Range-separated density-functional theory with the random-phase approximation: Detailed formalism and illustrative applications

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Using Green's-function many-body theory, we present the details of a formally exact adiabatic-connection fluctuation-dissipation density-functional theory based on range separation, which was sketched in Toulouse *et al.* [Phys. Rev. Lett. **102**, 096404 (2009)]. Range-separated density-functional theory approaches combining short-range density-functional approximations with long-range random-phase approximations (RPAs) are then obtained as well-identified approximations on the long-range Green's-function self-energy. Range-separated RPA-type schemes with or without long-range Hartree-Fock exchange response kernel are assessed on rare-gas and alkaline-earth-metal dimers and compared to range-separated second-order perturbation theory and range-separated coupled-cluster theory.

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I. INTRODUCTION

Range-separated density-functional theory has emerged as a powerful approach for improving the accuracy of standard Kohn-Sham (KS) density-functional theory [1,2] applied with usual local or semilocal density-functional approximations, in particular for electronic systems with strong (static) or weak (van der Waals) correlation effects. Based on a separation of the electron-electron interaction into long-range and short-range components, it permits a rigorous combination of a long-range explicit many-body approximation with a short-range density-functional approximation (see, e.g., Ref. [3] and references therein). Several many-body approximations have been considered for the long-range part: configuration interaction [4,5], multiconfiguration self-consistent-field theory [6–8], second-order perturbation theory [9–13], coupled-cluster theory [14–18], multireference second-order perturbation theory [19], and several variants of the random-phase approximation (RPA) [20–24].

In the context of the recent revived interest in RPA-type approaches to the electron correlation problem in atomic, molecular, and solid-state systems [25–48], several range-separated approaches using long-range RPA-type approximations have indeed been proposed and show promising results, in particular for describing weak intermolecular interactions. Toulouse *et al.* [20] have presented a range-separated RPA-type theory including the long-range Hartree-Fock exchange response kernel. Janesko *et al.* [21–23] have proposed a simpler range-separated RPA scheme with no exchange kernel and in which the RPA correlation energy has been rescaled by an empirical coefficient. Paier *et al.* [24] have added the so-called second-order screened exchange to the latter scheme, which appears to correct the self-interaction error. In all these cases, range separation tends to improve the corresponding full-range RPA-type approach, avoiding the inaccurate description and slow basis-set convergence of short-range correlations in RPA.

In Ref. [20], only the main lines of range-separated density-functional theory with long-range RPA were presented. In this work, we give now all the missing details of the theory. Using Green's-function many-body theory, we construct a formally exact adiabatic-connection fluctuation-dissipation density-functional theory based on range separation, without the need to maintain the one-particle density constant. Range-separated RPA-type schemes are then obtained as well-identified approximations on the long-range Green's-function self-energy. The range-separated RPA-type methods, with or without long-range Hartree-Fock exchange response kernel, are assessed on rare-gas and alkaline-earth-metal dimers and compared to range-separated second-order perturbation theory and range-separated coupled-cluster theory. The most tedious details of the theory are given in the appendixes.

II. THEORY

A. Range-separated density-functional theory

In range-separated density-functional theory (see, e.g., Ref. [3]), the exact ground-state energy of an N-electron system is expressed as the following minimization over multideterminant wave functions Ψ:

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n_{\Psi}] \right\}, \tag{1}$$

where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{ne}$ is the nuclei-electron interaction operator, $\hat{W}_{ee}^{\text{lr}} = (1/2)\iint d\mathbf{r}_1 d\mathbf{r}_2 w_{ee}^{\text{lr}}(r_{12})\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)$ is a long-range (lr) electron-electron interaction written with $w_{ee}^{\text{lr}}(r) = \text{erf}(\mu r)/r$ and the pair-density operator $\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)$, and $E_{\text{Hxc}}^{\text{sr}}[n]$ is the corresponding μ-dependent short-range (sr) Hartree-exchange-correlation (Hxc) density functional that Eq. (1) defines. The parameter μ in the error function controls the range of the separation. The minimizing wave function, denoted by Ψ^{lr}, yields the exact density. Several approximations [3,7,14,18,49–51] have been proposed for

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the short-range exchange correlation (xc) functional $E_{xc}^{sr}[n]$, and an approximate scheme must be used for the long-range wave-function part of the calculation.

