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Resolution of identity approach for the Kohn-Sham correlation energy within the exact-exchange random-phase approximation

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Two related methods to calculate the Kohn-Sham correlation energy within the framework of the adiabatic-connection fluctuation-dissipation theorem are presented. The required coupling-strength-dependent density-density response functions are calculated within exact-exchange time-dependent density-functional theory, i.e., within time-dependent density-functional response theory using the full frequency-dependent exchange kernel in addition to the Coulomb kernel. The resulting resolution-of-identity exact-exchange random-phase approximation (RI-EXXRP) methods in contrast to previous EXXRP methods employ an auxiliary basis set (RI basis set) to improve the computational efficiency, in particular, to reduce the formal scaling of the computational effort with respect to the system size N from N^6 to N^5 . Moreover, the presented RI-EXXRP methods, in contrast to previous ones, do not treat products of occupied times unoccupied orbitals as if they were linearly independent. Finally, terms neglected in previous EXXRP methods can be included, which leads to a method designated RI-EXXRP+, while the method without these extra terms is simply referred to as RI-EXXRP. Both EXXRP methods are shown to yield total energies, reaction energies of small molecules, and binding energies of noncovalently bonded dimers of a quality that is similar and in some cases even better than that obtained with quantum chemistry methods such as Møller-Plesset perturbation theory of second order (MP2) or with the coupled cluster singles doubles method. In contrast to MP2 and to conventional density-functional methods, the presented RI-EXXRP methods are able to treat static correlation. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3697845>]

I. INTRODUCTION

Recently, in Refs. 1 and 2, generally applicable Kohn Sham (KS) methods for molecules were introduced that treat the correlation energy within the random-phase approximation (RPA) on the basis of time-dependent density-functional theory (TDDFT) with the exact frequency-dependent exchange kernel.^{3–9} These exact-exchange RPA (EXXRP) methods show very promising first results. For closed shell organic molecules total energies were as accurate as those from the coupled cluster singles doubles (CCSD) method when compared with CCSD(T) (CCSD with perturbative triples contributions) reference results. With respect to CCSD(T) data, EXXRP reaction energies were slightly less accurate than CCSD ones but better than those from Møller-Plesset perturbation theory of second order (MP2) or conventional density-functional theory (DFT) methods such as the B3LYP method. In contrast to conventional DFT methods, the EXXRP approach can be applied to cases characterized by static correlation, i.e., to dissociation or bond breaking.² Moreover, the EXXRP approach can treat van der Waals interactions. In summary, first results suggest that the EXXRP method might be of comparable accuracy as high-level quantum chemistry approaches such as CCSD but more widely applicable, a quite remarkable characteristic for a DFT method.

In recent years a number of DFT based RPA approaches were presented.^{1,2,10–36} All these RPA approaches require two steps: (i) A self-consistent KS calculation is carried out to cal-

culate KS orbitals and eigenvalues. This step requires an approximation of the KS exchange-correlation potential.

(ii) From the orbitals and eigenvalues the total energy is calculated. All contributions to the total energy with the exception of the correlation energy are calculated exactly. This includes the exchange energy which is calculated by the exact expression of the exchange energy of a Slater determinant, here the KS determinant. The correlation energy is calculated within the RPA, that is by invoking TDDFT.^{37–39} This step requires an approximation of the exchange-correlation kernel, the frequency-dependent functional derivative of the exchange-correlation energy with respect to the electron density.

The various DFT based RPA methods differ in the approximations required in steps (i) and (ii). Most RPA methods in step (i) carry out a conventional KS calculation with one of the standard approximations for the exchange-correlation potential. Often the approximations due to Perdew, Burke, and Ernzerhof⁴⁰ (PBE) or Tao, Perdew, Staroverov, and Scuseria⁴¹ (TPSS) are employed. In the EXXRP methods, on the other hand, the exact local multiplicative KS exchange potential (EXX potential)^{42–48} is employed in step (i) while the correlation potential is neglected. In step (ii) most DFT based RPA methods completely neglect the exchange-correlation kernel and retain only the Coulomb kernel in the TDDFT calculation for the RPA correlation energy.^{11,15,17,49,50} RPA methods considering only the

Coulomb kernel shall be denoted direct RPA (dRPA) methods here. Some dRPA approaches are corrected such that the correlation energy is exact to second-order perturbation theory^{16,19,51} or are augmented with additional first-order singles terms.³²

Other DFT based RPA methods employ range-separation approaches in order to treat only parts of the correlation energy via the RPA, while other parts of the correlation energy are treated by approximate semilocal functionals of the density.^{20,21,28,29,52–54} The EXXRPA method distinguishes itself from other DFT based RPA methods by a number of unique properties:

(a) In the EXXRPA approach the choice for the approximations of the exchange-correlation potential and the exchange-correlation kernel is consistent. In both cases the exchange contribution is treated exactly and the correlation contribution is neglected. In methods based on dRPA the exchange-correlation kernel is completely neglected and only the Coulomb kernel is retained. If, consistently, the exchange-correlation potential was neglected in the self-consistent KS calculation then the latter would result in a Hartree calculation that could not be expected to give reasonable results. Therefore, some approximate exchange-correlation potential has to be chosen and combined with the dRPA calculation neglecting the exchange-correlation potential. Since there is no natural consistent choice, this choice is to some extent arbitrary. On the other hand, this choice has a significant effect on the accuracy of the resulting approach. The approach of Ref. 19, SOSEX, e.g., requires the PBE exchange-correlation potential in the KS calculation for the orbitals and their eigenvalues. If, instead, orbitals and eigenvalues are calculated with the exact-exchange-only KS method (EXX method), then quite poor results are obtained despite the fact that the EXX calculation in contrast to the PBE calculation yields a qualitatively correct orbital and eigenvalue spectrum.³³

(b) The EXXRPA method is rigorously self-interaction free in both of its steps. This is best seen at the example of a one-electron system. For a one-electron system the EXX potential exactly cancels the Coulomb potential and the EXX KS calculation reduces to solving the Schrödinger equation of the one-electron system and the exact orbitals and eigenvalues of the one-electron system are obtained. The EXXRPA correlation energy for a one-electron system is zero. Since the Hartree and exchange energies also cancel no energy contribution from an electron-electron self-interaction occurs. In summary, the exact eigenstates and eigenvalues of the one-electron system are obtained. In other DFT based RPA methods both steps of the RPA procedure, the KS calculation as well as the calculation of the RPA correlation energy, suffer from unphysical self-interactions. In a one-electron system the dRPA correlation energy, for example, is not equal to zero. Furthermore, depending on the choice for the exchange-correlation potential, the preceding KS calculation may not reduce to the Schrödinger equation of the one-electron system and therefore may yield orbitals and eigenvalues that differ from the exact ones.

(c) The EXXRPA method is free of parameters. In some of the other DFT based RPA methods empirical or technical parameters occur at the one or other point.

(d) The EXXRPA yields accurate total energies and accurate reaction energies. Other DFT based RPA methods such as the dRPA method only yield accurate reaction energies but quite poor total energies, which indicates that these methods rely on error cancellations. This point is related to point (b) above.

While the EXXRPA approach shows promising results and has conceptual and formal advantages compared to other DFT based RPA approaches, the two specific EXXRPA methods introduced in Refs. 1 and 2 suffer from a number of shortcomings. Most importantly, both methods exhibit a formal N^6 scaling of the computational effort with the system size N . This is the same scaling behaviour as in CCSD methods. Since EXXRPA methods seem to have comparable accuracy as CCSD methods they can be considered as competitive compared to standard methods such as CCSD. However, compared to standard KS methods with an effective scaling of the computational effort of N^3 or even below, the EXXRPA methods of Refs. 1 and 2 are computationally highly expensive. Another shortcoming of the EXXRPA methods of Refs. 1 and 2 is that one type of terms of the frequency-dependent exchange kernel was neglected. Thus, strictly speaking, both methods are not fully exact-exchange RPA methods. (Note that in Ref. 2 with H_2 a two-electron system was considered, for which the neglected term vanishes. Therefore, the label EXXRPA was fully justified in Ref. 2). The terms neglected in the EXXRPA methods of Refs. 1 and 2 are known to have only negligible effects on valence-valence excitations in TDDFT calculations and therefore can be assumed to also have very little effect on the EXXRPA correlation energy. Nevertheless, an incorporation of these terms seems to be desirable. Finally, the EXXRPA methods introduced in Refs. 1 and 2 treat products of occupied times unoccupied orbitals as if they were linearly independent. This, however, is not the case. In TDDFT calculations of valence-valence excitation energies it was shown⁹ that the linear dependence of the products of occupied times unoccupied orbitals has virtually no effect. Nevertheless, at least from a formal point of view, it seems to be desirable if products of occupied times unoccupied orbitals no longer had to be treated as linearly independent.

Here, we introduce an EXXRPA approach, termed RI-EXXRPA (resolution-of-the-identity EXXRPA), that employs an auxiliary basis set, the RI basis set, in order to increase the efficiency and that exhibits a formal N^5 scaling of the computational effort with the system size. This is the formal scaling of MP2 methods. The presented RI-EXXRPA methods, however, are more accurate than MP2 and, in contrast to MP2, are able to treat static correlation. The scaling of the presented RI-EXXRPA methods is still clearly less favourable than that of standard DFT methods. However, it should be pointed out that those computational steps exhibiting a high scaling of the computational effort have a small prefactor. Therefore, for small and medium size systems the presented RI-EXXRPA methods require only moderate computational effort. Indeed, all computations for this work could be carried out on single processor workstations. The presented RI-EXXRPA approach enables a treatment of all terms of the frequency-dependent exchange kernel. To keep in line with previous work we use the acronym RI-EXXRPA if the terms

neglected in the EXXRPAs of Refs. 1 and 2 are not considered while the acronym RI-EXXRPAs is used if these terms are taken into account. Because products of occupied and unoccupied orbitals are represented in the linearly independent RI basis set, the RI-EXXRPAs of this work no longer treat these products as if they were linearly independent.

The paper is organized as follows. Section II on formalism firstly briefly reviews the formal basis of DFT based RPA methods in general and EXXRPAs in particular. Then the basic RI-EXXRPAs method is introduced and next specific treatments and modifications of standard RI basis sets are presented that lead to an efficient and numerically stable RI-EXXRPAs implementation. Finally, it is discussed how the presented RI-EXXRPAs methods can be turned into a dRPA method by neglecting the terms originating from the exact-exchange kernel. Section III gives computational details. In Sec. IV firstly, in Subsection IV A, the numerical stability of the presented RI-EXXRPAs methods is investigated and then, in Subsection IV B, total energies, reaction and binding energies, and potential energy curves from RI-EXXRPAs methods are compared to those from conventional DFT and standard quantum chemistry methods (MP2, CCSD, CCSD(T)). Subsection IV A on the numerical stability is not required for an understanding of the following parts of the paper and therefore can be skipped by readers not interested in the investigation of the numerical stability of the presented methods. Finally, Sec. V gives a brief summary.

