog of the overlap matrix $\widetilde{\mathbf{S}}$ of Eq. (8) in case of the new auxiliary basis functions f_p, is a unit matrix. Moreover, the linear combination of auxiliary basis functions f_p that corresponds to a constant function is removed. (See Sec. II C for details on the construction of the new auxiliary basis functions f_p.) The matrix representation of the KS response function with respect to the new auxiliary

basis functions shall be denoted $\mathbf{X}_0(i\omega)$. Taking into account that $\mathbf{S} = \mathbf{1}$, Eq. (17) turns into

$$
E_c^{\mathrm{dRPA}} = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \mathrm{Tr}[[\mathbf{1} - \alpha \mathbf{X}_0(\nu)]^{-1}\mathbf{X}_0(i\omega) - \mathbf{X}_0(\nu)]
\tag{18}
$$

for the new auxiliary basis functions. Next we diagonalize the KS response matrix $\mathbf{X}_0(i\omega)$ and represent it by

$$
\mathbf{X}_0(i\omega) = \mathbf{V}(i\omega)\, \boldsymbol{\sigma}(i\omega)\, \mathbf{V}^T(i\omega).
\tag{19}
$$

In Eq. (19), the matrix $\mathbf{V}(i\omega)$ contains as columns the eigenvectors of the KS response matrix $\mathbf{X}_0(i\omega)$ while the diagonal matrix $\boldsymbol{\sigma}(i\omega)$ contains its eigenvalues. Inserting the representation (19) of the KS response matrix in Eq. (18) for the dRPA correlation energy yields the final expression

$$
\begin{aligned}
E_c^{\mathrm{dRPA}} &= \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \mathrm{Tr}[[\mathbf{1} - \alpha \mathbf{V}(i\omega)\boldsymbol{\sigma}(i\omega)\mathbf{V}^T(i\omega)]^{-1} \\
&\quad \times \mathbf{V}(i\omega)\boldsymbol{\sigma}(i\omega)\mathbf{V}^T(i\omega) - \mathbf{V}(i\omega)\boldsymbol{\sigma}(i\omega)\,\mathbf{V}^T(i\omega)] \\
&= \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \mathrm{Tr}[[\mathbf{1} - \alpha\boldsymbol{\sigma}(i\omega)]^{-1}\boldsymbol{\sigma}(i\omega) - \boldsymbol{\sigma}(i\omega)] \\
&= \frac{1}{2\pi} \int_0^\infty d\omega \mathrm{Tr}[\ln(|\mathbf{1} - \boldsymbol{\sigma}(i\omega)|) + \boldsymbol{\sigma}(i\omega)]
\end{aligned}
\tag{20}
$$

for the latter. In the last line of Eq. (20), the coupling strength integration has been carried out analytically. Equation (20) for the dRPA correlation energy can be carried out exceptionally easily. The computationally most demanding task is the construction of the KS response function $\mathbf{X}_0(i\omega)$ for as many frequencies as are needed in the frequency integration, which is carried out numerically, e.g., by a Gauss-Legendre[74] quadrature. The computational effort for the construction of $\mathbf{X}_0(i\omega)$ scales like N^4 with the system size N, however, with a moderate prefactor. All other steps in the calculation of the dRPA correlation energy, including the diagonalization of $\mathbf{X}_0(i\omega)$, exhibit a more favorable scaling of the computational effort with the system size.

B. Correlation potential in the random phase approximation

The dRPA correlation potential v_c^{dRPA} is defined as the functional derivative of the dRPA correlation energy E_c^{dRPA} with respect to the electron density $\rho(\mathbf{r})$, i.e., by

$$
v_c^{\mathrm{dRPA}}(\mathbf{r}) = \frac{\delta E_c^{\mathrm{dRPA}}}{\delta \rho(\mathbf{r})}.
\tag{21}
$$

The dRPA correlation energy E_c^{dRPA} is given in terms of KS orbitals and eigenvalues. The KS orbitals and eigenvalues are functionals of the ground state electron density $\rho(\mathbf{r})$. However, we do not know the form of these functionals. Therefore, we cannot evaluate the functional derivative $\delta E_c^{\mathrm{dRPA}}/\delta \rho(\mathbf{r})$ via the chain rule by first taking the derivative of E_c^{dRPA} with respect to the KS orbitals and their eigenvalues and by subsequently taking the functional derivative of the KS orbitals and

their eigenvalues with respect to the electron density. Instead, the dRPA correlation potential v_c^{dRPA} can be obtained via the optimized effective potential (OEP) method,[75–77] which yields the functional derivative with respect to the electron density of quantities that depend on KS orbitals and eigenvalues in form of an integral equation, the OEP equation. The OEP equation for the dRPA correlation potential v_c^{dRPA} assumes the form

$$\int d\mathbf{r}' \, \chi_0(0, \mathbf{r}, \mathbf{r}') \, v_c^{\text{dRPA}}(\mathbf{r}') \,=\, t_c^{\text{dRPA}}(\mathbf{r}) \qquad (22)$$

with

$$t_c^{\text{dRPA}}(\mathbf{r}) = \frac{\delta E_c^{\text{dRPA}}}{\delta v_s(\mathbf{r})}$$
$$= \sum_u \left[\int d\mathbf{r}' \, \frac{\delta E_c^{\text{dRPA}}}{\delta \varphi_u(\mathbf{r}')} \frac{\delta \varphi_u(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{\delta E_c^{\text{dRPA}}}{\delta \varepsilon_u} \frac{\delta \varepsilon_u}{\delta v_s(\mathbf{r})} \right]. \qquad (23)$$

In Eq. (22), v_s denotes the KS potential and $\chi_0(0, \mathbf{r}, \mathbf{r}')$ is the KS response function for a frequency of zero, i.e., the static KS response function.

In order to handle the OEP equation (22) computationally, we again invoke the auxiliary basis set $\{f_q\}$ and expand the dRPA correlation potential $v_c^{\text{dRPA}}(\mathbf{r})$ according to

$$v_c^{\text{dRPA}}(\mathbf{r}) = \sum_\nu v_{c,\nu}^{\text{dRPA}} \int d\mathbf{r}' \, \frac{f_\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad (24)$$

as a linear combination of electrostatic potentials of auxiliary basis functions f_ν. The corresponding linear combination

$$\rho_c^{\text{dRPA}}(\mathbf{r}) = \sum_\nu v_{c,\nu}^{\text{dRPA}} f_\nu(\mathbf{r}) \qquad (25)$$

of the auxiliary basis functions f_ν itself represents a correlation charge density $\rho_c^{\text{dRPA}}(\mathbf{r})$, the electrostatic potential of which is the dRPA correlation potential. By acting from the left with the resolution of the identity (6), or more precisely with the analog of (6) in the case of the new auxiliary basis functions f_ν, on the OEP equation (22) and by expressing v_c^{dRPA} according to Eq. (24), turns the OEP equation (22) into the matrix equation

$$\mathbf{X}_0(0) \, \mathbf{v}_c^{\text{dRPA}} = \mathbf{t}_c^{\text{dRPA}} \qquad (26)$$

with

$$t_{c,\nu}^{\text{dRPA}} = \int d\mathbf{r} d\mathbf{r}' \, \frac{f_\nu(\mathbf{r}') \delta E_c / \delta v_s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \qquad (27)$$

In order to calculate the elements $t_{c,\nu}^{\text{dRPA}}$ of the vector $\mathbf{t}_c^{\text{dRPA}}$ of the right hand side of the OEP equation (26), we consider an expansion of the KS potential v_s in the auxiliary basis functions f_ν, or more precisely in electrostatic potentials of the functions f_ν,

$$v_s(\mathbf{r}) = \sum_\nu v_{s,\nu} \int d\mathbf{r}' \, \frac{f_\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \qquad (28)$$

In actual KS calculations only parts of the KS potential v_s, the exchange and correlation contributions, are expanded in

the auxiliary basis set. This, however, does not affect the following arguments. The crucial point is that we will consider only changes of the KS potential $v_s(\mathbf{r})$ that can be expanded according to (28) when taking functional derivatives with respect to $v_s(\mathbf{r})$. The derivative of the dRPA correlation energy with respect to changes of the expansion coefficients $v_{s,\nu}$ in Eq. (28) yields the required vector elements $t_{c,\nu}^{\text{dRPA}}$ for the right hand side of the OEP equation (26) according to

$$\frac{\partial E_c^{\text{dRPA}}}{\partial v_{s,\nu}} = \int d\mathbf{r} \, \frac{\delta E_c^{\text{dRPA}}}{\delta v_s(\mathbf{r})} \frac{\delta v_s(\mathbf{r})}{\delta v_{s,\nu}}$$
$$= \int d\mathbf{r} \, \frac{\delta E_c^{\text{dRPA}}}{\delta v_s(\mathbf{r})} \int d\mathbf{r}' \, \frac{f_\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$= t_{c,\nu}^{\text{dRPA}}. \qquad (29)$$

Because standard perturbation theory gives access to the change of KS orbitals and eigenvalues in linear order with a change of the expansion coefficients $v_{s,\nu}$ of the KS potential and because the dRPA correlation energy depends on KS orbitals and eigenvalues we can calculate the derivative $\partial E_c^{\text{dRPA}} / \partial v_{s,\nu}$ and thus the required vector elements $t_{c,\nu}^{\text{dRPA}}$ in a straightforward though somewhat involved way. Below we will, step by step, develop an expression for this derivative that can be evaluated efficiently.