In a first step, the minimization in Eq. (1) is restricted to single-determinant wave functions Φ, leading to the range-separated hybrid (RSH) approximation [9],

$$E_{\mathrm{RSH}} = \min_{\Phi} \{ \langle \Phi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\mathrm{lr}} | \Phi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_{\Phi}] \}, \quad (2)$$

which does not include long-range correlation. The minimizing determinant Φ_0 is given by the self-consistent Euler-Lagrange equation,

$$\hat{H}_0 |\Phi_0\rangle = \mathcal{E}_0 |\Phi_0\rangle, \quad (3)$$

where $\mathcal{E}_0$ is the Lagrange multiplier for the normalization constraint and $\hat{H}_0$ is the RSH reference Hamiltonian,

$$\hat{H}_0 = \hat{T} + \hat{V}_{ne} + \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0] + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr}}[n_{\Phi_0}], \quad (4)$$

which includes the Hartree-Fock (HF)-type long-range Hartree-exchange (Hx) potential $\hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0]$ and the short-range local Hxc potential $\hat{V}_{\mathrm{Hxc}}^{\mathrm{sr}}[n] = \int d\mathbf{r} v_{\mathrm{Hxc}}^{\mathrm{sr}}[n](\mathbf{r}) \hat{n}(\mathbf{r})$, written with $v_{\mathrm{Hxc}}^{\mathrm{sr}}[n](\mathbf{r}) = \delta E_{\mathrm{Hxc}}^{\mathrm{sr}}[n]/\delta n(\mathbf{r})$ and the density operator $\hat{n}(\mathbf{r})$. As usual, $\hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}$ is the sum of a local Hartree part $\hat{V}_{\mathrm{H}}^{\mathrm{lr}} = \int d\mathbf{r}_1 v_{\mathrm{H}}^{\mathrm{lr}}(\mathbf{r}_1) \hat{n}(\mathbf{r}_1)$ with $v_{\mathrm{H}}^{\mathrm{lr}}(\mathbf{r}_1) = \int d\mathbf{r}_2 w_{ee}^{\mathrm{lr}}(r_{12}) \langle \Phi_0 | \hat{n}(\mathbf{r}_2) | \Phi_0 \rangle$ and a nonlocal exchange part $\hat{V}_{x,\mathrm{HF}}^{\mathrm{lr}} = \iint d\mathbf{x}_1 d\mathbf{x}_2 v_x^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_2) \hat{n}_1(\mathbf{x}_2,\mathbf{x}_1)$ written with $v_x^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_2) = -w_{ee}^{\mathrm{lr}}(r_{12}) \langle \Phi_0 | \hat{n}_1(\mathbf{x}_1,\mathbf{x}_2) | \Phi_0 \rangle$ and the one-particle density-matrix operator $\hat{n}_1(\mathbf{x}_1,\mathbf{x}_2)$ expressed with space-spin coordinates $\mathbf{x}_1 = (\mathbf{r}_1,s_1)$ and $\mathbf{x}_2 = (\mathbf{r}_2,s_2)$.

The RSH scheme does not yield the exact energy and density, even with the exact short-range functional $E_{\mathrm{Hxc}}^{\mathrm{sr}}[n]$. Nevertheless, the RSH approximation can be used as a reference to express the exact energy as

$$E = E_{\mathrm{RSH}} + E_c^{\mathrm{lr}}, \quad (5)$$

defining the long-range correlation energy E_c^{lr}, for which we now give an adiabatic connection formula. We introduce the following energy expression with a formal coupling constant λ:

$$E_\lambda = \min_{\Psi} \{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0] + \lambda \hat{W}^{\mathrm{lr}} | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_\Psi] \}, \quad (6)$$