II. FORMALISM

A. Adiabatic-connection fluctuation-dissipation theorem and exact-exchange time-dependent density-functional theory

Starting point for DFT based RPA methods is the adiabatic-connection fluctuation-dissipation theorem^{55,56} (AC-FDT)

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

that yields the correlation energy E_c as defined in the KS formalism of DFT. In order to calculate the correlation energy E_c from the AC-FDT the response functions χ_0 and χ_α are required. The response function χ_0 is the uncoupled frequency-dependent KS response function that is given in terms of KS orbitals and eigenvalues by

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

In Eq. (2) the abbreviation $\varphi_{ia}(\mathbf{r}) = \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r})$ is used for products of occupied times unoccupied KS orbitals φ_i and φ_a , respectively. Throughout the paper we consider non-spin-polarized electronic systems with real-valued KS orbitals. Spin is taken into account via appropriate prefactors. The frequency-dependent factors $\lambda_{ia}(\nu)$ in the KS response function χ_0 , Eq. (2), are given by

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

with $\varepsilon_{ia} = \varepsilon_a - \varepsilon_i$ denoting differences of the KS eigenvalues ε_a and ε_i of unoccupied and occupied KS orbitals, respectively. Throughout indices i, j denote occupied orbitals and indices a, b denote unoccupied orbitals. For the calculation of the uncoupled frequency-dependent response of the electron density of the KS model system the parameter ν would have to be set equal to a physical, i.e., real-valued, frequency ω , in the AC-FDT ν is set to complex-valued frequencies, i.e., is set to $i\omega$.

The response function χ_α depends on the coupling constant α and is the density-density (potential-density) response function corresponding to the ground state Ψ_0^α of a model electron system with an electron-electron interaction that is scaled by the coupling constant α with $0 < \alpha < 1$. The state Ψ_0^α is the ground state of the Schrödinger equation

$$[\hat{T} + \alpha \hat{V}_{ee} + \hat{v}_\alpha] \Psi_n^\alpha = E_n^\alpha \Psi_n^\alpha \quad (4)$$

that defines the adiabatic connection^{55,57,58} between the real, i.e., physical, electron system and the associated KS model system. In Eq. (4), $\hat{T}$ designates the operator of the kinetic energy, $\hat{V}_{ee}$ designates the operator of the electron-electron interaction, and $\hat{v}_\alpha$ designates the operator corresponding to a local multiplicative potential $v_\alpha(\mathbf{r})$ that depends on the coupling constant α and is defined up to an additive constant, via the Hohenberg-Kohn theorem, by the requirement that the ground state electron density along the adiabatic connection, i.e., the electron density of Ψ_0^α , equals the physical ground state electron density for all values of α . The Schrödinger equation (4) turns into the Schrödinger equation of the physical electron system for $\alpha = 1$, and into the corresponding many-electron KS equation for $\alpha = 0$. For $\alpha = 0$ the response function χ_α becomes the uncoupled KS response function χ_0 and for $\alpha = 1$ the response function χ_α equals the response function of the physical electron system.

The response function χ_α is formally given in terms of the eigenstates Ψ_n^α and eigenvalues E_n^α of Eq. (4) by the sum-over-states expression

$$\chi_\alpha(\nu, \mathbf{r}, \mathbf{r}') = \sum_{n \neq 0} -\frac{2(E_n^\alpha - E_0^\alpha)}{(E_n^\alpha - E_0^\alpha)^2 - \nu^2} \times \langle \Psi_0^\alpha | \hat{\rho}(\mathbf{r}) | \Psi_n^\alpha \rangle \langle \Psi_n^\alpha | \hat{\rho}(\mathbf{r}') | \Psi_0^\alpha \rangle. \quad (5)$$

The sum-over-states expression (5) is of little practical value because its evaluation requires the solution of the many-electron problem for each value of the coupling constant α . Moreover, constructing the potential v_α is not straightforward and again requires solutions of the many-electron Schrödinger equation (4).

Within DFT based RPA methods the response function χ_α is constructed within TDDFT.³⁷⁻³⁹ In the frequency domain, the basic equation of TDDFT or more precisely of density-functional response theory in first order is given by³⁸

$$\int d\mathbf{r}'' \left[\delta(\mathbf{r} - \mathbf{r}'') - \int d\mathbf{r}' \chi_0(\nu, \mathbf{r}, \mathbf{r}') f_{\text{Hx}}(\nu, \mathbf{r}', \mathbf{r}'') \right] \rho^{(1)}(\nu, \mathbf{r}'') = \int d\mathbf{r}' \chi_0(\nu, \mathbf{r}, \mathbf{r}') v^{(1)}(\nu, \mathbf{r}'). \quad (6)$$

For $\nu = \omega$, i.e., for a real-valued frequency, the frequency-dependent local multiplicative potential $v^{(1)}(\nu, \mathbf{r}') = v^{(1)}(\omega, \mathbf{r}')$

in Eq. (6) determines a time-dependent perturbation $v^{(1)}(\omega, \mathbf{r}') \exp[-i\omega t]$ of an electronic system. The linear response of the ground state electron density of the electronic system on this perturbation is given by $\rho^{(1)}(\omega, \mathbf{r}'') \exp[-i\omega t]$, i.e., for $\nu = \omega$ the quantity $\rho^{(1)}(\nu, \mathbf{r}'') = \rho^{(1)}(\omega, \mathbf{r}'')$ is the response of the density in the frequency domain. The quantity $f_{\text{Hx}}(\nu, \mathbf{r}, \mathbf{r}')$ is the sum of the Coulomb and exchange kernel, the frequency-dependent functional derivative of the Hartree and exchange potential with respect to the electron density. If the sum of f_{Hx} is supplemented by a correlation contribution to the kernel f_{Hxc} , the sum of Coulomb, exchange, and correlation kernel, then Eq. (6) is an exact equation that yields the exact frequency-dependent linear response of an electron system on a frequency-dependent perturbation.

Because f_{Hxc} is unknown approximations have to be made in practice. If the exchange-correlation contribution to f_{Hxc} are completely neglected and only the Coulomb kernel $f_{\text{H}}(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ is retained in the construction of the response function χ_α , then the RPA approach often referred to as dRPA results. In this work we focus on exact-exchange RPA, i.e., EXXRPAs. In EXXRPAs the correlation contribution to f_{Hxc} is neglected whereas the remaining sum f_{Hx} of the Coulomb and exchange kernel is treated exactly, including the frequency dependence of the exchange kernel f_{x} . (The Coulomb kernel does not depend on the frequency.)

The sum f_{Hx} of Coulomb and exchange kernel obeys the integral equation³⁻⁵

$$f_{\text{Hx}}(\nu, \mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' d\mathbf{r}''' \chi_0^{-1}(\nu, \mathbf{r}, \mathbf{r}'') h_{\text{Hx}}(\nu, \mathbf{r}'', \mathbf{r}''') \times \chi_0^{-1}(\nu, \mathbf{r}''', \mathbf{r}'). \quad (7)$$

The function h_{Hx} can be decomposed in two parts, h_{Hx}^{I} and $h_{\text{Hx}}^{\text{II}}$ according to

$$h_{\text{Hx}}(\nu, \mathbf{r}, \mathbf{r}') = h_{\text{Hx}}^{\text{I}}(\nu, \mathbf{r}, \mathbf{r}') + h_{\text{Hx}}^{\text{II}}(\nu, \mathbf{r}, \mathbf{r}'). \quad (8)$$

The contribution h_{Hx}^{I} is given by³⁻⁵

$$h_{\text{Hx}}^{\text{I}}(\nu, \mathbf{r}, \mathbf{r}') = \sum_{ia,jb} \varphi_{ia}(\mathbf{r}) \lambda_{ia}(\nu) X_{ia,jb}^{\text{Hx}}(\nu) \lambda_{jb}(\nu) \varphi_{jb}(\mathbf{r}') \quad (9)$$

with

$$X_{ia,jb}^{\text{Hx}}(\nu) = \frac{1}{4}(A_{ia,jb} + B_{ia,jb} + \Delta_{ia,jb}) + \nu^2 \frac{1}{4} \varepsilon_{ia}^{-1} (A_{ia,jb} - B_{ia,jb} + \Delta_{ia,jb}) \varepsilon_{jb}^{-1} \quad (10)$$

and

$$A_{ia,jb} = 2(ai|jb) - (ab|ji), \quad (11)$$

$$B_{ia,jb} = 2(ai|bj) - (aj|bi), \quad (12)$$

$$\Delta_{ia,jb} = \delta_{ij} \langle \varphi_a | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_b \rangle - \delta_{ab} \langle \varphi_i | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_j \rangle \quad (13)$$

with integrals of the type $(ai|jb)$ being defined according to $\int d\mathbf{r} d\mathbf{r}' \varphi_a(\mathbf{r}) \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}') \varphi_b(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$, $\hat{v}_{\text{x}}^{\text{NL}}$ being the nonlocal

exchange operator defined by its kernel $\sum_i \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$, and $\hat{v}_{\text{x}}$ being the local multiplicative KS exchange potential.

The second contribution $h_{\text{Hx}}^{\text{II}}$ of h_{Hx} is given by³⁻⁵

$$h_{\text{Hx}}^{\text{II}}(\nu, \mathbf{r}, \mathbf{r}') = \sum_{ia,j} \varphi_{ia}(\mathbf{r}) \lambda_{ia}(\nu) \langle \varphi_a | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_j \rangle \varepsilon_{ja}^{-1} \varphi_{ji}(\mathbf{r}') + \sum_{ia,j} \varphi_{ij}(\mathbf{r}) \varepsilon_{ja}^{-1} \langle \varphi_j | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_a \rangle \lambda_{ia}(\nu) \varphi_{ia}(\mathbf{r}') - \sum_{ia,b} \varphi_{ia}(\mathbf{r}) \lambda_{ia}(\nu) \langle \varphi_b | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_i \rangle \varepsilon_{ib}^{-1} \varphi_{ab}(\mathbf{r}') - \sum_{ia,b} \varphi_{ba}(\mathbf{r}) \varepsilon_{ib}^{-1} \langle \varphi_i | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_b \rangle \lambda_{ia}(\nu) \varphi_{ia}(\mathbf{r}') \quad (14)$$

with the abbreviations $\varphi_{ij}(\mathbf{r}) = \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r})$ and $\varphi_{ab}(\mathbf{r}) = \varphi_a(\mathbf{r}) \varphi_b(\mathbf{r})$.