Because the correlation energy according to Eq. (20) depends exclusively on the diagonal matrix $\boldsymbol{\sigma}(i\omega)$ containing the eigenvalues $\sigma_n(i\omega)$ of the KS response matrix $\mathbf{X}_0(i\omega)$ we need the derivatives $\sigma'_{n,\nu}(i\omega)$ of the eigenvalues $\sigma_n(i\omega)$ with respect to the coefficients $v_{s,\nu}$ in order to obtain the corresponding derivative $\boldsymbol{\sigma}'_\nu(i\omega)$ of $\boldsymbol{\sigma}(i\omega)$. With $\boldsymbol{\sigma}'_\nu(i\omega)$ the first order change $t_{c,\nu}^{\text{dRPA}}$ of E_c^{dRPA} is given by

$$t_{c,\nu}^{\text{dRPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \, \text{Tr}\left[\frac{-\boldsymbol{\sigma}(i\omega) \, \boldsymbol{\sigma}'_\nu(i\omega)}{\mathbf{1} + \boldsymbol{\sigma}(i\omega)} \right]$$
$$= \int_0^\infty d\omega \, t_{c,\nu}(i\omega) \qquad (30)$$

with

$$t_{c,\nu}(i\omega) = \frac{1}{2\pi} \text{Tr}\left[\frac{-\boldsymbol{\sigma}(i\omega) \, \boldsymbol{\sigma}'_\nu(i\omega)}{\mathbf{1} + \boldsymbol{\sigma}(i\omega)} \right]. \qquad (31)$$

According to basic perturbation theory, the derivative $\sigma'_{n,\nu}(i\omega)$ is given by

$$\sigma'_{n,\nu}(i\omega) = \mathbf{v}_n^T(i\omega) \, \mathbf{X}'_{0,\nu}(i\omega) \, \mathbf{v}_n(i\omega), \qquad (32)$$

with $\mathbf{X}'_{0,\nu}(i\omega)$ being the derivative of $\mathbf{X}_0(i\omega)$ with respect to the coefficients $v_{s,\nu}$ and with $\mathbf{v}_n(i\omega)$ denoting the eigenvectors of $\mathbf{X}_0(i\omega)$.

Next we define integrals

$$(\varphi_s \, \varphi_t | f_p) = \int d\mathbf{r} d\mathbf{r}' \, \frac{\varphi_s(\mathbf{r}) \varphi_t(\mathbf{r}) \, f_p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad (33)$$

with the indices s and t referring to arbitrary, i.e., occupied or unoccupied, orbitals. For $s = i$ and $t = a$ the integrals $(\varphi_s \, \varphi_t | f_p)$

are the analog of the integrals $(\varphi_i \varphi_a | \tilde{f}_p)$ of Eq. (12) with the difference that the latter contain the original RI functions $\tilde{f}_p$ whereas the former contain the actually used linear combinations f_p, i.e., the actually used auxiliary basis functions, see Sec. II C for details. The elements $X_{0,pq}(i\omega)$ of the dynamic KS response function are given by

$$X_{0,pq}(i\omega) = \sum_{ia} (\varphi_i \varphi_a | f_p) \, \lambda_{ia}(i\omega) \, (\varphi_i \varphi_a | f_q) . \quad (34)$$

Equation (34) is the analog of Eq. (13) for $\nu = i\omega$ after switching from the original RI basis functions $\tilde{f}_p$ to the actually used auxiliary basis functions f_p.

Starting from Eqs. (32) and (34) the derivative $\sigma'_{n,\nu}(i\omega)$ can be expressed as

$$\sigma'_{n,\nu}(i\omega)$$

$$= \sum_k \sum_\ell v_{k,n}(i\omega) \, X^{(1)}_{0,k\ell,\nu}(i\omega) \, v_{\ell,n}(i\omega)$$

$$= \sum_k \sum_\ell v_{k,n}(i\omega) \sum_i \sum_a [2(\varphi'_{i,\nu}\varphi_a|f_k)\lambda_{ia}(\varphi_i\varphi_a|f_\ell)$$

$$+ 2 (\varphi_i \varphi'_{a,\nu} | f_k) \, \lambda_{ia} \, (\varphi_i \varphi_a | f_\ell)$$

$$+ (\varphi_i \varphi_a | f_k) \, \lambda'_{ia,\nu} \, (\varphi_i \varphi_a | f_\ell)]v_{\ell,n}(i\omega). \quad (35)$$

The required derivatives $\varphi'_{i,\nu}$, $\varphi'_{a,\nu}$, and $\lambda'_{ia,\nu}$ of the KS orbitals φ_i and φ_a, and the energy factor λ_{ia} with respect to the coefficients $v_{s,\nu}$ are obtained by standard perturbation theory as

$$(\varphi'_{i,\nu} \varphi_a | f_p) = \sum_{s \neq i} (\varphi_s \varphi_a | f_p) \, \frac{(\varphi_s \varphi_i | f_\nu)}{\varepsilon_i - \varepsilon_s}$$

$$= \sum_s N_{sa,p} \, M_{si,\nu}, \quad (36)$$

with

$$N_{st,p} = (\varphi_s \varphi_t | f_p) \quad (37)$$

and

$$M_{st,p} = \begin{array}{ll} \frac{N_{st,p}}{\varepsilon_t - \varepsilon_s} & \text{for } s \neq t \\ 0 & \text{for } s = t . \end{array} \quad (38)$$

Similarly we obtain

$$(\varphi_i \varphi'_{a,\nu} | f_p) = \sum_{s \neq a} (\varphi_i \varphi_s | f_p) \, \frac{(\varphi_s \varphi_a | f_\nu)}{\varepsilon_a - \varepsilon_s}$$

$$= \sum_s N_{si,p} \, M_{sa,\nu} \quad (39)$$

and

$$\lambda'_{ia,\nu}(i\omega) = \gamma_{ia}(i\omega) \, [(\varphi_a \varphi_a | f_\nu) - (\varphi_i \varphi_i | f_\nu)]$$

$$= \gamma_{ia}(i\omega) \, [N_{aa,\nu} - N_{ii,\nu}] \quad (40)$$

with

$$\gamma_{ia}(i\omega) = \frac{d\lambda_{ia}}{d\varepsilon_{ia}}$$

$$= \frac{-4}{\varepsilon_{ia}^2 + \omega^2} + \frac{8\varepsilon_{ia}^2}{\left(\varepsilon_{ia}^2 + \omega^2\right)^2}. \quad (41)$$

If we substitute Eqs. (36), (39), and (40) into Eq. (35), then the derivative $\sigma'_{n,\nu}(i\omega)$ assumes the form

$$\sigma'_{n,\nu}(i\omega) = \sum_p \sum_q v_{p,n}(i\omega)$$

$$\times \sum_i \sum_a \left[2 \sum_s [N_{sa,p}M_{si,\nu}\lambda_{ia}(i\omega)N_{ia,q} + N_{si,p} \, M_{sa,\nu} \, \lambda_{ia}(i\omega) \, N_{ia,q}] \right.$$

$$\left. + N_{ai,p} \, \gamma_{ia}(i\omega) \, [N_{aa,\nu} - N_{ii,\nu}] \, N_{ia,q} \right] v_{q,n}(i\omega)$$

$$= 2 \sum_i \sum_s \left[\sum_a \left[\sum_p v_{p,n}(i\omega) \, N_{sa,p} \right] \lambda_{ia}(i\omega) \left[\sum_q v_{q,n}(i\omega) \, N_{ia,q} \right] \right] M_{si,\nu}$$

$$+ 2 \sum_a \sum_s \left[\sum_i \left[\sum_p v_{p,n}(i\omega) \, N_{si,p} \right] \lambda_{ia}(i\omega) \left[\sum_q v_{q,n}(i\omega) \, N_{ia,q} \right] \right] M_{sa,\nu}$$

$$+ 2 \sum_i \sum_a \left[\sum_p v_{p,n}(i\omega) \, N_{ia,p} \right] \gamma_{ia}(i\omega) \, [N_{aa,\nu} - N_{ii,\nu}] \left[\sum_q v_{q,n}(i\omega) \, N_{ia,q} \right]. \quad (42)$$

In order to evaluate Eq. (42) in a computationally efficient way we now define intermediate quantities that can be calculated with a computational effort scaling at most with N^4 with the system size N. First, we define quantities $F_{st,n}(i\omega)$ by

$$F_{st,n}(i\omega) = \sum_p v_{p,n}(i\omega) N_{st,p} \qquad (43)$$

and substitute them into Eq. (42) to obtain

$$\sigma'_{n,v}(i\omega) = 2 \sum_i \sum_s \left[\sum_a F_{sa,n}(i\omega)\lambda_{ia}(i\omega)F_{ia,n}(i\omega) \right] M_{si,v}$$
$$+ 2 \sum_a \sum_s \left[\sum_i F_{si,n}(i\omega)\lambda_{ia}(i\omega)F_{ia,n}(i\omega) \right] M_{sa,v}$$
$$+ \sum_i \sum_a F_{ia,n}(i\omega)\gamma_{ia}(i\omega)[N_{aa,v} - N_{ii,v}]F_{ia,n}(i\omega). \qquad (44)$$

Next we define quantities $T_{si,n}(i\omega)$ and $T_{sa,n}(i\omega)$ by

$$T_{si,n}(i\omega) = \sum_a F_{sa,n}(i\omega) \lambda_{ia}(i\omega) F_{ia,n}(i\omega) \qquad (45)$$

and

$$T_{sa,n}(i\omega) = \sum_i F_{si,n}(i\omega) \lambda_{ia}(i\omega) F_{ia,n}(i\omega) \qquad (46)$$

and substitute them into Eq. (44) to obtain

$$\sigma'_{n,v}(i\omega) = 2 \sum_i \sum_s T_{si,n}(i\omega) M_{si,v}$$
$$+ 2 \sum_a \sum_s T_{sa,n}(i\omega) M_{sa,v}$$
$$+ \sum_i \sum_a F_{ia,n}(i\omega)\gamma_{ia}(i\omega)F_{ia,n}(i\omega)[N_{aa,v} - N_{ii,v}]. \qquad (47)$$