where the minimization is done over multideterminant wave functions Ψ, $\hat{W}^{\mathrm{lr}}$ is the long-range Møller-Plesset-type fluctuation perturbation operator

$$\hat{W}^{\mathrm{lr}} = \hat{W}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0], \quad (7)$$

and $E_{\mathrm{Hxc}}^{\mathrm{sr}}$ is the previously defined λ-independent short-range Hxc functional. The minimizing wave function, denoted by $\Psi_\lambda^{\mathrm{lr}}$, is given by the self-consistent Euler-Lagrange equation

$$\hat{H}_\lambda^{\mathrm{lr}} |\Psi_\lambda^{\mathrm{lr}}\rangle = \mathcal{E}_\lambda^{\mathrm{lr}} |\Psi_\lambda^{\mathrm{lr}}\rangle, \quad (8)$$

where $\mathcal{E}_\lambda^{\mathrm{lr}}$ is the Lagrange multiplier for the normalization constraint and $\hat{H}_\lambda^{\mathrm{lr}}$ is the long-range interacting effective Hamiltonian along the adiabatic connection

$$\begin{aligned} \hat{H}_\lambda^{\mathrm{lr}} &= \hat{T} + \hat{V}_{ne} + \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0] + \hat{V}_{\mathrm{Hx}c}^{\mathrm{sr}}[n_{\Psi_\lambda^{\mathrm{lr}}}] + \lambda \hat{W}^{\mathrm{lr}} \\ &= \hat{H}_0 + \lambda \hat{W}^{\mathrm{lr}} + \left(\hat{V}_{\mathrm{Hx}c}^{\mathrm{sr}}[n_{\Psi_\lambda^{\mathrm{lr}}}] - \hat{V}_{\mathrm{Hx}c}^{\mathrm{sr}}[n_{\Phi_0}] \right). \end{aligned} \quad (9)$$

For $\lambda = 1$, Eq. (6) reduces to Eq. (1), and so the physical energy $E = E_{\lambda=1}$ and density are recovered. For $\lambda = 0$, the minimizing wave function is the RSH determinant $\Psi_{\lambda=0}^{\mathrm{lr}} = \Phi_0$ and the Hamiltonian of Eq. (9) reduces to the RSH reference Hamiltonian, $\hat{H}_{\lambda=0}^{\mathrm{lr}} = \hat{H}_0$. Note that, because the density at $\lambda = 0$ is not exact, the density necessarily varies along this adiabatic connection. Taking the derivative of E_λ with respect to λ, noting that E_λ is stationary with respect to $\Psi_\lambda^{\mathrm{lr}}$, and reintegrating between $\lambda = 0$ and $\lambda = 1$ gives

$$E = E_{\lambda=0} + \int_0^1 d\lambda \, \langle \Psi_\lambda^{\mathrm{lr}} | \hat{W}^{\mathrm{lr}} | \Psi_\lambda^{\mathrm{lr}} \rangle, \quad (10)$$

with $E_{\lambda=0} = \langle \Phi_0 | \hat{T} + \hat{V}_{ne} + \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0] | \Phi_0 \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_{\Phi_0}] = E_{\mathrm{RSH}} - \langle \Phi_0 | \hat{W}^{\mathrm{lr}} | \Phi_0 \rangle$. Thus, the long-range correlation energy is

$$E_c^{\mathrm{lr}} = \int_0^1 d\lambda \left[\langle \Psi_\lambda^{\mathrm{lr}} | \hat{W}^{\mathrm{lr}} | \Psi_\lambda^{\mathrm{lr}} \rangle - \langle \Phi_0 | \hat{W}^{\mathrm{lr}} | \Phi_0 \rangle \right], \quad (11)$$

or, equivalently,

$$\begin{aligned} E_c^{\mathrm{lr}} = \frac{1}{2} \int_0^1 d\lambda \int & d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' w^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') \\ & \times P_{c,\lambda}^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2'), \end{aligned} \quad (12)$$