An evaluation of the integral equation (7) is numerically problematic due to the occurrence of the inverse of the KS response function χ_0 . In order to avoid a direct use of the kernel f_{Hx} and the necessity to solve the integral equation (7) we switch from the basic DFT response equation (6) to a response equation for the effective KS potential.⁶⁻⁹ To that end we exploit that the response $\rho^{(1)}$ of the electron density can be obtained within the KS reference system according to

$$\rho^{(1)}(\nu, \mathbf{r}) = \int d\mathbf{r}' \chi_s(\nu, \mathbf{r}, \mathbf{r}') v_s^{(1)}(\nu, \mathbf{r}') \quad (15)$$

from the frequency-dependent first-order change $v_s^{(1)}$ of the KS potential corresponding to the perturbing external potential $v^{(1)}$ of the physical system. If Eq. (15) is inserted into the DFT response equation (6), then the equation

$$\int d\mathbf{r}' [\chi_0(\nu, \mathbf{r}, \mathbf{r}') - h_{\text{Hx}}(\nu, \mathbf{r}, \mathbf{r}')] v_s^{(1)}(\nu, \mathbf{r}') = \int d\mathbf{r}' \chi_0(\nu, \mathbf{r}, \mathbf{r}') v^{(1)}(\nu, \mathbf{r}') \quad (16)$$

is obtained,⁶⁻⁹ an equation for the response $v_s^{(1)}$ of the effective KS potential. Equation (16) does not contain an inverse KS response function and was used as basis for time-dependent exact-exchange methods to calculate electronic excitation energies in Refs. 6–9. In Refs. 1 and 2 EXXRPAs methods with a N^6 scaling with the system size N were developed on the basis of Eq. (16). Starting from Eqs. (15) and (16) we here present a resolution-of-identity EXXRPAs method (RI-EXXRPAs method) that exhibits a N^5 scaling with system size due to the use of an auxiliary basis set (RI basis set).

B. Basic RI-EXXRPAs method

We introduce an auxiliary basis set, the RI basis set, by the unsymmetric resolution-of-the-identity

$$\delta(\mathbf{r} - \mathbf{r}') = \sum_{pq} \tilde{f}_p(\mathbf{r}) [\tilde{\mathbf{S}}^{-1}]_{pq} \int d\mathbf{r}'' \frac{\tilde{f}_q(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \quad (17)$$

$$= \sum_{pq} \int d\mathbf{r}'' \frac{\tilde{f}_p(\mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|} [\tilde{\mathbf{S}}^{-1}]_{pq} \tilde{f}_q(\mathbf{r}') \quad (18)$$

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

$$\tilde{S}_{pq} = \int d\mathbf{r} d\mathbf{r}' \frac{\tilde{f}_p(\mathbf{r}) \tilde{f}_q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (19)$$

The tilde on $\tilde{f}_p$ and $\tilde{\mathbf{S}}$ indicates that the original RI basis functions and their overlap matrix are preliminary quantities that, later on, will be modified to the auxiliary basis functions and overlap matrix actually used. Note that the use of auxiliary basis sets in conjunction with the Coulomb norm has a long tradition in DFT methods and is frequently used successfully in various approaches.^{59–62} We now act from left with the resolution-of-the-identity (17) on Eqs. (15) and (16) and additionally insert the resolution-of-the-identity (18) before the potentials $v_s^{(1)}$ and $v^{(1)}$ to obtain

$$\tilde{\mathbf{S}}^{-1} \tilde{\rho}^{(1)}(v) = \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(v) \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{v}}_s^{(1)}(v) \quad (20)$$

and

$$\tilde{\mathbf{S}}^{-1} [\tilde{\mathbf{X}}_0(v) - \tilde{\mathbf{H}}(v)] \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{v}}_s^{(1)}(v) = \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(v) \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{v}}^{(1)}(v) \quad (21)$$

with the vectors $\tilde{\mathbf{v}}^{(1)}(v)$, $\tilde{\mathbf{v}}_s^{(1)}(v)$, and $\tilde{\rho}^{(1)}(v)$ defined by their elements

$$\tilde{v}_p^{(1)}(v) = \int d\mathbf{r} \tilde{f}_p(\mathbf{r}) v^{(1)}(v, \mathbf{r}), \quad (22)$$

$$\tilde{v}_{s,p}^{(1)}(v) = \int d\mathbf{r} \tilde{f}_p(\mathbf{r}) v_s^{(1)}(v, \mathbf{r}), \quad (23)$$

and

$$\tilde{\rho}_p^{(1)}(v) = \int d\mathbf{r} d\mathbf{r}' \frac{\tilde{f}_p(\mathbf{r}') \rho^{(1)}(v, \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (24)$$

Note that the elements $\tilde{v}_p^{(1)}(v)$ and $\tilde{v}_{s,p}^{(1)}(v)$ of the vectors $\tilde{\mathbf{v}}^{(1)}(v)$ and $\tilde{\mathbf{v}}_s^{(1)}(v)$ representing the first-order changes $v^{(1)}(v, \mathbf{r})$ and $v_s^{(1)}(v, \mathbf{r})$ of the external and the KS potential, respectively, are defined by integrals with respect to the overlap norm, whereas the elements $\tilde{\rho}_p^{(1)}(v)$ of the vector $\tilde{\rho}^{(1)}(v)$ representing the response $\rho^{(1)}(v, \mathbf{r})$ of the electron density are defined with respect to the Coulomb norm. This is a consequence of using the unsymmetric resolutions-of-the-identity (17) and (18). The matrix elements of the matrices $\tilde{\mathbf{X}}_0(v)$ and $\tilde{\mathbf{H}}(v)$ are given by

$$\tilde{X}_{0,pq}(v) = \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \frac{\tilde{f}_p(\mathbf{r}''') \chi_0(v, \mathbf{r}'', \mathbf{r}') \tilde{f}_q(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'| |\mathbf{r}'' - \mathbf{r}'''|} \quad (25)$$

and

$$\tilde{H}_{pq}(v) = \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \frac{\tilde{f}_p(\mathbf{r}''') h_{\text{Hx}}(v, \mathbf{r}'', \mathbf{r}') \tilde{f}_q(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'| |\mathbf{r}'' - \mathbf{r}'''|}, \quad (26)$$

respectively.

In order to calculate the matrices $\tilde{\mathbf{X}}_0(v)$ and $\tilde{\mathbf{H}}(v)$, the matrix $\tilde{\mathbf{D}}$ with matrix elements

$$\tilde{D}_{ia,p} = \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \tilde{f}_p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (27)$$

is defined. The matrix $\tilde{\mathbf{D}}$ is a rectangular matrix with the first index, the superindex ia , running over all products of occu-

pied times unoccupied orbitals and the second index p referring to the RI basis functions. With the matrix $\tilde{\mathbf{D}}$ the matrix $\tilde{\mathbf{X}}_0(v)$ representing the uncoupled KS response function can be calculated according to

$$\tilde{\mathbf{X}}_0(v) = \tilde{\mathbf{D}}^T \lambda(v) \tilde{\mathbf{D}} \quad (28)$$

with the diagonal matrix $\lambda(v)$ being defined with Eq. (3) according to $\lambda_{ia,jb}(v) = \delta_{ia,jb} \lambda_{ia}(v)$. The matrix $\tilde{\mathbf{H}}(v)$ is constructed according to

$$\tilde{\mathbf{H}}(v) = \tilde{\mathbf{H}}^I(v) + \tilde{\mathbf{H}}^{II}(v) \quad (29)$$

from two parts $\tilde{\mathbf{H}}^I(v)$ and $\tilde{\mathbf{H}}^{II}(v)$ that correspond to the two functions $h_{\text{Hx}}^I(v, \mathbf{r}, \mathbf{r}')$ and $h_{\text{Hx}}^{II}(v, \mathbf{r}, \mathbf{r}')$ in Eq. (8) for the sum $h_{\text{Hx}}(v, \mathbf{r}, \mathbf{r}')$ of Coulomb and exchange kernel. The first part $\tilde{\mathbf{H}}^I(v)$ is given by

$$\begin{aligned} \tilde{\mathbf{H}}^I(v) = & \frac{1}{4} \tilde{\mathbf{D}}^T \lambda(v) [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \lambda(v) \tilde{\mathbf{D}} \\ & + v^2 \frac{1}{4} \tilde{\mathbf{D}}^T \lambda(v) \epsilon^{-1} [\mathbf{A} - \mathbf{B} + \mathbf{\Delta}] \epsilon^{-1} \lambda(v) \tilde{\mathbf{D}} \end{aligned} \quad (30)$$

with the matrix elements of the matrices $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{\Delta}$ defined in Eqs. 11, 12, and 13.

In order to calculate the second part $\tilde{\mathbf{H}}^{II}(v)$ of $\tilde{\mathbf{H}}(v)$ we first construct the rectangular matrices $\tilde{\mathbf{M}}$ and $\tilde{\mathbf{N}}$ with matrix elements

$$\tilde{M}_{ia,p}(i\omega) = \sum_j \frac{\langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | j \rangle}{\epsilon_a - \epsilon_j} \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}) \tilde{f}_p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (31)$$

and

$$\tilde{N}_{ia,p}(i\omega) = - \sum_b \frac{\langle b | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle}{\epsilon_b - \epsilon_i} \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_a(\mathbf{r}) \varphi_b(\mathbf{r}) \tilde{f}_p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (32)$$

and then obtain $\tilde{\mathbf{H}}^{II}(v)$ according to

$$\begin{aligned} \tilde{\mathbf{H}}^{II}(v) = & \tilde{\mathbf{D}}^T \lambda(v) \tilde{\mathbf{M}} + \tilde{\mathbf{M}}^T \lambda(v) \tilde{\mathbf{D}} \\ & + \tilde{\mathbf{D}}^T \lambda(v) \tilde{\mathbf{N}} + \tilde{\mathbf{N}}^T \lambda(v) \tilde{\mathbf{D}}. \end{aligned} \quad (33)$$

Having considered the calculations of the quantities entering Eq. (21) we now rearrange the latter in order to obtain $\tilde{\mathbf{v}}_s^{(1)}(v)$ as

$$\tilde{\mathbf{v}}_s^{(1)}(v) = \tilde{\mathbf{S}} [\tilde{\mathbf{X}}_0(v) - \tilde{\mathbf{H}}(v)]^{-1} \tilde{\mathbf{X}}_0(v) \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{v}}^{(1)}(v). \quad (34)$$

Substitution of Eq. (34) in Eq. (20) then leads to

$$\begin{aligned} \tilde{\mathbf{S}}^{-1} \tilde{\rho}^{(1)}(v) = & \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(v) [\tilde{\mathbf{X}}_0(v) - \tilde{\mathbf{H}}(v)]^{-1} \\ & \times \tilde{\mathbf{X}}_0(v) \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{v}}^{(1)}(v). \end{aligned} \quad (35)$$

From the definition of the resolution of identity (17) follows that the response $\rho^{(1)}(v, \mathbf{r})$ of the electron density within the RI basis set is given by

$$\rho^{(1)}(v, \mathbf{r}) = \sum_p \tilde{f}_p(\mathbf{r}) [\tilde{\mathbf{S}}^{-1} \tilde{\rho}^{(1)}(v)]_p. \quad (36)$$