Equation (47) could be used to calculate the derivatives $\sigma'_{n,v}(i\omega)$. Then in a second step the trace of $[-\boldsymbol{\sigma}(i\omega)\boldsymbol{\sigma}'_v(i\omega)]/[1 + \boldsymbol{\sigma}(i\omega)]$ that occurs in the expression of Eq. (30) for the elements $t_{c,v}^{\text{dRPA}}$ of the right hand side of the OEP equation had to be taken. However, it is computationally more efficient to interchange the order of these steps. We, therefore, define the quantities

$$R_{si}(i\omega) = \sum_n \frac{-\sigma_n(i\omega) T_{si,n}(i\omega)}{1 + \sigma_n(i\omega)}, \qquad (48)$$

$$R_{sa}(i\omega) = \sum_n \frac{-\sigma_n(i\omega) T_{sa,n}(i\omega)}{1 + \sigma_n(i\omega)}, \qquad (49)$$

and

$$Y_{ia}(i\omega) = \sum_n \frac{-\sigma_n(i\omega)F_{ia,n}(i\omega)\gamma_{ia}(i\omega)F_{ia,n}(i\omega)}{1 + \sigma_n(i\omega)}, \qquad (50)$$

and then directly calculate the integrand $t_{c,v}(i\omega)$, Eq. (31), of the frequency integration (30) for the elements $t_{c,v}^{\text{dRPA}}$ of the right hand side $\mathbf{t}_c^{\text{dRPA}}$ of the OEP equation (26) for the dRPA

correlation potential

$$t_{c,v}(i\omega) = \frac{1}{2\pi} \text{Tr} \left[\frac{-\boldsymbol{\sigma}(i\omega)\,\boldsymbol{\sigma}_v^{(1)}(i\omega)}{1 + \boldsymbol{\sigma}(i\omega)} \right]$$
$$= \frac{1}{2\pi} \left[2 \sum_i \sum_s R_{si}(i\omega) M_{si,v} \right.$$
$$+ 2 \sum_a \sum_s R_{sa}(i\omega)M_{sa,v}$$
$$\left. + \sum_i \sum_a Y_{ia}(i\omega)[N_{aa,v} - N_{ii,v}] \right]. \qquad (51)$$

The calculation of the right hand side of the OEP equation (26) is the most demanding task in the construction of the dRPA correlation potential. The KS response matrix $\mathbf{X}_0(0)$ is readily constructed according to Eq. (34). The solution vector $\mathbf{v}_c^{\text{dRPA}}$ of the OEP matrix equation then contains as elements the expansion coefficients $v_{c,v}^{\text{dRPA}}$ of the dRPA correlation potential in terms of electrostatic potentials of the auxiliary basis functions f_v, Eq. (24), and thus determines the dRPA correlation potential. The dRPA correlation potential is then transformed back to an expansion with respect to the original RI basis set $\{\tilde{f}_p\}$ which then finally is used to calculate the contribution of the dRPA correlation potential to the KS Hamiltonian matrix. These steps are discussed in detail in Sec. II C.

C. Processing of auxiliary basis sets and regularization of the OEP equation

As discussed in Secs. II A and II B, the actually used auxiliary basis functions f_p are linear combinations of standard RI basis functions $\tilde{f}_p$. The construction of the employed auxiliary basis functions f_p from the original RI basis sets $\{\tilde{f}_p\}$ is carried out as described in Ref. 46. In Ref. 46, in several steps, a rectangular transformation matrix $\mathbf{W}$ is constructed that contains in its columns the coefficients of linear combinations of the original basis functions $\tilde{f}_p$ that define the new basis functions f_p. The transformation matrix $\mathbf{W}$ is constructed in such a way that the overlap matrix $\mathbf{S}$ with respect to the Coulomb norm in the new auxiliary basis set is a unit matrix, i.e.,

$$\mathbf{W}^T \tilde{\mathbf{S}} \mathbf{W} = \mathbf{S} = \mathbf{1}. \qquad (52)$$

In the process of orthonormalizing the original overlap matrix $\tilde{\mathbf{S}}$ eigenvectors with eigenvalues below a threshold t_S can be removed. In this way it can be guaranteed that the actual used auxiliary basis set $\{f_p\}$ is sufficiently linearly independent. Moreover, the linear combination of original auxiliary basis functions that corresponds to the representation of a constant function is removed. As a result the actually used basis functions f_p are all orthogonal to a constant function. This is important because a constant function is an eigenfunction of the KS response function with eigenvalue zero which would make the OEP equation (26) for the correlation potential singular.

The input data for the calculation of the dRPA correlation energy and potential are the KS eigenvalues and the integrals

$N_{st,p} = (\varphi_s \varphi_t \mid f_p)$ of Eq. (37). These are obtained from integrals $\widetilde{N}_{st,q} = (\varphi_s \varphi_t \mid \tilde{f}_q)$ by

$$N_{st,p} = \sum_q W_{qp} \, \widetilde{N}_{st,q}. \tag{53}$$

The integrals $\widetilde{N}_{st,q} = (\varphi_s \varphi_t \mid \tilde{f}_q)$ are calculated from standard three-center integrals with respect to the orbital and RI basis sets by a transformation from orbital basis functions to molecular orbitals (AO-MO transformation).

A crucial point to consider in OEP methods is their numerical accuracy. For Gaussian basis set methods this is known to be quite critical and a lot of work has been devoted to this point.[77–87] It turned out that the auxiliary basis set and the orbital basis set have to be balanced such that the orbital basis set is sufficiently converged for a given auxiliary basis set. If the auxiliary basis set is increased for a given orbital basis set then OEP methods become numerically unstable. In Ref. 85, balanced auxiliary and orbital basis set are presented. The orbital basis sets, however, are large uncontracted basis set, which would lead to considerable computational effort if employed in RPA methods. In order to be able to use standard orbitals basis sets of Dunning type with core polarization functions[88] together with the corresponding standard RI basis sets,[72,73] we invoke regularization techniques when solving the OEP equation.[81] The interplay of these regularization techniques with the above described processing of the original RI basis set to construct the actually used auxiliary basis functions shall be discussed in detail elsewhere. Here, we will only briefly discuss how the OEP equation is actually solved.

With the spectral representation of the KS response matrix $\mathbf{X}_0(0)$ given in Eq. (19) the solution $\mathbf{v}_c^{\mathrm{dRPA}}$ of the OEP equation (26) is given by

$$\mathbf{v}_c^{\mathrm{dRPA}} = \mathbf{V}(0) \, \boldsymbol{\sigma}^{-1}(0) \, \mathbf{V}^T(0) \, \mathbf{t}_c^{\mathrm{dRPA}}. \tag{54}$$

As regularization we modify the inverse eigenvalues $\sigma_n^{-1}(0)$ of the static KS response matrix in Eq. (54). That is we either replace them by

$$\begin{aligned}
\sigma_n^{-1}(0) &= \sigma_n^{-1}(0) && \text{for } \sigma_n(0) > t_{SVD}^{OEP}, \\
\sigma_n^{-1}(0) &= 0 && \text{for } \sigma_n(0) \le t_{SVD}^{OEP},
\end{aligned} \tag{55}$$

which corresponds to a singular value decomposition or by

$$\sigma_n^{-1}(0) = \frac{1}{\beta + \sigma_n(0)}, \tag{56}$$

which corresponds to a Tikhonov regularization, with the regularization factor β. Note that the regularization is exclusively carried out for the static KS response matrix in the OEP equation, the dynamic response matrices required for the dRPA energy and the right hand side of the OEP equation remain unchanged.

Finally, we have to calculate the contribution $\mathbf{H}_c^{\mathrm{dRPA}}$ of the dRPA correlation potential to the KS Hamiltonian matrix. To that end we first transform the solution $\mathbf{v}_c^{\mathrm{dRPA}}$ of the OEP equation which refers to the auxiliary basis functions f_p back to a vector $\tilde{\mathbf{v}}_c^{\mathrm{dRPA}}$ which contains the expansion coefficients $\tilde{v}_{c,\nu}^{\mathrm{dRPA}}$ of the dRPA correlation potential with respect to the original RI basis functions $\tilde{f}_p$ or more precisely their

electrostatic potential, compare with Eq. (24) for the expansion of the dRPA correlation potential with respect to the new auxiliary basis functions f_p. This backtransformation is given by

$$\tilde{\mathbf{v}}_c^{\mathrm{dRPA}} = \mathbf{W} \, \mathbf{v}_c^{\mathrm{dRPA}} \tag{57}$$

and the elements $H_{c,mn}^{\mathrm{dRPA}}$ of the contribution $\mathbf{H}_c^{\mathrm{dRPA}}$ of the dRPA correlation to the KS Hamiltonian matrix is given by

$$H_{c,mn}^{\mathrm{dRPA}} = \sum_\nu \tilde{v}_{c,\nu}^{\mathrm{dRPA}} \, (\chi_m \chi_n \mid \tilde{f}_\nu) \tag{58}$$

with the integrals $(\chi_m \chi_n \mid \tilde{f}_\nu) = \int d\mathbf{r}\, d\mathbf{r}'\, \chi_m(\mathbf{r})\, \chi_n(\mathbf{r})\, \tilde{f}_\nu(\mathbf{r}')/ |\mathbf{r} - \mathbf{r}'|$ containing orbitals basis functions χ_m and χ_n.

III. COMPUTATIONAL DETAILS

The method was implemented in the development version of the Molpro quantum chemistry package,[89] with which all calculations of this work were performed. Core electrons were fully taken into account in all calculations. The set of 21 organic molecules for which total energies as well as selected reaction energies were calculated is the same as in Ref. 46. The geometries of the S22 benchmark database were taken from Hobza *et al.*,[90] we chose the CCSD(T) values of Takatani *et al.*[91] as complete-basis-set (CBS) reference.