Inserting Eq. (35) into Eq. (36) leads together with Eq. (22) to

$$\begin{aligned} \rho^{(1)}(\nu, \mathbf{r}) &= \sum_p \tilde{f}_p(\mathbf{r}) [\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu) [\tilde{\mathbf{X}}_0(\nu) - \tilde{\mathbf{H}}(\nu)]^{-1} \\ &\quad \times \tilde{\mathbf{X}}_0(\nu) \tilde{\mathbf{S}}^{-1} \tilde{\mathbf{v}}^{(1)}(\nu)]_p \\ &= \int d\mathbf{r}' \sum_p \sum_q \tilde{f}_p(\mathbf{r}) [\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu) [\tilde{\mathbf{X}}_0(\nu) \\ &\quad - \tilde{\mathbf{H}}(\nu)]^{-1} \tilde{\mathbf{X}}_0(\nu) \tilde{\mathbf{S}}^{-1}]_{pq} \tilde{f}_q(\mathbf{r}') \nu^{(1)}(\nu, \mathbf{r}'), \end{aligned} \quad (37)$$

which implies that the response function $\chi_{\alpha=1}(\nu, \mathbf{r}, \mathbf{r}')$, i.e., the response function for a value of the coupling constant α of one, is given by

$$\begin{aligned} \chi_{\alpha=1}(\nu, \mathbf{r}, \mathbf{r}') &= \sum_p \sum_q \tilde{f}_p(\mathbf{r}) [\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu) [\tilde{\mathbf{X}}_0(\nu) - \tilde{\mathbf{H}}(\nu)]^{-1} \\ &\quad \times \tilde{\mathbf{X}}_0(\nu) \tilde{\mathbf{S}}^{-1}]_{pq} \tilde{f}_q(\mathbf{r}'). \end{aligned} \quad (38)$$

The sum f_{Hx} of the Coulomb and exchange kernel depends linearly on the coupling constant α . Therefore, the coupling-constant-dependent response function $\chi_{\alpha}(\nu, \mathbf{r}, \mathbf{r}')$ is obtained by simply scaling the matrix $\tilde{\mathbf{H}}(\nu)$ in Eq. (38) by α , leading to

$$\begin{aligned} \chi_{\alpha}(\nu, \mathbf{r}, \mathbf{r}') &= \sum_p \sum_q \tilde{f}_p(\mathbf{r}) [\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu) [\tilde{\mathbf{X}}_0(\nu) - \alpha \tilde{\mathbf{H}}(\nu)]^{-1} \\ &\quad \times \tilde{\mathbf{X}}_0(\nu) \tilde{\mathbf{S}}^{-1}]_{pq} \tilde{f}_q(\mathbf{r}'). \end{aligned} \quad (39)$$

In the AC-FDT equation (1) the integral

$$\begin{aligned} \int d\mathbf{r} d\mathbf{r}' \frac{\chi_{\alpha}(\nu, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} &= \sum_{pq} [\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu) [\tilde{\mathbf{X}}_0(\nu) - \alpha \tilde{\mathbf{H}}(\nu)]^{-1} \\ &\quad \times \tilde{\mathbf{X}}_0(\nu) \tilde{\mathbf{S}}^{-1}]_{pq} \tilde{S}_{pq} \\ &= \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu) [\tilde{\mathbf{X}}_0(\nu) \\ &\quad - \alpha \tilde{\mathbf{H}}(\nu)]^{-1} \tilde{\mathbf{X}}_0(\nu)] \end{aligned} \quad (40)$$

occurs. For $\alpha = 0$ Eq. (39) gives the uncoupled KS response function $\chi_0(\nu, \mathbf{r}, \mathbf{r}')$ and Eq. (40) turns into the integral

$$\int d\mathbf{r} d\mathbf{r}' \frac{\chi_0(\nu, \mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(\nu)]. \quad (41)$$

Setting $\nu = i\omega$ and inserting Eqs. (40) and (41) into the AC-FDT (1) leads to the expression

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^{\infty} d\omega \int_0^1 d\alpha \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(i\omega) [\tilde{\mathbf{X}}_0(i\omega) \\ &\quad - \alpha \tilde{\mathbf{H}}(i\omega)]^{-1} \tilde{\mathbf{X}}_0(i\omega)] \\ &\quad + \frac{1}{2\pi} \int_0^{\infty} d\omega \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(i\omega)] \end{aligned} \quad (42)$$

for the correlation energy E_c . In the second term on the right hand side of Eq. (42) the coupling-constant integration was carried out exploiting that the integrand in Eq. (41) is independent of α .

Next, the coupling-constant integration in the first term on the right hand side of Eq. (42) is carried out. To that end we

exploit that the matrix $\tilde{\mathbf{X}}_0(i\omega)$ is negative definite. A spectral representation

$$\tilde{\mathbf{X}}_0(i\omega) = -\tilde{\mathbf{V}}(i\omega) \tilde{\boldsymbol{\sigma}}(i\omega) \tilde{\mathbf{V}}^T(i\omega) \quad (43)$$

of $\tilde{\mathbf{X}}_0(i\omega)$ contains only positive entries $\sigma_n(i\omega)$ in the diagonal matrix $\tilde{\boldsymbol{\sigma}}(i\omega)$ and we can calculate the square root of $-\tilde{\mathbf{X}}_0(i\omega)$ according to

$$[-\tilde{\mathbf{X}}_0(i\omega)]^{1/2} = \tilde{\mathbf{L}}(i\omega) = \tilde{\mathbf{V}}(i\omega) \tilde{\boldsymbol{\sigma}}(i\omega)^{1/2} \tilde{\mathbf{V}}^T(i\omega). \quad (44)$$

With the matrix $\tilde{\mathbf{L}}(i\omega)$ expression (42) for the correlation energy can be rewritten as

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^{\infty} d\omega \int_0^1 d\alpha \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{L}}(i\omega) \\ &\quad \times [-\mathbf{1} - \alpha \tilde{\mathbf{L}}^{-1}(i\omega) \tilde{\mathbf{H}}(i\omega) \tilde{\mathbf{L}}^{-1}(i\omega)]^{-1} \tilde{\mathbf{L}}(i\omega)] \\ &\quad + \frac{1}{2\pi} \int_0^{\infty} d\omega \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(i\omega)]. \end{aligned} \quad (45)$$

Diagonalization of $\tilde{\mathbf{L}}^{-1}(i\omega) \tilde{\mathbf{H}}(i\omega) \tilde{\mathbf{L}}^{-1}(i\omega)$ yields its spectral representation

$$\tilde{\mathbf{L}}^{-1}(i\omega) \tilde{\mathbf{H}}(i\omega) \tilde{\mathbf{L}}^{-1}(i\omega) = \tilde{\mathbf{U}}(i\omega) \tilde{\boldsymbol{\tau}}(i\omega) \tilde{\mathbf{U}}^T(i\omega) \quad (46)$$

that can be used to express $[-\mathbf{1} - \alpha \tilde{\mathbf{L}}^{-1}(i\omega) \tilde{\mathbf{H}}(i\omega) \tilde{\mathbf{L}}^{-1}(i\omega)]^{-1}$ as $\tilde{\mathbf{U}}(i\omega) [-\mathbf{1} - \alpha \tilde{\boldsymbol{\tau}}(i\omega)]^{-1} \tilde{\mathbf{U}}^T(i\omega)$ and to subsequently carry out the integration over the coupling constant analytically to obtain the expression

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^{\infty} d\omega \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{L}}(i\omega) \tilde{\mathbf{U}}(i\omega) \\ &\quad \times [-\tilde{\boldsymbol{\tau}}^{-1}(i\omega) \ln[|\mathbf{1} + \tilde{\boldsymbol{\tau}}(i\omega)|]] \tilde{\mathbf{U}}^T(i\omega) \tilde{\mathbf{L}}(i\omega)] \\ &\quad + \frac{1}{2\pi} \int_0^{\infty} d\omega \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{X}}_0(i\omega)] \\ &= \frac{-1}{2\pi} \int_0^{\infty} d\omega \text{Tr}[\tilde{\mathbf{S}}^{-1} \tilde{\mathbf{L}}(i\omega) \tilde{\mathbf{U}}(i\omega) \\ &\quad \times [-\tilde{\boldsymbol{\tau}}^{-1}(i\omega) \ln[|\mathbf{1} + \tilde{\boldsymbol{\tau}}(i\omega)|] + \mathbf{1}] \tilde{\mathbf{U}}^T(i\omega) \tilde{\mathbf{L}}(i\omega)] \end{aligned} \quad (47)$$

for the KS correlation energy. In the analytic integration over the coupling constant it is exploited that $[-\mathbf{1} - \alpha \tilde{\boldsymbol{\tau}}(i\omega)]$ is a diagonal matrix.

C. Processing of auxiliary basis sets for an efficient and numerically stable RI-EXXRP implementation

Equation (47) for the RI-EXXRP correlation energy implicitly contains the inverse of the square root $\tilde{\mathbf{L}}(i\omega)$ of the negative $-\tilde{\mathbf{X}}_0(i\omega)$ of the uncoupled KS response function, see Eqs. (43), (44), and (46). It is known from optimized effective potential (OEP) methods, e.g., the EXX method, that the use of the inverse of the KS response function can lead to numerical instabilities.^{47,63–68} In OEP methods the inverse of the static KS response function instead of the inverse of the square root of the KS response functions for complex-valued frequencies is required. Moreover, the inverse is used for a very different purpose. Nevertheless, a specifically adapted

construction of the auxiliary basis set and a careful construction of the inverse of the square root of the uncoupled KS response function turned out to be important for the numerical stability and the efficiency of the RI-EXXRP method. This construction of the actually used auxiliary basis is carried out in three steps elucidated in the following.

Starting point of the construction of the auxiliary basis set are standard RI basis sets.^{69,70} In a first step the overlap matrix $\tilde{\mathbf{S}}$ of the RI basis functions with respect to the Coulomb norm, see Eq. (19), is conditioned such that its diagonal elements become equal to one, i.e., we define an intermediate overlap matrix $\mathbf{S}'$ according to

$$\mathbf{S}' = \boldsymbol{\mu}^{-1/2} \tilde{\mathbf{S}} \boldsymbol{\mu}^{-1/2} \quad (48)$$

with the elements μ_{pq} of the diagonal matrix $\boldsymbol{\mu}$ being given by $\mu_{pq} = \delta_{pq} \tilde{S}_{pp}$.

In the second step, the spectral representation of the overlap matrix $\mathbf{S}'$ is calculated according to

$$\mathbf{S}' = \mathbf{P} \mathbf{v} \mathbf{P}^T. \quad (49)$$

By removing those rows in $\mathbf{P}$ and those rows and columns in $\mathbf{v}$ that belong to eigenvalues v_{pp} lower than a chosen threshold t_S we obtain the rectangular matrix $\tilde{\mathbf{P}}$ and the diagonal matrix $\tilde{\mathbf{v}}$. The transformation

$$\tilde{\mathbf{v}}^{-1/2} \tilde{\mathbf{P}}^T \mathbf{S}' \tilde{\mathbf{P}} \tilde{\mathbf{v}}^{-1/2} = \mathbf{E} \quad (50)$$

of $\mathbf{S}'$ leads to a unit matrix $\mathbf{E}$ of a dimension that is smaller than that of $\tilde{\mathbf{S}}$ and $\mathbf{S}'$ due to the removal of linear combinations of basis functions corresponding to an eigenvalue of the overlap matrix $\mathbf{S}'$ smaller than t_S .

Finally, in a third step, we remove contributions from a constant function from the auxiliary basis set. The reason is that constant functions are eigenfunctions of the KS response function with an eigenvalue of zero. This means in order for the KS response function to be invertible we have to remove constant functions from the domain the response function acts on. To that end we need the vector $\tilde{\mathbf{y}}$ defined by its elements

$$\tilde{y}_p = \int d\mathbf{r} \tilde{f}_p(\mathbf{r}), \quad (51)$$

i.e., the elements $\tilde{y}_p$ are simply the integrals over the original RI basis function $\tilde{f}_p(\mathbf{r})$. Next we calculate a transformed vector $\mathbf{y}^{\text{II}}$ according to

$$\mathbf{y}^{\text{II}} = \tilde{\mathbf{v}}^{-1/2} \tilde{\mathbf{P}}^T \tilde{\boldsymbol{\mu}}^{-1/2} \tilde{\mathbf{y}} \quad (52)$$

with the transformation matrices defined in the first two steps above. Next we construct a matrix $\mathbf{T}$ with columns

$$\mathbf{t}_p = \mathbf{e}_p - \frac{y_p^{\text{II}}}{\mathbf{y}^{\text{II}T} \mathbf{y}^{\text{II}}} \mathbf{y}^{\text{II}} \quad (53)$$

with $\mathbf{e}_p$ denoting the p th unit vector. The normalized vector $(1/\sqrt{\mathbf{y}^{\text{II}T} \mathbf{y}^{\text{II}}}) \mathbf{y}^{\text{II}}$ represents a constant function, or, perhaps more precisely, all vectors orthogonal to this vector are orthogonal to constant functions in the sense that integrals of a constant function with functions represented by those vectors orthogonal to $(1/\sqrt{\mathbf{y}^{\text{II}T} \mathbf{y}^{\text{II}}}) \mathbf{y}^{\text{II}}$ equal zero. We then diagonalize $\mathbf{T}^T \mathbf{T}$

$$\mathbf{T}^T \mathbf{T} = \mathbf{Q} \boldsymbol{\gamma} \mathbf{Q}^T. \quad (54)$$

The diagonal elements γ_{pp} of the diagonal matrix $\boldsymbol{\gamma}$ all equal one except one diagonal element that equals zero. By removing the row in $\mathbf{Q}$ and the row and column in $\boldsymbol{\gamma}$ that belong to the eigenvalue v_{pp} equaling zero we obtain the rectangular projection matrix $\tilde{\mathbf{Q}}$ and the matrix $\boldsymbol{\gamma}$ turns into a unit matrix of smaller dimension.

In summary, we have constructed the final auxiliary basis set by three successive steps. The first step was a pure scaling of the original basis set, the last two steps were transformations combined with eliminations of basis functions. In summary we transformed the original overlap matrix $\tilde{\mathbf{S}}$ according to

$$\tilde{\mathbf{Q}}^T \tilde{\mathbf{v}}^{-1/2} \tilde{\mathbf{P}}^T \boldsymbol{\mu}^{-1/2} \tilde{\mathbf{S}} \boldsymbol{\mu}^{-1/2} \tilde{\mathbf{P}} \tilde{\mathbf{v}}^{-1/2} \tilde{\mathbf{Q}} = \mathbf{E} \quad (55)$$

into a unit matrix. The matrix $\tilde{\mathbf{D}}$ of Eq. (27) needs to be transformed accordingly into

$$\mathbf{D} = \tilde{\mathbf{D}} \boldsymbol{\mu}^{-1/2} \tilde{\mathbf{P}} \tilde{\mathbf{v}}^{-1/2} \tilde{\mathbf{Q}}. \quad (56)$$

Equation (47) for the RI-EXXRP correlation energy then assumes the form

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \text{Tr}[\mathbf{L}(i\omega) \mathbf{U}(i\omega) \times [-\boldsymbol{\tau}^{-1}(i\omega) \ln[|\mathbf{1} + \boldsymbol{\tau}(i\omega)|] + \mathbf{1}] \mathbf{U}^T(i\omega) \mathbf{L}(i\omega)]. \quad (57)$$

In Eq. (57), in contrast to Eq. (47), no inverse of an overlap matrix $\mathbf{S}$ corresponding to the overlap matrix $\tilde{\mathbf{S}}$ of Eq. (47) occurs because the overlap matrix has been transformed into a unit matrix. Moreover, the matrices $\tilde{\boldsymbol{\tau}}(i\omega)$, $\tilde{\mathbf{U}}(i\omega)$, and $\tilde{\mathbf{L}}(i\omega)$ referring to the original RI basis set are replaced by the matrices $\boldsymbol{\tau}(i\omega)$, $\mathbf{U}(i\omega)$, and $\mathbf{L}(i\omega)$ referring to the transformed RI basis set, i.e., the actually used auxiliary basis set. More generally, in Subsection II B, i.e., in Eqs. (27)–(33), the matrix $\tilde{\mathbf{D}}$ has to be replaced by the matrix $\mathbf{D}$ and subsequently the matrices, $\tilde{\mathbf{X}}_0(i\omega)$, $\tilde{\boldsymbol{\sigma}}(i\omega)$, $\tilde{\mathbf{V}}(i\omega)$, $\tilde{\mathbf{L}}(i\omega)$, $\tilde{\boldsymbol{\tau}}(i\omega)$, and $\tilde{\mathbf{U}}(i\omega)$ of Eqs. (21)–(47) that are calculated using the matrix $\tilde{\mathbf{D}}$ turn to corresponding matrices $\mathbf{X}_0(i\omega)$, $\boldsymbol{\sigma}(i\omega)$, $\mathbf{V}(i\omega)$, $\mathbf{L}(i\omega)$, $\boldsymbol{\tau}(i\omega)$, and $\mathbf{U}(i\omega)$, calculated using the matrix $\mathbf{D}$. Additionally, in Eqs. (17)–(47), that is, the complete Subsection II B, the overlap matrix $\tilde{\mathbf{S}}$ is replaced by a unit matrix, i.e., it does no longer explicitly occur.

As mentioned above, besides a suitable construction of the auxiliary basis set, the square root $\mathbf{L}(i\omega)$ of the negative of the KS response matrix $\mathbf{X}_0(i\omega)$ and its inverse $\mathbf{L}^{-1}(i\omega)$ have to be calculated with special care in order to obtain a numerical stable procedure. The square root $\mathbf{L}(i\omega)$ of the negative of $\mathbf{X}_0(i\omega)$ is calculated from the spectral representation $\mathbf{V}(i\omega) \boldsymbol{\sigma}(i\omega) \mathbf{V}^T(i\omega)$ of $-\mathbf{X}_0(i\omega)$. Because the matrix $-\mathbf{X}_0(i\omega)$ is positive definite, in principle, it is straightforward to calculate the matrices $\mathbf{L}(i\omega)$ and $\mathbf{L}^{-1}(i\omega)$ by taking the square root of the diagonal matrix $\boldsymbol{\sigma}(i\omega)$ or the inverse of the square root of $\boldsymbol{\sigma}(i\omega)$, respectively. In practice, however, the matrix $-\mathbf{X}_0(i\omega)$ may contain very small eigenvalues with magnitudes smaller than 10^{-15} . The magnitude of these eigenvalues lies below the usual computational accuracy and the eigenvalues therefore are not necessarily physically meaningful. Indeed, it may happen that some of these small eigenvalues are even negative and therefore obviously unphysical. Generally, small eigenvalues of $-\mathbf{X}_0(i\omega)$ may be

of questionable accuracy and can lead to numerical instabilities. Therefore, a threshold t_{SVD} is introduced and eigenvalues of $-\mathbf{X}_0(i\omega)$ below this threshold are set to zero when taking the square root and the inverse of the square root of $\sigma(i\omega)$. In the calculation of the matrices $\mathbf{L}(i\omega)$ and $\mathbf{L}^{-1}(i\omega)$ these eigenvalues remain untouched and retain their value of zero, i.e., a singular value decomposition of $-\mathbf{X}_0(i\omega)$ is carried out.

The threshold t_S for the reduction of the auxiliary basis set and the threshold t_{SVD} for the singular value decomposition interact in such a way that for a larger threshold t_S leading to the elimination of more auxiliary basis functions the negative $-\mathbf{X}_0(i\omega)$ of the KS response function has a smaller number of small eigenvalues falling under the threshold t_{SVD} . The optimal choice and the influence of the thresholds t_S and t_{SVD} is discussed in Sec. IV A.

D. RI-dRPA method

For test purposes we implemented also a version of the RPA approach presented here that yields the dRPA correlation energy. To that end only the matrix $\tilde{\mathbf{H}}(i\omega)$ representing the function $h_{\text{HX}}(\nu, \mathbf{r}, \mathbf{r}')$ has to be replaced in Subsection II B by a matrix $\mathbf{H}^{\text{dRPA}}(i\omega)$ representing only the contribution $h_{\text{H}}(\nu, \mathbf{r}, \mathbf{r}')$ of the Coulomb kernel to $h_{\text{HX}}(\nu, \mathbf{r}, \mathbf{r}')$. The contribution $h_{\text{H}}(\nu, \mathbf{r}, \mathbf{r}')$ depends according to

$$h_{\text{H}}(\nu, \mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' d\mathbf{r}''' \frac{\chi_0(\nu, \mathbf{r}, \mathbf{r}'') \chi_0(\nu, \mathbf{r}''', \mathbf{r}')}{|\mathbf{r}'' - \mathbf{r}'''|} \quad (58)$$

on the Coulomb kernel $1/|\mathbf{r}'' - \mathbf{r}'''|$ and the uncoupled KS response function χ_0 . From Eq. (58) follows that the required matrix $\mathbf{H}^{\text{dRPA}}(i\omega)$ can simply be obtained by modifying Eq. (30) to

$$\mathbf{H}^{\text{dRPA}}(\nu) = \mathbf{D}^T \boldsymbol{\lambda}(\nu) \mathbf{C} \boldsymbol{\lambda}(\nu) \mathbf{D} \quad (59)$$

with the matrix $\mathbf{C}$ being defined by its matrix elements $C_{ia,jb}$ given by

$$C_{ia,jb} = (ai|jb). \quad (60)$$

By replacing Eqs. (29)–(33) of the RI-EXXRP method by Eq. (59) a RI-dRPA method is obtained. (In Eq. (59) matrices without a tilde occur. This means Eq. (59) refers to the actually used auxiliary basis set not the original RI basis set.)