All OEP equations in this work were solved invoking the Tikhonov regularization, Eq. (56), with $\beta = 10^{-3}$ for aug-cc-pCVDZ and aug-cc-pCVTZ and $\beta = 8 \times 10^{-4}$ for the aug-cc-pCVQZ basis sets,[88] if not stated otherwise. The cutoff parameter t_S defined in Ref. 46, which regulates the removal of auxiliary basis functions was set to zero in all self-consistent EXX and dRPA calculations, i.e., no functions were removed beforehand, unless stated otherwise. As auxiliary basis sets (for representing the exchange and correlation potentials, the static and the frequency-dependent KS response functions, and the right hand side of the OEP equation for the potential for the evaluation of the RPA correlation energy) we did not choose aug-cc-pwCVXZ MP2fit basis sets[73] (X = D,T,Q), which could be considered as natural choice to match the employed aug-cc-pCVXZ (X = D,T,Q) orbital basis sets. We found, however, that the steep functions in these RI basis sets render the OEP calculations numerically unstable, which is always the case if the auxiliary basis is too large.[77–83,85–87] The smaller aug-cc-pVXZ MP2fit basis sets[72] turned out to be better balanced with the employed aug-cc-pCVXZ orbital basis sets than their larger counterparts with more core functions.

For the calculations of the reference potentials in Sec. IV we employed large even-tempered orbital basis sets accompanied by an even tempered RI basis set in the case of the neon atom and a modified aug-cc-pV5Z MP2fit basis sets in the case of CO and C_2H_2.[92]

In case of a subsequent calculation of the EXXRPA+ correlation energy with EXX or dRPA orbitals and eigenvalues the values for the cutoffs t_S and t_{SVD} determining the removal of linear dependencies in the auxiliary basis set and the threshold in the singular values decomposition of the frequency-dependent response functions, respectively, were adopted from Ref. 46, i.e., $t_S = 10^{-6}$ and $t_{SVD} = 10^{-4}$. Note that the choices for the two cutoffs exclusively influence

the response functions required in the calculation of the EXXRPA+ correlation energy but not any response functions occurring in the preceding self-consistent dRPA or EXX calculations, see above the technical details of these calculations.

In the self-consistent EXX and dRPA calculations Hartree Fock orbitals were used as starting point and the DIIS[93] method was employed to converge the calculations. The maximum number of 15–20 iterations to converge the self-consistency process was required for the largest complexes of the S22 set, other molecules exhibited a faster convergence. Preliminary tests indicate that the convergence of dRPA calculations could be further accelerated by starting them from EXX orbitals and eigenvalues. A numerical integration over the imaginary frequencies ω is necessary in the self-consistent dRPA calculation, as well as in the possibly following EXXRPA+ calculations. In both cases we used a Gauss-Legendre quadrature scheme,[74] employing 30 grid points.

When calculating the EXXRPA+ energies of the S22 set, which contains a number of somewhat large dimer systems, we invoked an additional RI in the treatment of the two-electron integrals required in the evaluation of the EXXRPA+ correlation energy, see Eqs. (11) and (12) of Ref. [46]. That is, the two-electron integrals were evaluated according to $(ai|jb) = \sum_{pq}(ai|p)(p|q)^{-1}(p|jb)$. For this evaluation of the integrals $(ab|ji)$ to be sufficiently accurate, we had to use aug-cc-pV5Z MP2fit basis-sets supplemented by some additional s-functions, which are listed in the supplementary material.[92] These RI basis sets were used in all calculations of EXXRPA+ energies independently of the choice of the orbital basis set. For the latter always the same basis set as in the preceding self-consistent EXX or dRPA calculations was chosen. In this way the accuracy of the EXXRPA+ energies only varies with the quality of the orbital basis set and the RI basis set of the preceding self-consistent EXX or dRPA calculations but not with the RI set employed in the EXXRPA+ energy calculation because the latter was fixed to the large supplemented aug-cc-pV5Z MP2fit basis set.

IV. EXEMPLARY CORRELATION POTENTIALS IN THE RANDOM PHASE APPROXIMATION AND TESTS OF THE NUMERICAL STABILITY

In order to test our implementation, we compare the correlation potential and energy as well as the ionization potential of the neon atom to data from the numerical grid approach of Ref. [32]. For this purpose we employed large even-tempered orbital and RI basis sets. By using a large orbital basis a smaller number of unphysically small eigenvalues $\sigma_n(0)$ of the static response matrix was obtained such that we could reduce the factor β of the Tikhonov regularization to a value of $\beta = 10^{-4}$ in the solution of the OEP equation. Our correlation energy of 0.591 hartree and the ionization potential (IP) of 0.795 hartree deviate by only 5 mhartree and 1 mhartree, respectively, from the values of Ref. [32], i.e., are in good agreement. In Fig. 1, the dRPA correlation potential is compared to the exact KS correlation potential of Ref. [64] and the Perdew, Burke, and Ernzerhof (PBE) and the Perdew-Wang 92 local-density approximation (PW92 LDA) correlation functionals.
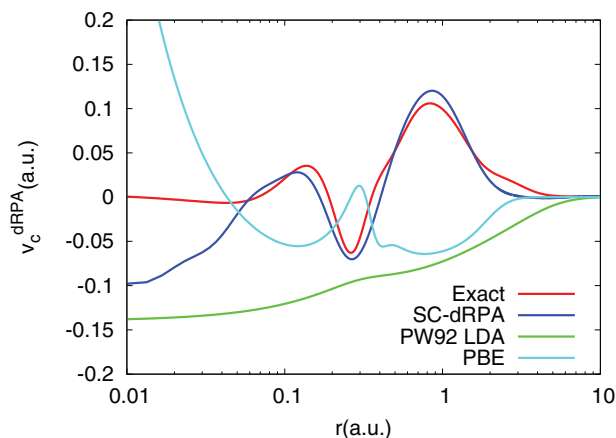

FIG. 1. Self-consistent dRPA, LDA (PW92), and PBE correlation potentials for the neon atom compared to the exact one of Ref. [64]. The self-consistent dRPA potential was obtained with even-tempered orbital and RI basis sets. Thresholds of $t_S = 10^{-6}$ in the removal of linear dependencies of the auxiliary basis set and of $\beta = 10^{-4}$ in the Tikhonov regularization applied in the construction of exact exchange potential and the dRPA correlation potential were used.

As evident in Fig. 1 the latter two conventional correlation potentials have little in common with the exact correlation potential. This is in line with earlier findings on the quality of LDA and GGA correlation potentials.[64] The dRPA correlation potential of Ne, on the other hand, represents a reasonable approximation to the true correlation potential and thus can be considered as physically meaningful.[44,45] In Figs. 2 and 3, we show exchange and dRPA correlation potentials for CO and the acetylene molecule. In order to provide converged benchmark results we employed large even-tempered orbital basis sets as well as modified aug-cc-pV5Z MP2fit basis sets as RI basis sets and a threshold of $t_s = 10^{-6}$ in the removal of linear dependent functions of the auxiliary basis set in conjunction with a factor of $\beta = 3 \times 10^{-3}$ in the Tikhonov regularization of the OEP equation. For the case of CO we also show potentials obtained with factors of $\beta = 10^{-5}$ and $\beta = 3 \times 10^{-2}$ in the Tikhonov regularization that either lead to oscillations or
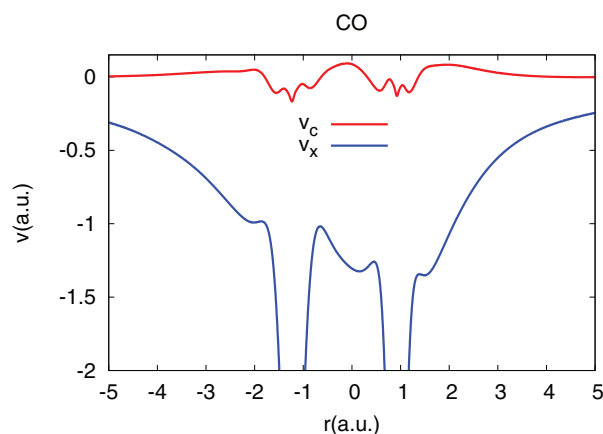

FIG. 2. Exchange and correlation potential for CO. An even tempered orbital basis set in conjunction with a modified aug-cc-pV5Z MP2fit basis set employed as auxiliary basis set was used. The factor β in the Tikhonov regularization applied in the construction of exact exchange potential and the dRPA correlation potential was set to $\beta = 3 \times 10^{-3}$ and the cutoff parameter t_S to remove linear dependencies of the RI basis set was set to 10^{-6}.
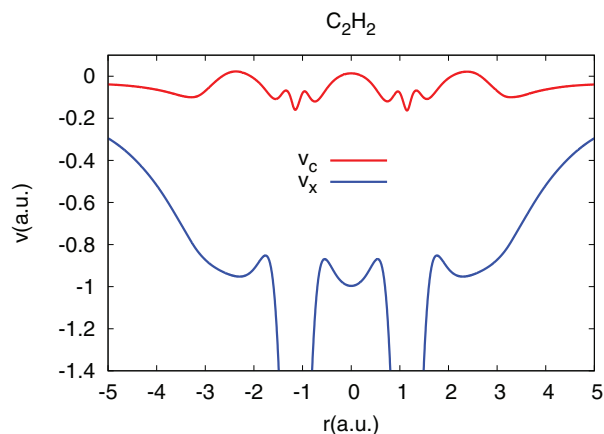
FIG. 3. Exchange and correlation potential for C_2H_2. An even tempered orbital basis set in conjunction with a modified aug-cc-pV5Z MP2fit basis set employed as RI basis set was used. The factor β in the Tikhonov regularization applied in the construction of exact exchange potential and the dRPA correlation potential was set to $\beta = 3 \times 10^{-3}$ and the cutoff parameter t_S to remove linear dependencies of the RI basis set was set to 10^{-6}.