The RI-dRPA procedure obtained from the RI-EXXRP method in the way described above is of interest only for test purposes, i.e., for testing the numerical stability of the steps it has in common with the RI-dRPA method, see Sec. IV A, but not as a practical method. The reason is that more efficient RI methods exist in the special case of dRPA, see Refs. 17, 23, and 36. For example, the approach of Ref. 23 is related to the current approach, but in addition to expanding the response equation in an auxiliary basis set it also employs the RI a second time to approximate the Coulomb kernel matrix. With this the expression for the dRPA correlation energy simplifies and an inversion of the square root of $-\mathbf{X}_0(i\omega)$ can be avoided.

III. COMPUTATIONAL DETAILS

The geometries of the 21 organic molecules for which the total energies and the correlation energies were calculated are

the same as those used in Ref. 1. In Sec. IV B where the CH_2 -groups of the ethene molecule are twisted around the carbon-carbon bond we set the CH bond length to 1.09 Å and the HCH angle to 120°.

To assess the performance of our RI-EXXRP methods for intermolecular interaction energies, a subset of seven small dimers from the S22 benchmark database of Hobza *et al.*⁷¹ has been considered, namely, the hydrogen-bridged dimers $(\text{H}_2\text{O})_2$, $(\text{NH}_3)_2$, $(\text{HCOOH})_2$, and $(\text{CHONH}_2)_2$, the mixed-type system $\text{C}_2\text{H}_4 \dots \text{C}_2\text{H}_2$, and the two dispersion dominated dimers $(\text{CH}_4)_2$ and $(\text{C}_2\text{H}_4)_2$. The complete basis set (CBS) extrapolated CCSD(T) reference values were taken from the work of Takatani *et al.*⁷²

The exact-exchange Kohn-Sham (EXX) orbitals and eigenvalues that entered the RPA calculations were obtained completely analogously to those in Ref. 1. Accordingly, we performed a numerically stable EXX calculation with the method described in Ref. 73 consisting of two steps. Firstly, the exact local KS exchange potential was computed with the balanced uncontracted triple-zeta orbital and auxiliary basis sets of Ref. 73. In the next step the actually used EXX orbitals and eigenvalues were calculated by a KS calculation keeping fixed the exact local KS exchange potential represented in the auxiliary basis of the first step, but with a contracted aug-cc-pVXZ (Ref. 74) orbital basis set with $X = \text{T}$ and Q . In the second step only the Coulomb potential was optimized self-consistently. The correlation energies were computed with the resulting EXX orbitals and eigenvalues post-self-consistently.

The integration over the imaginary frequencies ω was performed using a Gauss-Legendre quadrature scheme⁷⁵ where we used 30 integration points in case of the 21 organic molecules and 40 points for the larger systems of the S22 set. Increasing the number of gridpoints for the largest system of the 21 organic molecules lead to a change of energy in the range of 10^{-6} Hartree, implying a sufficiently large integration grid. However, the situation is different in the case of static correlation, where the HOMO-LUMO gap is vanishing. In the case of twisting the CH_2 groups in ethene described in Sec. IV B we had to enlarge the grid up to 80 integration points.

We implemented the method in the development version of the Molpro quantum chemistry package,⁷⁶ with which we also performed the MP2, CCSD, CCSD(T), multireference self-consistent field (MC-SCF) (number of active orbitals = 12), and B3LYP (Refs. 77 and 78) calculations. All electrons including core electrons were correlated in the EXXRP and dRPA calculations as well as in the MP2, CCSD, and CCSD(T) calculations.

IV. PERFORMANCE OF THE RI-EXXRP METHOD

A. Numerical stability of the RI-EXXRP method

In this subsection the numerical stability of the RPA approach presented here is investigated and suitable values for the two thresholds t_{SVD} and t_S are identified. We start by comparing dRPA correlation energies of the RI-dRPA approach of Subsection II D with those from the RPA method of Ref. 2, which shall be denoted simply dRPA method here. The

latter calculates the dRPA correlation energy from the excitation energies and corresponding eigenvectors of a TDDFT calculation employing exclusively the Coulomb kernel but no exchange-correlation kernel. The approach of Ref. 2 scales with N^6 with the system size N and thus is computationally quite inefficient, but it does not invoke a RI basis set and therefore can provide reference data for the approach introduced here. The reason for comparing the RI-dRPA approach with the dRPA method of Ref. 2 instead of comparing the RI-EXXRP method, which is the method we are actually interested in, with the EXXRP method of Ref. 2 is that in the EXXRP method of Ref. 2, in contrast to the RI-EXXRP presented here, products of occupied times unoccupied orbitals are treated as if they were linearly independent although they are not. While this can be assumed to have little effect it still makes the EXXRP method of Ref. 2 less ideal as reference method to check the numerical stability of the methodical framework of the approaches introduced here.

In Fig. 1 the differences of the dRPA correlation energies $E_c^{\text{RI-dRPA}}$ and E_c^{dRPA} of the RI-dRPA method of Subsection II D and the dRPA method of Ref. 2, respectively, are displayed for different values of the threshold t_{SVD} of the singular value decomposition used in the calculation of the inverse of the square root of the KS response functions for a number of molecules. The second threshold t_s was set to zero. This means in the orthonormalization step in the construction of the actually used auxiliary basis set from the initial RI basis set no basis functions were removed. For Fig. 1 an aug-cc-pVTZ orbital basis set was combined with an initial RI basis set of aug-cc-pV5Z quality. The combination of a large RI basis set with a moderate orbital basis set was chosen because it is known from OEP methods that inversions of the KS response matrix become numerically more critical if the auxiliary basis set becomes large. The combination of an aug-cc-pVTZ orbital basis set with an aug-cc-pV5Z RI basis set thus should be numerically more demanding than the combination of orbital and RI basis sets of comparable quality that is used later on.

Figure 1 shows that the results of the RI-dRPA approach do not depend at all on the value of the singular value decomposition threshold t_{SVD} for values of t_{SVD} between 10^{-14} and 10^{-4} . This shows that the RI-dRPA approach is remarkably stable. Even if eigenvalues of the KS response matrix as small as 10^{-14} , i.e., eigenvalues close to the computational accuracy, are retained in the construction of the inverse of the square root of the KS response matrix the approach remains numerically stable. In many cases, eigenvalues smaller than 10^{-9} did not occur. In these cases results for values of $10^{-14} \leq t_{\text{SVD}} \leq 10^{-9}$, of course, are identical. The deviations from the reference values lie between 10^{-6} and 10^{-5} Hartree and thus are negligible. At a singular value decomposition threshold t_{SVD} of 10^{-2} the resulting correlation energies deviate from the reference values and become too small in magnitude. This is not surprising because with increasing t_{SVD} more and more contributions to the correlation energy are removed and the correlation energy eventually has to approach zero. Figure 1 suggests to use a singular value decomposition threshold t_{SVD} of 10^{-4} because this is the largest value that does not yet affect the RI-dRPA correlation energies. This means for

FIG. 1. Numerical stability of the RI-dRPA method (resolution-of-identity direct RPA method), influence of the threshold t_{SVD} of the singular values decomposition, Eq. (43), of the KS response function: Displayed is the logarithm of deviations $\Delta E = E^{\text{RI-dRPA}} - E^{\text{dRPA}}$ of total energies $E^{\text{RI-dRPA}}$ from the RI-dRPA method of this work that employs a RI approximation to reference direct RPA total energies E^{dRPA} calculated without RI approximation for various values of t_{SVD} . An aug-cc-pVTZ orbital basis and an aug-cc-pV5Z RI basis was employed. The threshold t_s controlling the removal of basis functions in the orthonormalization of the RI basis set was set to zero, i.e., no basis functions were removed in this step.

this choice of t_{SVD} the largest number of contributions to the response function with small eigenvalues are removed in the singular value decomposition which potentially increases the numerical stability of the approach. While this is not an issue in the case of RI-dRPA due to the high numerical stability, it may be of interest if instead of the dRPA correlation energy other DFT based RPA correlation energies are calculated within the framework of the presented method, see below.

As mentioned above, the question of numerical stability, in principle, should be less critical for the combination of aug-cc-pVQZ orbital and aug-cc-pVQZ RI basis sets than for the combination of aug-cc-pVTZ orbital and aug-cc-pV5Z RI basis sets considered in Fig. 1. However, already the latter potentially less stable combination of basis sets turned out to be perfectly stable with respect to the choice of the singular value decomposition threshold t_{SVD} , down to values of $t_{\text{SVD}} = 10^{-14}$. We therefore expect the combination of aug-cc-pVQZ orbital and aug-cc-pVQZ RI basis sets to be also perfectly stable with respect to the choice of t_{SVD} . In order to check this we repeated the investigation of the influence of the threshold t_{SVD} for the combination of aug-cc-pVQZ orbital and aug-cc-pVQZ RI basis sets. The results shown in Fig. 2 are quite similar to those of Fig. 1. Indeed, the range of stability with respect to t_{SVD} again stretches from 10^{-4} to 10^{-14} . The deviations of RI-dRPA total energies from the reference dRPA total energies obtained without RI approximation are larger for the combination of aug-cc-pVQZ orbital and aug-cc-pVQZ RI basis sets, Fig. 2, than for the combination of aug-cc-pVTZ orbital and aug-cc-pV5Z RI basis sets, Fig. 1. This, however, is not a question of the numerical stability with respect to the singular value decomposition threshold t_{SVD} but of the error due to the RI approximation. The latter is larger for aug-cc-pVQZ RI basis sets than for aug-cc-pV5Z RI basis sets.

FIG. 2. Numerical stability of the RI-dRPA method (resolution-of-identity direct RPA method), influence of the threshold t_{SVD} of the singular values decomposition, Eq. (43), of the KS response function: Displayed is the logarithm of deviations $\Delta E = E^{\text{RI-dRPA}} - E^{\text{dRPA}}$ of total energies $E^{\text{RI-dRPA}}$ from the RI-dRPA method of this work that employs a RI approximation to reference direct RPA total energies E^{dRPA} calculated without RI approximation for various values of t_{SVD} . An aug-cc-pVQZ orbital basis and an aug-cc-pVQZ RI basis was employed. The threshold t_{S} controlling the removal of basis functions in the orthonormalization of the RI basis set was set to zero, i.e., no basis functions were removed in this step.

In Fig. 3 for the same setup as in Figs. 1 and 2 the singular value decomposition threshold t_{SVD} was fixed at a value of 10^{-8} and the threshold t_{S} determining the removal of auxiliary basis functions in the orthonormalization of the auxiliary basis set was varied from zero (no functions removed) to 10^{-2} . Figure 3 shows that up to a threshold of 10^{-6} the RI-dRPA correlation energies are not affected. Because a removal of auxiliary basis functions increases the general numerical stability of approaches involving an inversion of the KS response matrix we set, from now on, the threshold t_{S} to 10^{-6} , the largest value the dRPA correlation energy is not yet affected.

In Fig. 4 the influence of the quality of the initial RI basis set is shown for a given aug-cc-pVTZ orbital basis set. The RI-dRPA correlation energies approach their reference dRPA values with increasing quality of the initial RI basis set when going from an aug-cc-pVTZ over an aug-cc-pVQZ to an aug-cc-pV5Z RI basis set. For the aug-cc-pVTZ RI basis set the deviations from the reference values of up to about 1 kcal/mol can occur. For the two better RI basis sets the deviations are much smaller and therefore negligible. From now on aug-cc-pVQZ RI basis sets will be used with which the RI error should be insignificant. We note, in this context, that if reaction energies instead of total energies or total correlation energies are considered errors due to the RI basis set quality may cancel to some extent. An accurate calculation of correlation energies, on the other hand, requires orbital basis sets of good quality, i.e., basis sets of aug-cc-pVQZ quality or beyond, and this suggests the use of RI basis sets of the same quality. In this work the combination of aug-cc-pVQZ orbital and aug-cc-pVQZ RI basis sets will be employed from now on.

In Fig. 5 the influence of the singular value decomposition threshold t_{SVD} of the RI-EXXRP method is shown. To

FIG. 3. Numerical stability of the RI-dRPA method (resolution-of-identity direct RPA method), influence of the threshold t_{S} controlling the removal of basis functions in the orthonormalization, Eq. (49), of the RI basis set: Displayed is the logarithm of deviations $\Delta E = E^{\text{RI-dRPA}} - E^{\text{dRPA}}$ of total energies $E^{\text{RI-dRPA}}$ from the RI-dRPA method of this work that employs a RI approximation to reference direct RPA total energies E^{dRPA} calculated without RI approximation for various values of t_{S} . An aug-cc-pVTZ orbital basis and an aug-cc-pV5Z RI basis was employed. The threshold t_{SVD} of the singular values decomposition of the KS response function was set to $t_{\text{SVD}} = 10^{-8}$.

that end, total energies of the RI-EXXRP method are compared to those from the EXXRP method of Refs. 1 and 2. The EXXRP method of Refs. 1 and 2, in contrast to the RI-EXXRP method of this work, does not require an auxiliary basis set. Figure 5 shows again that RI-RPA approaches can be numerically remarkable stable. For values of t_{SVD} between 10^{-14} and 10^{-4} almost identical results are obtained. At a value of $t_{\text{SVD}} = 10^{-2}$ results start to differ from those in the range of stability of t_{SVD} . For $t_{\text{SVD}} > 10^{-1}$ again that many contributions of the correlation energy are removed that

FIG. 4. Numerical stability of the RI-dRPA method (resolution-of-identity direct RPA method), influence of the quality of the RI basis set: Displayed is the logarithm of deviations $\Delta E = E^{\text{RI-dRPA}} - E^{\text{dRPA}}$ of total energies $E^{\text{RI-dRPA}}$ from the RI-dRPA method of this work that employs a RI approximation to reference direct RPA total energies E^{dRPA} calculated without RI approximation for different RI basis sets, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z. An aug-cc-pVTZ orbital basis was employed. The threshold t_{SVD} of the singular values decomposition of the KS response function was set to $t_{\text{SVD}} = 10^{-4}$. The threshold t_{S} controlling the removal of basis functions in the orthonormalization of the RI basis set was set to $t_{\text{S}} = 10^{-6}$.

FIG. 5. Numerical stability of the RI-EXXRP method (resolution-of-identity exact-exchange RPA method), influence of the threshold t_{SVD} of the singular values decomposition, Eq. (43), of the KS response function: Displayed is the logarithm of deviations $\Delta E = E^{\text{RI-EXXRP}} - E^{\text{EXXRP}}$ of total energies $E^{\text{RI-EXXRP}}$ from the RI-EXXRP method of this work that employs a RI approximation to total energies E^{EXXRP} calculated with the EXXRP method of Ref. 2 without RI approximation for various values of t_{SVD} . An aug-cc-pVQZ orbital basis and an aug-cc-pVQZ RI basis was employed. The threshold t_{S} controlling the removal of basis functions in the orthonormalization of the RI basis set was set to $t_{\text{S}} = 10^{-6}$.

it becomes too small in magnitude by a significant amount and begins to approach zero. In the range of stability, i.e., for $10^{-14} \leq t_{\text{SVD}} \leq 10^{-4}$, the RI-EXXRP results deviate from the EXXRP results by up to about 3 kcal/mol and thus clearly stronger than the RI-dRPA from the dRPA results. Because the RI-EXXRP method seems to be numerically similarly stable as the RI-dRPA method the larger deviation to the EXXRP method might originate in the fact that the EXXRP method in contrast to the RI-EXXRP methods treat products of occupied times unoccupied orbitals as if they were linearly independent even though they are not. Indeed, RI-EXXRP total energies lie somewhat closer at CCSD(T) reference energies as EXXRP ones, see below. In this respect the RI-EXXRP method would yield somewhat better results than the EXXRP method despite the fact that a RI approximation is invoked in the former approach because of the proper handling of the linear dependencies of products of occupied times unoccupied orbitals. However, it cannot completely be ruled out that errors due to the RI approximation are larger in the RI-EXXRP method than in the RI-dRPA method and fortuitously lead to results in better agreement with reference data.

Figure 6 gives information on the numerical stability of the RI-EXXRP+ approach. The RI-EXXRP+ approach differs from the RI-EXXRP approach because it takes into account the terms of Eq. (33) that are neglected in the latter. The RI-EXXRP+ approach therefore represents a complete

FIG. 6. Numerical stability of the RI-EXXRP+ method (resolution-of-identity exact-exchange RPA method including the terms of Eq. (33)), influence of the threshold t_{SVD} of the singular values decomposition, Eq. (43), of the KS response function: Displayed are deviations $\Delta E = E^{\text{RI-EXXRP+}} - E^{\text{CCSD(T)}}$ of total energies $E^{\text{RI-EXXRP+}}$ from the RI-EXXRP+ method of this work to CCSD(T) total energies $E^{\text{CCSD(T)}}$ for various values of t_{SVD} . An aug-cc-pVQZ orbital basis and an aug-cc-pVQZ RI basis was employed. The threshold t_{S} controlling the removal of basis functions in the orthonormalization of the RI basis set was set to $t_{\text{S}} = 10^{-6}$.

exact-exchange RPA method in the sense that all contributions to the frequency-dependent exchange kernel are taken into account. The inclusion of the terms of Eq. (33) lead to a clearly reduced numerical stability as can be concluded from the dependence of differences of RI-EXXRP+ and CCSD(T) total energies on the singular value decomposition threshold t_{SVD} , displayed in Fig. 6. The reason for this reduced numerical stability most likely is that the additional terms in the RI-EXXRP+ approach contain products of two unoccupied orbital, see Eq. (32) that cannot be represented very good by the employed standard RI basis sets. Small values of t_{SVD} , i.e., values of 10^{-5} or below, lead to significant changes in the results. For a range of stability for $10^{-4} \leq t_{\text{SVD}} \leq 10^{-2}$ quite similar total energies are obtained. For $t_{\text{SVD}} = 10^{-4}$ and $t_{\text{SVD}} = 10^{-3}$ total energies are obtained that are very close. For $t_{\text{SVD}} = 10^{-2}$ slight deviations of the total energies from the values for $t_{\text{SVD}} = 10^{-4}$ and $t_{\text{SVD}} = 10^{-3}$ can be observed that, however, are negligible compared to the deviations to the CCSD(T) reference values. A choice of $t_{\text{SVD}} = 10^{-4}$, like in the RI-EXXRP case therefore seems to be suitable also for the RI-EXXRP+ approach.

B. Comparison of the accuracy of RI-EXXRP and other methods

In Figs. 7 and 8 EXXRP total energies are compared with total energies from RI-dRPA and from a number of standard methods for a number of organic compounds (see Fig. 7 for list of compounds). Figure 8 shows that all three EXXRP methods, the one of Ref. 2 that does not use RI basis sets and scales with N^6 with the system size N as well as the RI methods of this work with N^5 scaling, RI-EXXRP and RI-EXXRP+, yield total energies that are closer to the reference CCSD(T) values than all other considered methods including the CCSD method. Comparing the results of the

FIG. 7. Performance of EXXRPA methods compared to standard quantum chemistry methods: Displayed are deviations $\Delta E = E^{\text{Method}} - E^{\text{CCSD(T)}}$ of total energies E^{Method} from various methods (EXXRPA, RI-EXXRPA, RI-EXXRPA+, MP2, and CCSD) to CCSD(T) total energies $E^{\text{CCSD(T)}}$. An aug-cc-pVQZ orbital basis and, for the RI-EXXRPA and RI-EXXRPA+ method, an aug-cc-pVQZ RI basis was employed. The thresholds t_{SVD} and t_{S} of the RI-EXXRPA and RI-EXXRPA+ method were set to $t_{\text{SVD}} = 10^{-4}$ and $t_{\text{S}} = 10^{-6}$, respectively.

EXXRPA method of Ref. 2 and the RI-EXXRPA method of this work Fig. 8 shows that the latter is slightly more accurate. As discussed above, the reason might be that the RI-EXXRPA method in contrast to the EXXRPA method does not treat products of occupied times unoccupied orbitals as linearly independent although they are not. In any case differences between the two methods are very small demonstrating again that the RI approximation can be safely made. The inclusion of the extra terms of Eq. (33) in the treatment of the frequency-dependent exchange kernel in the RI-EXXRPA+ approach leads to further improvements of the total energies. The finding that the RI-EXXRPA+ total energies deviate less from the CCSD(T) reference values by almost a factor of two compared to the CCSD total energies is quite remarkable for a DFT method. The RI-dRPA total energies exhibit by far the largest deviations from the reference. This confirms earlier findings^{11,33} that DFT-based dRPA total energies as well as atomization energies are of poor quality.

In Fig. 7 individual deviations of total energies from the CCSD(T) reference values for the molecules considered in Fig. 8 are shown. Values for B3LYP and RI-dRPA are not shown in Fig. 7 because of their large deviations from the reference values. The EXXRPA variants in most cases underestimate the magnitude of the correlation energy like MP2 and CCSD. This is in marked difference to dRPA correlation energies (not shown) that strongly overestimate the magnitude of the correlation energy due to the missing exchange terms in the pure Coulomb kernel.