damp the correlation potential, see Fig. 4. We note that the setups described in Sec. III which are more suitable for practical applications and which are used later on lead to potentials (not displayed here) that do not perfectly match the converged potentials of Fig. 2 obtained with the large even-tempered basis sets. On the one hand, this indicates a basis-set dependence
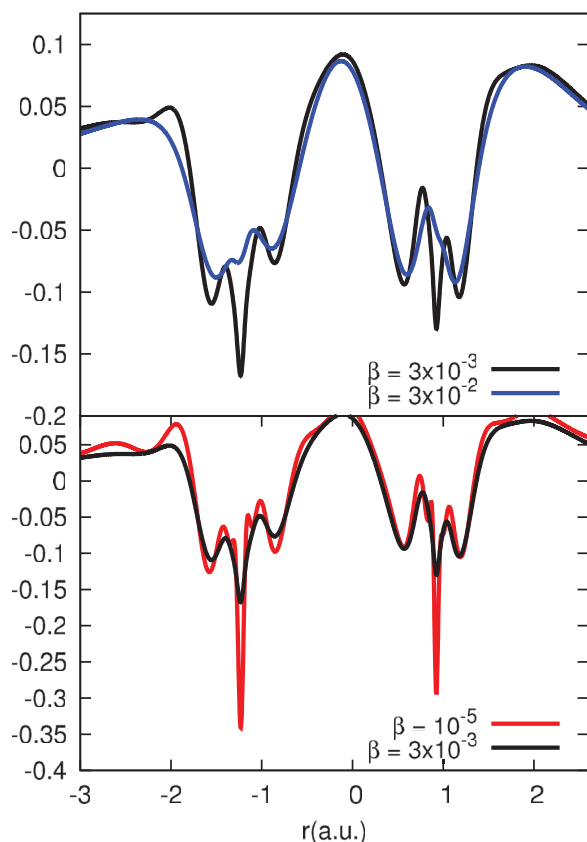

FIG. 4. Dependence of the correlation potential of CO on the factor β in the Tikhonov regularization applied in the construction of exact exchange potential and the dRPA correlation potential. An even tempered orbital basis set in conjunction with a modified aug-cc-pV5Z MP2fit basis set employed as auxiliary basis set were used. The cutoff parameter t_S to remove linear dependencies of the RI basis set was set to 10^{-6}.

of the correlation potential and on the other hand this might be due to the balancing of orbital and auxiliary basis sets. The balancing of orbital and auxiliary basis sets is a long standing problem in OEP methods for the exchange potential[77–83,85–87] and may be similar or even more critical for the correlation potential. The correlation potential is smaller by an order of magnitude compared to the exchange potential but exhibits oscillations in the core region[64,94] in contrast to the latter.

The question is now, how the technical quality of the exchange and correlation potential affects quantities like the total energy or orbital energies. In Table I, we show total energies and IPs for the CO molecule corresponding to eight different values of the Tikhonov regularization factor β. Table I shows that the total energy is very stable for a region of $10^{-5} \geq \beta \geq 3 \times 10^{-4}$ with changes below 0.1 mhartree. The ionization energy calculated as the negative of the eigenvalue of the highest occupied molecular orbital (HOMO) is distinctively less stable. This demonstrates that the eigenvalues are quite sensitive to details of the correlation potential. For three representative values of β (10^{-5}, 3×10^{-3}, 3×10^{-2}) the corresponding dRPA correlation potentials are displayed in Fig. 4. The three factors were chosen such that three different types of potentials were obtained. The largest value of $\beta = 3 \times 10^{-2}$ corresponds to a potential, which is smooth but too much damped and, therefore, exhibits a correlation potential with less pronounced features. Whereas the smallest value of $\beta = 10^{-5}$ leads to an oscillatory potential. The intermediate value of $\beta = 3 \times 10^{-3}$ yields a potential with pronounced features but no unphysical oscillations, see Fig. 4.

The self-consistent dRPA method considered here is a variational method that determines the exchange-correlation potential within the OEP framework. This means, within the self-consistency process, that effective KS potential is searched for that leads to orbitals and eigenvalues minimizing the dRPA total energy expression. In other words in the self-consistency process those orbitals and eigenvalues are determined that minimize the dRPA total energy expression but obey the constraint to be eigenfunctions and eigenenergies of a one-electron Hamiltonian operator with a local multiplicative effective potential, the optimized effective potential constituting the effective KS potential. In accordance with the

TABLE I. Dependence of the self-consistent dRPA total energy and of the ionization potential (a.u.) calculated as the negative of the HOMO eigenvalue on the choice of the parameter β of the Tikhonov regularization employed in the construction of the exact exchange potential and the dRPA correlation potential for the CO molecule. Even tempered orbital and modified aug-cc-pV5Z MP2fit basis sets were used. The cutoff parameter t_S in the removal of linear dependencies in the RI basis set was set to 10^{-6}.

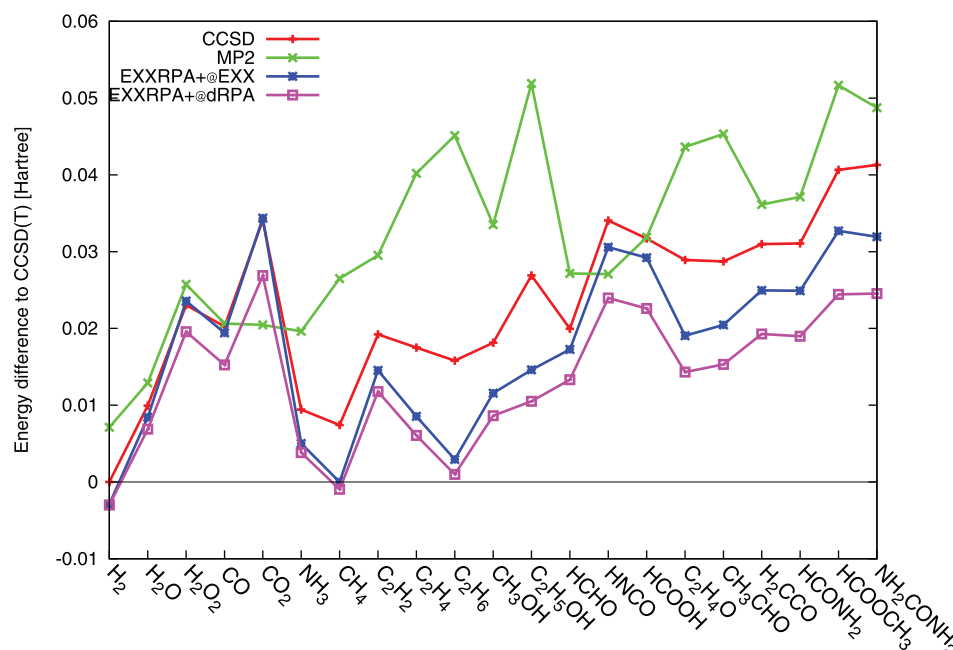| β	E_{total}	IP
10^{-5}	−113.606 546	−0.531 225
3×10^{-5}	−113.606 543	−0.533 234
10^{-4}	−113.606 529	−0.535 784
3×10^{-4}	−113.606 455	−0.538 745
10^{-3}	−113.606 012	−0.540 738
3×10^{-3}	−113.604 036	−0.542 625
10^{-2}	−113.593 570	−0.545 301
3×10^{-2}	−113.561 124	−0.549 859

FIG. 5. EXXRPA+@dRPA and EXXRPA+@EXX total energies in comparison to standard quantum chemistry methods: Displayed are deviations $\Delta E = E^{Method} - E^{CCSD(T)}$ of total energies E^{Method} to CCSD(T) total energies $E^{CCSD(T)}$. Aug-cc-pCVQZ orbital basis sets were used. The exchange and correlation potentials were expanded in aug-cc-pVQZ MP2fit basis sets. For the calculation of the RI-EXXRPA+ correlation energy the aug-cc-pCVQZ orbital basis sets were used in conjunction with supplemented aug-cc-pV5Z MP2fit basis sets employed as RI basis sets (see Sec. III for further technical details).

variational principle, the total energy rises as one increases the threshold in the Tikhonov regularization of the OEP equation, see Eq. (56), since the variational freedom of the exchange-correlation potential and thus of the effective KS potential, which is optimized, is reduced more and more. The energy belonging to the oscillatory potential of the lowest Tikhonov factor deviates less from the converged value than the smooth potential, whereas the IP differs more. This is a behavior known from exact-exchange-only OEP methods. In this case the total energy depends only on the occupied orbitals and with larger auxiliary basis set the total energy always becomes smaller and eventually approaches a lower limit at the expense of an unphysical potential accompanied by an unphysical eigenvalue spectrum. This means, the price for tiny, in the end insignificant changes of the total energy are highly oscillatory unphysical exchange potentials.[83, 86, 87] To a lesser extent this seems also to happen in the case of dRPA total energy in which the energy not only depends on the occupied orbitals but also on the virtual orbitals and their eigenvalues. The fact that the too small and too large values for the factor β of the Tikhonov regularization lead to only moderate changes of the total energy indicates that the presented self-consistent dRPA method is numerically reasonably stable.

V. SELF-CONSISTENT DIRECT RPA ENERGIES, IONIZATION POTENTIALS, AND HOMO LUMO GAPS AND EXXRPA ENERGIES BASED ON DIRECT RPA ORBITALS

In Figs. 5 and 6, we compare dRPA and EXXRPA + total energies based on EXX and dRPA orbitals to standard quantum chemistry methods using data from CCSD(T) (coupled cluster singles doubles with perturbative triples) as reference. The four combinations are denoted dRPA@EXX, dRPA@dRPA, EXXRPA+@EXX, and EXXRPA+@dRPA. Both EXXRPA methods, EXXRPA+@EXX and EXXRPA+@dRPA, perform better than all other considered methods. The use of dRPA orbitals and eigenvalues as input reduces the error of EXXRPA+ total energies with
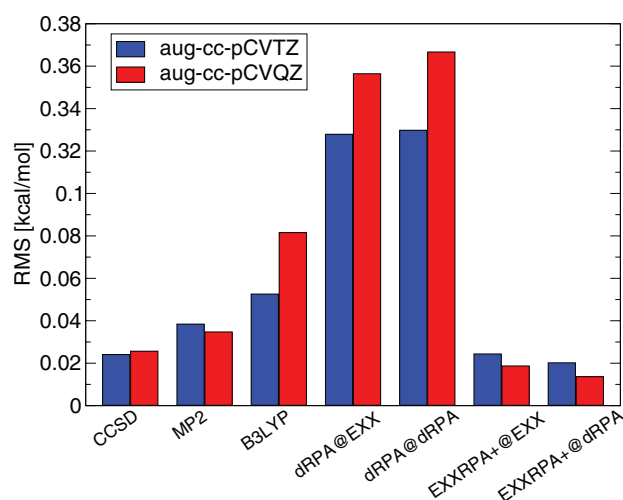

FIG. 6. Total energies: Performance of different RPA methods compared to standard quantum chemistry methods: Root-mean-squared errors (RMS) of deviations of total energies from various methods (EXXRPA+@EXX, dRPA@EXX, EXXRPA+@dRPA, dRPA@dRPA, B3LYP, MP2, and CCSD) to the corresponding CCSD(T) total energies. Aug-cc-pCVTZ and aug-cc-pCVQZ orbital basis sets were used. The exchange and correlation potentials were expanded in aug-cc-pVXZ MP2fit and basis sets, where X corresponds to the employed orbital basis set. For the calculation of RI-EXXRPA+ correlation energy the aug-cc-pCVQZ and aug-cc-pCVTZ orbital basis sets were used in conjunction with supplemented aug-cc-pV5Z MP2fit basis sets employed as RI basis sets (see Sec. III for further technical details).
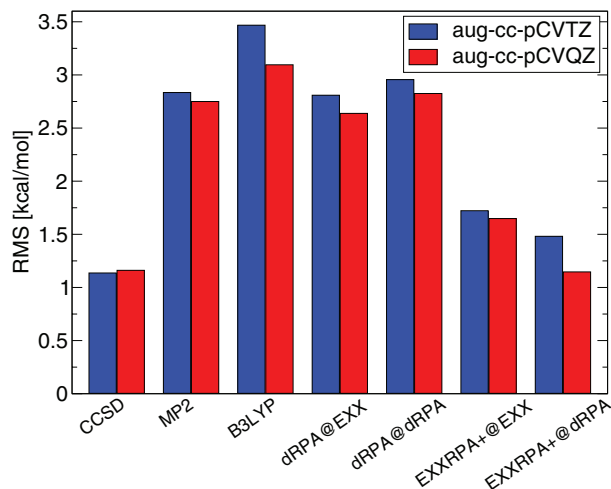
FIG. 7. Reaction energies: Performance of different RPA methods compared to standard quantum chemistry methods: Root-mean-squared errors (RMS) of deviations of 15 reaction energies (see Table II for considered reactions) from various methods (EXXRPA+@EXX, dRPA@EXX, EXXRPA+@dRPA, dRPA@dRPA, B3LYP, MP2, and CCSD) to the corresponding CCSD(T) reaction energies. Aug-cc-pCVTZ and aug-cc-pCVQZ orbital basis sets were used. The exchange and correlation potentials were expanded in aug-cc-pVXZ MP2fit and basis sets, where X corresponds to the employed orbital basis set. For the calculation of RI-EXXRPA+ correlation energy the aug-cc-pCVQZ and aug-cc-pCVTZ orbital basis sets were used in conjunction with supplemented aug-cc-pV5Z MP2fit basis sets employed as RI basis sets (see Sec. III for further technical details).

respect to the CCSD(T) reference by almost a factor of two compared to EXX input orbitals and eigenvalues for the aug-cc-pCVQZ orbital basis set, see Fig. 6. As a consequence of the self-consistency, the dRPA@dRPA as well as the EXXRPA+@dRPA energies are lowered, which constitutes a worsening in the first case, since dRPA methods overestimate the magnitude of the correlation energy drastically. Comparing the error bars in Fig. 6, one can see that all methods except B3LYP and the dRPA methods benefit from a larger orbital basis. The finding that dRPA results worsen with larger basis sets could be expected since the overestimation of the correlation energy grows with the size of the basis set.

In Fig. 7, selected reaction energies calculated with the same methods are compared to CCSD(T) reference values (see Table II for a list of the reactions). It can be seen that the use of dRPA instead of EXX orbitals improves the reaction energies for the EXXRPA+ method, leading to an accuracy lying in the range of that of the CCSD method. The latter seems to benefit the most from error cancellations in the calculation of reaction energies as compared to total energies.

TABLE II. Considered reactions.

$C_2H_2 + H_2 \rightarrow C_2H_4$	$HCOOH + NH_3$
	$\rightarrow HCONH_2 + H_2O$
$C_2H_6 + H_2 \rightarrow 2CH_4$	$CO + H_2 \rightarrow HCHO$
$H_2CO + H_2 \rightarrow CH_3OH$	$H_2O_2 + H_2 \rightarrow 2H_2O$
$C_2H_2 + H_2O \rightarrow CH_3CHO$	$C_2H_4 + H_2O \rightarrow C_2H_5OH$
$CH_3CHO + H_2 \rightarrow C_2H_5OH$	$CO + NH_3 \rightarrow HCONH_2$
$CO + H_2O \rightarrow CO_2 + H_2$	$HNCO + NH_3 \rightarrow NH_2CONH_2$
$CH_3OH + CO \rightarrow HCOOCH_3$	$CO + H_2O_2 \rightarrow CO_2 + H_2O$
$H_2CCO + HCHO \rightarrow C_2H_4O + CO$	$C_2H_4 + H_2 \rightarrow C_2H_6$

TABLE III. Ionization potentials (eV) of 24 molecules from the GW27 set. The *G0W0*, PBE, and experimental values were taken from Ref. 98. PBE, dRPA@dRPA, and EXX ionization potentials were calculated as negatives of the HOMO eigenvalues. Aug-cc-pCVTZ orbital basis sets in conjunction with aug-cc-pVTZ MP2fit basis sets were used for the dRPA@dRPA and EXX calculations (see Sec. III for further technical details).

System	Exp IP	PBE	G0W0[98]	dRPA@dRPA	EXX
H_2	15.42	10.25	15.73	16.51	15.96
Li_2	5.11	3.21	4.90	6.03	4.88
Na_2	4.89	3.13	4.74	4.42	4.50
F_2	15.70	8.97	14.44	15.21	17.6
N_2	15.58	10.20	14.51	15.83	17.18
BF	11.00	6.80	10.50	11.09	11.06
LiH	7.90	4.36	6.644	7.99	8.17
CO_2	13.78	9.02	12.79	13.64	14.77
H_2O	12.62	7.02	11.76	12.91	13.89
NH_3	10.85	6.02	10.10	10.90	11.71
SiH_4	12.30	8.47	12.23	13.14	13.09
SF_4	12.30	8.09	11.79	12.58	13.83
Methane	13.60	9.44	13.84	14.57	14.7
Ethane	12.00	8.13	12.27	12.86	13.16
Propane	11.51	7.67	11.60	12.23	12.51
Butane	11.09	7.58	11.16	12.03	12.44
Isobutane	11.13	7.60	11.19	12.03	12.37
Ethylene	10.68	6.78	10.22	10.49	10.35
Acetone	9.70	5.59	8.58	10.00	11.15
Acrolein	10.11	5.96	8.91	10.60	11.42
Benzene	9.24	6.39	8.65	9.27	9.20
Naphthalen	8.09	5.50	7.49	7.83	7.91
Anthracene	7.40	4.96	6.65	6.82	6.95
Naphthacene	6.97	4.65	6.12	6.19	6.36
MAE		3.88	0.59	0.50	0.87

Regarding the influence of the orbital basis set, all methods, except CCSD, which remains virtually unchanged, improve with the larger orbital basis set, see Fig. 7. The reaction energies of the self-consistent dRPA method are comparable to the ones of the MP2 method and better than the ones of B3LYP, but slightly inferior to the non-self-consistent dRPA results.

It is known that in KS-DFT the negative of the eigenvalue of the HOMO equals the IP.[95, 96] This indicates that there is a relationship between the quality of the exchange-correlation-potential and the accuracy of corresponding IPs. In Table III, we compare IPs obtained with our self-consistent dRPA method to IPs from the *G0W0* method (an approximate method to calculate the Green's function) of Ref. 97, the PBE method, and our EXX method with experimental values. The geometries, the *G0W0* results, and the PBE results were taken from Ref. 97. We had to neglect systems like Cs_2, Au_2, and Au_4 containing heavy elements for technical reasons, e.g., the non-availability of suitable basis sets. Both, EXX as well as SC-dRPA perform significantly better than the PBE functional, which is not surprising. It is known that local-, or semi-local exchange-correlation-functionals are plagued by spurious self-interactions leading to eigenvalue spectra of little physical meaning.[47, 48] Compared to the *G0W0* method, the SC-dRPA performs remarkably well, exhibiting a slightly smaller mean absolute error (MAE) than *G0W0*. This confirms that our exchange-correlation potentials should resemble the exact ones quite well as already illustrated in

TABLE IV. HOMO-LUMO gaps (eV) of 24 molecules from the GW27-set. Aug-cc-pCVTZ orbital basis sets were used. The EXX exchange and the dRPA correlation potentials were expanded in aug-cc-pVTZ MP2fit basis sets (see Sec. III for further technical details).