In Fig. 9 B3LYP, MP2, CCSD RI-dRPA, EXXRPA, RI-EXXRPA, and RI-EXXRPA+ reaction energies of the 16 reactions of Table I are compared to CCSD(T) reference values. The picture for reaction energies is different from that of total energies: Now CCSD yields the results closest to the reference values while the EXXRPA variants come in second. This means that CCSD benefits more from error cancellations than the EXXRPA methods when taking energy differences for

FIG. 8. Performance of EXXRPA methods compared to standard quantum chemistry methods: Root-mean-squared errors (RMS) of deviations of total energies from various methods (EXXRPA, RI-EXXRPA, RI-EXXRPA+, RI-dRPA, B3LYP, MP2, and CCSD) to CCSD(T) total energies. An aug-cc-pVQZ orbital basis and, for the RI-EXXRPA, RI-EXXRPA+, and RI-dRPA method, an aug-cc-pVQZ RI basis was employed. The thresholds t_{SVD} and t_{S} of the RI-EXXRPA, RI-EXXRPA+, and RI-dRPA method were set to $t_{\text{SVD}} = 10^{-4}$ and $t_{\text{S}} = 10^{-6}$, respectively.

calculating reaction energies. Both RI-EXXRPA approaches give slightly better results than the EXXRPA approach without the RI approximation, however, now the additional terms of Eq. (33) taken into account in the RI-EXXRPA+ approach do no longer lead to an improvement. The RI-dRPA method benefits strongly from error cancellation and yields reaction energies better than B3LYP and MP2 but inferior

FIG. 9. Performance of EXXRPA methods compared to standard quantum chemistry methods: Root-mean-squared errors (RMS) of deviations of 16 reaction energies (see Table I for considered reactions) from various methods (EXXRPA, RI-EXXRPA, RI-EXXRPA+, RI-dRPA, B3LYP, MP2, and CCSD) to the corresponding CCSD(T) reaction energies. An aug-cc-pVQZ orbital basis and, for the RI-EXXRPA, RI-EXXRPA+, and RI-dRPA method, an aug-cc-pVQZ RI basis was employed. The thresholds t_{SVD} and t_{S} of the RI-EXXRPA, RI-EXXRPA+, and RI-dRPA method were set to $t_{\text{SVD}} = 10^{-4}$ and $t_{\text{S}} = 10^{-6}$, respectively.

TABLE I. Considered reactions.

$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$
$\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$	$\text{CO} + \text{H}_2 \rightarrow \text{HCHO}$
$\text{H}_2\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$	$\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$
$\text{C}_2\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO}$	$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$
$\text{CH}_3\text{CHO} + \text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH}$	$\text{CO} + \text{NH}_3 \rightarrow \text{HCONH}_2$
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$\text{HNCO} + \text{NH}_3 \rightarrow \text{NH}_2\text{CONH}_2$
$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{HCOOCH}_3$	$\text{CO} + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
$\text{H}_2\text{CCO} + \text{HCHO} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{CO}$	$\text{HCOOH} + \text{NH}_2 \rightarrow \text{HCONH}_2 + \text{H}_2\text{O}$

to the EXXRPA variants. The finding that RI-dRPA reaction energies are quite accurate again is in line with earlier findings.^{33,35}

Figure 10 shows potential energy surfaces for the twisting of the CH_2 groups of ethene against each other around the carbon-carbon bond. At a twisting angle of 90° the wave function of ethene is of multireference character with two dominating Slater determinants, one, the Kohn-Sham ground state one, with the π -orbital doubly occupied and the π^* -orbital unoccupied, and the other one with the π -orbital unoccupied and the π^* -orbital doubly occupied. It is known from Ref. 2 that EXXRPA methods can treat static correlation, i.e., multireference cases, occurring in the dissociation of molecules. Here, with the twisting of ethene another example for the ability of EXXRPA methods to treat static correlation is given. Figure 10 shows that single reference methods such as the CCSD, the B3LYP, the Hartree-Fock (HF), or the exact-exchange only (EXX) KS method cannot treat correctly the multireference character of the ethene wave function for a twisting angle around 90° . This shows in the kink of the corresponding potential energy curves at a bending angle of 90° . The RI-EXX-RPA+ method as well as the MC-SCF method is able to correctly take into account the multireference character of ethene at a twisting angle of 90° . This is remarkable because the EXX calculation for the orbitals and eigenvalues entering the RI-EXXRPA+ method is a single reference method. Indeed, the EXX potential energy curve, see Fig. 10, does not reflect the multireference character of ethene at a twisting angle around 90° . This means static correlation is exclusively taken into account via the EXXRPA correlation energy. The mechanism how EXXRPA methods account for static correlation is explained in Ref. 2.

The interaction energies of non-covalently bonded molecules listed in Table II were computed with aug-cc-pVXZ ($X = 3, 4$) orbital basis sets and the corresponding RI basis. For a better comparison with the CBS reference values we extrapolated the correlation energy according to Ref. 79. The interaction energy was then computed with the extrapolated values of the correlation energy and the energy of the single determinant reference in the aug-cc-pVQZ basis. In order to account for the basis set superposition error, we used the Boys-Bernardi counterpoise correction.⁸⁰

In addition, we performed explicitly correlated F12-CCSD (Refs. 81–83) calculations in the aug-cc-pVTZ orbital basis set⁷⁴ for comparison. The F12a model was used in the calculations as this is known to yield results slightly overestimating the complete basis set limit results if large basis sets

FIG. 10. Potential energy curve of ethene for a twisting of the CH_2 -groups around the carbon-carbon bond for different methods. An aug-cc-pVQZ orbital basis and, for the RI-EXXRPA+ method, an aug-cc-pVQZ RI basis was employed. The thresholds t_{SVD} and t_{S} of the RI-EXXRPA+ method were set to $t_{\text{SVD}} = 10^{-4}$ and $t_{\text{S}} = 10^{-6}$, respectively.

are used so that an error compensation occurs if the small aug-cc-pVTZ basis set is used. The complementary auxiliary basis set singles correction was included in the reference energy as proposed in Refs. 81 and 82. We also compare our values to the RI-dRPA method of Ref. 23 (denoted here as TPSS-RI-dRPA), which was also tested on the S22 database using orbitals generated with the TPSS functional⁴¹ as input for the RPA calculation.³⁵

In Table II RI-EXXRPA+, RI-EXXRPA, RI-dRPA, MP2, F12-CCSD, and TPSS-RI-dRPA interaction energies are compared to the CCSD(T) reference from Ref. 72. As recent results already showed for the dRPA case,^{32,35,36} RPA-methods yield quite accurate interaction energies for non-covalent and weakly bonded dimers. This is confirmed here. The RI-EXXRPA+ approach yields results clearly superior to those from dRPA or CCSD methods and of the same accuracy as MP2, which is known to yield accurate interaction energies for hydrogen bonded systems. In contrast to the reaction energies, where the inclusion of the additional terms to the exchange kernel of Eq. (33) in the EXXRPA+ approach had only negligible effect, they improve the interaction energies significantly. Besides this, the influence of the input orbitals in dRPA calculations can be seen by comparing the RI-dRPA values of this work based on EXX orbitals and eigenvalues with the TPSS-RI-dRPA results of Ref. 35 based on orbitals and eigenvalues obtained with the TPSS exchange-correlation functional.⁴¹

TABLE II. Interaction energies in kcal/mol of seven non-covalently bonded systems of the S22 set taken from Ref. 71 with extrapolated complete basis set (CBS) CCSD(T) reference values from Ref. 72. RI-EXXRPA, RI-EXXRPA+, and RI-dRPA calculations were carried out with EXX orbitals and eigenvalues obtained with aug-cc-pVXZ ($X = 3, 4$) orbital basis sets. In the RPA calculations corresponding aug-cc-pVXZ ($X = 3, 4$) RI basis sets were employed as auxiliary basis sets. The F12-CCSD and MP2 calculations were performed starting from HF orbitals and with aug-cc-pVTZ orbital and RI basis sets in case of F12-CCSD and aug-cc-pVXZ ($X = 3, 4$) orbital basis sets for MP2. The acronym TPSS-RI-dRPA denotes dRPA results from the supporting information of Ref. 35, which were obtained with orbitals and eigenvalues calculated with the TPSS exchange-correlation functional (Ref. 41).

Complex	Basis	Reference	MP2	F12-CCSD	TPSS-RI-dRPA (Ref. 35)	RI-dRPA	RI-EXXRPA	RI-EXXRPA+
(NH ₃) ₂	3		3.00			2.33	2.54	2.76
	4		3.11			2.46	2.61	2.83
	CBS	3.15	3.18	2.88	2.74	2.58	2.70	2.92
(H ₂ O) ₂	3		4.72			3.73	4.29	4.55
	4		5.02			4.24	4.60	4.86
	CBS	5.07	5.21	4.74	4.52	4.59	4.81	5.06
(HCONH ₂) ₂	3		15.08			13.43	14.87	15.27
	4		15.57			14.23	15.42	15.84
	CBS	16.11	15.86	15.28	15.42	15.28	15.77	16.21
(HCOOH) ₂	3		17.61			15.25	17.40	17.90
	4		18.23			16.24	18.06	18.46
	CBS	18.81	18.61	17.92	17.91	16.91	18.50	18.81
(C ₂ H ₄) ₂	3		1.47			0.93	1.04	1.14
	4		1.55			1.04	1.13	1.24
	CBS	1.48	1.60	1.14	1.20	1.13	1.19	1.33
C ₂ H ₄ ...C ₂ H ₂	3		1.59			1.21	1.34	1.45
	4		1.64			1.26	1.37	1.46
	CBS	1.50	1.67	1.31	1.27	1.31	1.41	1.49
(CH ₄) ₂	3		0.46			0.29	0.30	0.37
	4		0.48			0.33	0.34	0.36
	CBS	0.53	0.49	0.41	0.40	0.35	0.36	0.34
RMS	3		0.61			1.80	0.83	0.55
RMS	4		0.31			1.29	0.50	0.25
RMS	CBS		0.15	0.51	0.52	0.94	0.29	0.13

V. SUMMARY

The resolution-of-identity exact-exchange RPA methods, RI-EXXRPA and RI-EXXRPA+, presented in this work were shown to be potential alternatives to standard wave function methods such as MP2 or CCSD. The formal computational scaling of the EXXRPA methods with the system size is that of the MP2 method, the accuracy, however, is superior and resembles that of the CCSD approach which exhibits a steeper scaling of the computational effort with the system size. In contrast to the MP2 method and conventional DFT methods the presented EXXRPA methods can treat static correlation, i.e., bond breaking, and thus seem to be more widely applicable.

So far there is only limited experience with the new methods and more tests and applications are required for a final assessment of their capabilities. However, even on the basis of the results presented here, it seems justified to state that EXXRPA methods seem to be able to compete with high-level standard quantum chemistry methods, such as CCSD, which is quite remarkable for a DFT method. This to some extent opens up a new playground for DFT methods. While conventional DFT methods are computationally cheap methods with limited accuracy and range of applicability, the methods presented here provide quite high accuracy and broad applicability, albeit at the prize of higher computational cost.

This means the potential field of application of the presented EXXRPA methods is that of MP2 and CCSD and not that of conventional DFT methods.

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