System	EXX	dRPA@dRPA	PBE
H_2	11.51	11.59	10.45
Li_2	1.46	1.23	1.36
Na_2	1.35	1.18	1.30
F_2	6.70	4.00	4.77
N_2	9.18	8.05	8.13
BF	5.03	4.37	4.61
LiH	3.73	2.94	2.73
CO_2	9.65	8.56	8.14
H_2O	8.49	7.48	6.39
NH_3	7.03	6.38	5.48
SiH_4	8.88	8.78	7.97
SF_4	6.64	5.68	5.37
Methane	10.41	10.20	9.07
Ethane	8.97	8.70	7.72
Propane	8.39	8.13	7.19
Butane	8.39	8.06	7.13
Isobutane	8.30	8.00	7.07
Ethylene	6.12	5.86	5.77
Acetone	5.58	4.34	4.11
Acrolein	4.97	3.72	3.54
Benzene	5.31	5.19	5.16
Naphthalen	3.70	3.52	3.48
Anthracene	2.48	2.30	2.27
Naphthacene	1.77	1.61	1.59

Fig. 1. The connection between physically correct exchange-correlation potentials and accurate IPs also shows by comparing EXX IPs with SC-dRPA IPs, i.e., by comparing IPs obtained exclusively with the exact-exchange-only potential with results obtained with the exact exchange potential plus the dRPA correlation potential. The MAE is more than 50% smaller for the approach including the dRPA correlation potential, which indicates that this approach yields a KS potential closer to the true one.

In Table IV, HOMO-LUMO (lowest unoccupied molecular orbital) gaps of a number of molecules obtained by the EXX, the self-consistent dRPA and the PBE method are compared. In solid state physics there is a longstanding discussion of how large the true KS bandgap is Ref. 98–108. Table IV shows the well known fact that EXX HOMO-LUMO gaps are always larger than GGA HOMO-LUMO gaps, here PBE HOMO-LUMO gaps. Comparing EXX and dRPA HOMO-LUMO gaps, Table IV shows that the latter are always smaller than the former except for H_2. The amount of the reduction of the HOMO-LUMO gap when going from EXX to dRPA, however, varies strongly with the system. Sometimes dRPA HOMO-LUMO gaps are closer to EXX sometimes closer to PBE gaps, in a number of cases the dRPA HOMO-LUMO gaps are even smaller than the PBE ones.

The S22 database of Hobza et al.[90] is established as a standard benchmark set for describing noncovalent intermolecular interaction energies. It represents a well-balanced test set, including various types of interaction like hydrogen-bonded, dispersion-dominated, and mixed-type

dimers. In Table V, we compare dRPA@dRPA, dRPA@EXX, EXXRPA+@dRPA, EXXRPA+@EXX, and MP2 noncovalent dimer binding energies of the S22 data set to the complete-basis set extrapolated (CBS) reference CCSD(T) values. The MP2 and CCSD(T) values were taken from Ref. 91. To estimate the basis set limit in our calculations we used the two point extrapolation formula of Ref. 109. Note that the original purpose of this formula was the extrapolation of energies of wave-function based methods and results from an application of this formula to dRPA and EXXRPA+ energies, therefore, have to be treated with caution.[110] Moreover, we employ in our approach an auxiliary basis set which is not taken into account by the extrapolation formula. Since the S22 set also contains rather large molecules like the adenine-thymine (AT) complex we extrapolated from an aug-cc-pCVDZ to an aug-cc-pCVTZ basis for the larger systems. In the remaining cases the extrapolation was performed from aug-cc-pCVTZ to aug-cc-pCVQZ. The basis set superposition error (BSSE) was removed using the Boys-Bernadi counterpoise correction.[111]

In Table V, we show the extrapolated CBS results, as well as the results with the largest orbital basis we used. In some cases the extrapolated binding energies are smaller than those obtained with the largest basis set, which is uncommon for dimer binding energies. The reason may be the above mentioned problems with using the two point extrapolation formula. As a consequence the MAE for EXXRPA+@dRPA is larger in the CBS limit than for the corresponding largest basis set, whereas all other methods improve or remain unchanged upon extrapolation. All dRPA methods underestimate the binding energy for all complexes. This is also true for the EXXRPA+ methods except for the H-bonded complexes in the EXXRPA+@dRPA approach. All in all the EXXRPA+ methods clearly outperform the dRPA methods, dRPA@EXX and dRPA@dRPA, which are both of similar accuracy. These results are also in line with the literature, according to which going beyond dRPA improves the accuracy significantly.[43,112]

VI. CONCLUDING REMARKS

The presented self-consistent dRPA method makes it possible to routinely and efficiently calculate correlation potentials for molecules that, concluding from comparison with exact reference potentials, can be assumed to be in fair agreement with the exact correlation potential. Indeed, we find that the negatives of the self-consistent dRPA eigenvalues of the highest occupied molecular orbitals of a set of test molecules are in as close an agreement with experimental ionization potentials as those from GW calculations, which indicates that self-consistent dRPA exchange-correlation potentials are quite accurate. Considering that the commonly employed GGA correlation potentials are known to be qualitatively wrong, the good quality of dRPA correlation potentials is a clear strength of the new method that could be beneficial if the orbitals and eigenvalues are used as input for subsequent calculations, e.g., TDDFT calculations for excitation energies. Indeed, first results from TDDFT calculations employing dRPA orbitals and eigenvalues that will be published elsewhere are encouraging.[113]

TABLE V. Interaction energies (kcal/mol) of the S22 set of noncovalently bound dimers. Depending on the system size calculations with aug-cc-pCVDZ and aug-cc-pCVTZ orbital basis sets or with aug-cc-pCVTZ and aug-cc-pCVQZ basis sets were carried out and used for the extrapolation to the complete basis set limit, which is listed together results from the largest orbital basis set for each system. The last two lines contain the MAE of the respective largest basis set and the complete basis set limit (CBS).

| Complex | Basis | Reference | dRPA | | EXXRPA+ | | MP2 |
			@dRPA	@EXX	@dRPA	@EXX	
NH_3 (C_{2h})	4	. . .	2.56	2.52	2.96	2.83	
	CBS	3.15	2.65	2.63	2.97	2.83	3.16
$(H_2O)_2(C_s)$	4	. . .	4.33	4.25	5.07	4.92	
	CBS	5.07	4.47	4.42	5.10	4.97	4.96
$(HCOOH)_2$ (C_{2h})	4	. . .	16.96	16.45	19.33	18.78	
	CBS	18.81	17.50	17.03	19.63	18.67	18.52
$(CHONH_2)_2$	4	. . .	14.68	14.38	16.40	16.01	
	CBS	16.11	15.09	14.82	16.66	15.46	15.79
Uracil-Uracil (C_{2h})	3	. . .	18.10	17.75	21.11	20.60	
	CBS	20.69	17.69	18.48	21.95	21.33	20.37
2-Pyridoxine-2-Aminopyridine	3	. . .	14.89	14.37	17.08	16.63	
	CBS	17.00	14.72	15.06	17.83	17.22	17.34
AT (WC)	3	. . .	14.57	13.90	16.69	16.08	
	CBS	16.74	14.21	14.63	17.23	16.82	16.52
$(CH_4)_2$ (D_{3d})	4	. . .	0.32	0.35	0.37	0.43	
	CBS	0.53	0.36	0.36	0.33	0.42	0.49
$(C_2H_4)_2$ (D_{2d})	4	. . .	1.06	1.09	1.42	1.40	
	CBS	1.48	1.07	1.16	1.45	1.42	1.58
Bz-CH_4 (C_3)	4	. . .	1.04	1.11	1.01	1.04	
	CBS	1.45	1.02	1.17	1.04	1.11	1.81
Bz-Bz (C_{2h})	3	. . .	1.74	1.91	1.97	2.11	
	CBS	2.62	1.79	2.20	2.12	2.07	4.96
Pyrazine-Pyrazine (C_s)	3	. . .	3.06	3.24	3.22	3.33	
	CBS	4.20	3.09	3.48	3.32	3.47	6.91
Uracil-Uracil (C_2)	3	. . .	8.18	7.67	7.92	8.64	
	CBS	9.74	8.29	8.13	7.91	9.07	11.11
Indole-Bz (stacked)	3	. . .	3.23	3.36	3.52	3.64	
	CBS	4.59	3.22	3.73	3.63	3.96	8.08
AT (stacked)	3	. . .	9.57	8.98	10.67	10.17	
	CBS	11.66	9.33	10.73	10.90	10.71	14.86
$C_2H_4 \cdots C_2H_2$ (C_{2v})	4	. . .	1.22	1.32	1.54	1.54	
	CBS	1.50	1.23	1.38	1.55	1.62	1.66
Bz-H_2O (C_s)	4	. . .	2.71	2.71	3.05	3.00	
	CBS	3.29	2.73	2.80	2.98	3.06	3.54
Bz-NH_3 (C_s)	4	. . .	1.85	1.89	2.32	2.04	
	CBS	2.32	1.88	1.97	2.33	2.06	2.66
Bz-HCN (C_s)	4	. . .	3.82	3.92	4.34	4.39	
	CBS	4.55	3.87	3.83	4.36	4.47	5.17
Bz-Bz (C_{2v})	3	. . .	2.56	2.61	2.87	2.96	
	CBS	2.71	2.38	2.29	2.82	2.82	3.63
Indole-Bz (T-shaped)	3	. . .	4.68	4.66	5.29	5.31	
	CBS	5.62	4.64	4.99	5.50	5.62	6.98
Phenole-Phenole	3	. . .	5.99	5.79	7.05	6.84	
	CBS	7.09	5.88	6.04	7.39	7.21	7.74
MAE	3/4	. . .	1.08	1.21	0.40	0.40	
MAE	CBS	. . .	1.08	0.89	0.49	0.32	0.88

Another area in which dRPA orbitals and eigenvalues can be used as input quantities is the evaluation of orbital-dependent exchange-correlation functionals. Here, we investigated the evaluation of the EXXRPA+ correlation energy with orbitals from the self-consistent dRPA method presented here. This leads to a KS approach, abbreviated as EXXRPA@dRPA approach, that is complementary to conventional GGA or hybrid methods. While the latter are computationally highly efficient but of quite limited accuracy and plagued by systematic shortcomings, the EXXRPA@dRPA approach is free of these deficiencies and can compete with high-level quantum chemistry methods like the CCSD method as far as accuracy is concerned. Considering computational effort the self-consistent dRPA method and the

EXXRPA@dRPA approach with a computational effort scaling of N^4 and N^5, respectively, with the system size N are more demanding than conventional GGA and hybrid methods but more efficient than high-level quantum chemistry methods like CCSD. This qualifies the EXXRPA@dRPA approach as alternative to the latter.

The natural next step to be made after devising a self-consistent dRPA method is to develop a complete self-consistent EXXRPA+ method. Work to that end is under way.

ACKNOWLEDGMENTS

APPENDIX: COMPUTATIONAL STEPS IN A SELF-CONSISTENT dRPA CALCULATION

In this Appendix, the computational steps required to carry out a self-consistent dRPA calculation are listed. More precisely, we consider the additional steps required to supplement an exact exchange-only KS method, e.g., the implementation of Ref. 85 by the dRPA correlation energy and potential. We assume that integrals $(\chi_m \chi_n | \tilde{f}_p)$ between an auxiliary basis function from a RI basis set and two orbitals basis functions χ_m and χ_n, see end of Sec. II, and overlap integrals $\widetilde{S}_{pq}$ between RI basis functions with respect of the Coulomb norm, see Eq. (8), are available. The latter are required in a first step that can be carried out before the self-consistency process of the KS calculation:

(1) *Preprocessing of the auxiliary basis functions*
Calculate the transformation matrix $\mathbf{W}$ to transform from the original RI basis functions $\tilde{f}_\nu$ to the actually used auxiliary basis functions f_ν as described in Ref. 46.

These integrals $(\chi_m \chi_n | \tilde{f}_\nu)$ and the transformation matrix $\mathbf{W}$ together with the coefficient vectors of the KS orbitals and the KS orbital eigenvalues are the input data for a dRPA module that has to be called in each self-consistency cycle of a KS calculation and that carries out the following steps:

(2) *AO-MO transformation of three-index integrals*
Calculate integrals $\widetilde{N}_{st,q} = (\varphi_s \varphi_t | \tilde{f}_q)$ by an AO-MO transformation from the basic three-index-integrals $(\chi_m \chi_n | \tilde{f}_q)$

(3) *Transformation of three-index integrals to auxiliary basis functions f_p*
Calculate integrals $N_{st,p} = (\varphi_s \varphi_t | f_p)$ containing the actually used auxiliary basis functions f_p from the integrals $\widetilde{N}_{st,q} = (\chi_m \chi_n | \tilde{f}_p)$ containing of the original RI basis functions $\tilde{f}_p$ with the help of the transformation matrix $\mathbf{W}$ according to Eq. (53).

1. The following steps 4–12 have to be carried out in a loop over the frequencies ω

(4) *Energy factors $\lambda_{ia}(\nu)$ with $\nu = i\omega$*
Calculate the energy factors $\lambda_{ia}(\nu)$ with $\nu = i\omega$ according to Eq. (3) for the current frequency ω.

(5) *Dynamic KS response matrix $\mathbf{X}_0(i\omega)$*
Calculate the elements $X_{0,pq}(i\omega)$ of the dynamic KS response matrix $\mathbf{X}_0(i\omega)$ according to Eq. (34) using the integrals $N_{ia,p} = (\varphi_i \varphi_a | f_p)$ and the energy factors $\lambda_{ia}(\nu)$ with $\nu = i\omega$.

(6) *Diagonalization of the dynamic KS response matrix $\mathbf{X}_0(i\omega)$*
Diagonalize the dynamic KS response matrix $\mathbf{X}_0(i\omega)$ in order to obtain its eigenvalues $\sigma_n(i\omega)$ and eigenvectors $\mathbf{v}_n(i\omega)$, see Eq. (19).

(7) *Contribution to frequency integration of dRPA correlation energy*
Calculate according to Eq. (20) the contribution $\mathrm{Tr}\,[\,\ln(|\mathbf{1} - \boldsymbol{\sigma}(i\omega)|) + \boldsymbol{\sigma}(i\omega)\,]$ to the frequency integral of the dRPA correlation energy for the current frequency ω.

(8) *Matrix elements $M_{st,p}$ and energy factors $\gamma_{ia}(i\omega)$*
Calculate matrix elements $M_{st,p}$ and energy factors $\gamma_{ia}(i\omega)$ according to Eqs. (38) and (41), respectively.

(9) *Intermediate quantities $F_{st,n}(i\omega)$*
Calculate the intermediate quantities $F_{st,n}(i\omega)$ according to Eq. (43) from the integrals $N_{st,p}$ and the eigenvectors $v_{p,n}(i\omega)$ of the dynamic KS response matrix.

(10) *Intermediate quantities $T_{si,n}(i\omega)$ and $T_{sa,n}(i\omega)$*
Calculate according Eqs. (45) and (46) the intermediate quantities $T_{si,n}(i\omega)$ and $T_{sa,n}(i\omega)$ from the quantities $F_{st,n}(i\omega)$ of the previous step and the energy factors $\lambda_{ia}(i\omega)$.

(11) *Intermediate quantities $R_{si}(i\omega)$, $R_{sa}(i\omega)$, and $Y_{ia}(i\omega)$*
Calculate according to Eqs. (48)–(50) the intermediate quantities $R_{si}(i\omega)$, $R_{sa}(i\omega)$, and $Y_{ia}(i\omega)$ from the quantities $T_{si,n}(i\omega)$ and $T_{sa,n}(i\omega)$ of the previous step and the matrix elements $M_{st,p}$ and energy factors $\gamma_{ia}(i\omega)$.

(12) *Integrand $t_{c,\nu}(i\omega)$ of the frequency integration for the elements of right hand side of OEP equation for the dRPA correlation potential*
For the current frequency ω, calculate according to Eq. (51) the integrand $t_{c,\nu}(i\omega)$ of the frequency integration (30) for the elements $t_{c,\nu}^{\mathrm{dRPA}}$ of the right hand side $\mathbf{t}_c^{\mathrm{dRPA}}$ of the OEP equation (26) for the dRPA correlation potential.

2. End of loop over frequencies

(13) *dRPA correlation energy E_c^{dRPA}*
Carry out the frequency integration of the contributions $\mathrm{Tr}\,[\,\ln(|\mathbf{1} - \boldsymbol{\sigma}(i\omega)|) + \boldsymbol{\sigma}(i\omega)\,]$ to obtain the correlation energy E_c^{dRPA} according to Eq. (20).

(14) *Right hand side $\mathbf{t}_c^{\mathrm{dRPA}}$ of OEP equation for correlation potential*
Carry out the frequency integration (30) of the integrand $t_{c,\nu}(i\omega)$ to obtain the elements $t_{c,\nu}^{\mathrm{dRPA}}$ of the right hand side $\mathbf{t}_c^{\mathrm{dRPA}}$ of the OEP equation (26) for the correlation potential.

(15) *Static KS response matrix $\mathbf{X}_0(0)$*
Calculate the elements $X_{0,pq}(0)$ of the static KS response matrix $\mathbf{X}_0(0)$ according to Eq. (34) using the

integrals $N_{ia,p} = (\varphi_i \varphi_a | f_p)$ and the energy factors $\lambda_{ia}(\nu)$ of Eq. (3) with $\nu = 0$.

(16) *Solution of the OEP equation for the correlation potential*

Solve the OEP equation (26) with the help of the regularizations (55) or (56) in order to obtain the vector $\mathbf{v}_c^{dRPA}$ containing the coefficients $v_{c,\nu}^{dRPA}$ of the expansion (24) of the dRPA correlation potential in terms of electrostatic potentials of the auxiliary basis functions f_ν.

(17) *Backtransformation to original RI basis functions*

Carry out the backtransformation (57) to obtain the coefficients $\tilde{v}_{c,\nu}^{dRPA}$ of the expansion of the dRPA correlation potential in terms of electrostatic potentials of the original RI basis functions $\tilde{f}_\nu$.

(18) *Contribution $\mathbf{H}_c^{dRPA}$ of the dRPA correlation potential to the KS Hamiltonian matrix*

Calculate the elements $H_{c,mn}^{dRPA}$ of the contribution $\mathbf{H}_c^{dRPA}$ of the dRPA correlation potential to the KS Hamiltonian matrix according to Eq. (58).

The integrals $\widetilde{N}_{st,q} = (\varphi_m \varphi_n | \tilde{f}_q)$ can be distributed in batches over the index s among several computation nodes via the Message Passing Interface (MPI). On each node the remaining batches can again be distributed among several Open MP processes. Therefore, steps 2, 3, and 8–11 can be parallelized over the index s via a mixed MPI/Open MP scheme. The batches over the index s can be further distributed in subbatches that are treated consecutive in order to further the reduce the storage requirements for the integrals $(\varphi_m \varphi_n | \tilde{f}_q)$. The storage requirements of the present dRPA implementation are determined by the integrals $(\varphi_i \varphi_a | \tilde{f}_p)$ needed for the intermediate quantities $F_{ia,n}(i\omega)$, which have to be kept in memory on each node, with i referring to occupied, a to unoccupied orbitals, and p to auxiliary basis functions.

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