where $w^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = w_{ee}^{\mathrm{lr}}(r_{12}) \delta(\mathbf{x}_1 - \mathbf{x}_1') \delta(\mathbf{x}_2 - \mathbf{x}_2') - 1/(N-1)[v_{\mathrm{H}}^{\mathrm{lr}}(\mathbf{r}_1) \delta(\mathbf{x}_1 - \mathbf{x}_1') + v_{\mathrm{x}}^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_1')] \delta(\mathbf{x}_2 - \mathbf{x}_2')$ is the potential corresponding to the perturbation operator $\hat{W}^{\mathrm{lr}}$ and $P_{c,\lambda}^{\mathrm{lr}}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')$ is the correlation part of the two-particle density matrix along the adiabatic connection.

B. Long-range many-body perturbation theory

We now derive a formally exact many-body perturbation theory to calculate the long-range correlation two-particle density matrix $P_{c,\lambda}^{\mathrm{lr}}$. Details are given in Appendix A.

The one-particle Green's function $G_\lambda^{\mathrm{lr}}(1,2)$ along the adiabatic connection of Eq. (9) in terms of space-spin-time coordinates $1 = (\mathbf{x}_1,t_1)$ and $2 = (\mathbf{x}_2,t_2)$ satisfies the following Dyson equation:

$$\left(G_\lambda^{\mathrm{lr}} \right)^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma_\lambda^{\mathrm{lr}}(1,2) - \Delta\Sigma_\lambda^{\mathrm{sr}}(1,2), \quad (13)$$

where $G_0(1,2)$ is the reference Green's function corresponding to the RSH Hamiltonian $\hat{H}_0$, $\Sigma_\lambda^{\mathrm{lr}}(1,2)$ is the self-energy corresponding to the long-range perturbation operator $\lambda \hat{W}^{\mathrm{lr}}$, and $\Delta\Sigma_\lambda^{\mathrm{sr}}(1,2)$ is the self-energy correction associated with the short-range potential variation term $\hat{V}_{\mathrm{Hx}c}^{\mathrm{sr}}[n_{\Psi_\lambda^{\mathrm{lr}}}] - \hat{V}_{\mathrm{Hx}c}^{\mathrm{sr}}[n_{\Phi_0}]$ due to the variation of the density [52]. The long-range self-energy corresponding to the perturbation operator $\lambda(\hat{W}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\Phi_0])$ is decomposed into Hartree, exchange, and correlation contributions as

$$\begin{aligned}\Sigma^{\rm lr}_\lambda(1,2) &= \Sigma^{\rm lr}_{{\rm Hx}c,\lambda}\big[G^{\rm lr}_\lambda\big](1,2) - \Sigma^{\rm lr}_{{\rm Hx},\lambda}[G_0](1,2)\\ &= \lambda\big\{\Sigma^{\rm lr}_{\rm Hx}\big[G^{\rm lr}_\lambda\big](1,2) - \Sigma^{\rm lr}_{\rm Hx}[G_0](1,2)\big\}\\ &\quad + \Sigma^{\rm lr}_{c,\lambda}\big[G^{\rm lr}_\lambda\big](1,2),\end{aligned} \tag{14}$$

where $\Sigma^{\rm lr}_{\rm Hx}[G](1,2)$ is the sum of a long-range Hartree self-energy,

$$\begin{aligned}\Sigma^{\rm lr}_{\rm H}[G](1,2) &= -i\int d3\, d4\, w^{\rm lr}_{ee}(1,3)\delta(1,2)\delta(3,4)G(4,3^+)\\ &= -i\delta(1,2)\int d3\, w^{\rm lr}_{ee}(1,3)G(3,3^+)\\ &= \delta(1,2)\int d\mathbf{r}_3\, w^{\rm lr}_{ee}(r_{13})n(\mathbf{r}_3)\\ &= \delta(1,2)v^{\rm lr}_{\rm H}[n](\mathbf{r}_1),\end{aligned} \tag{15}$$

with the instantaneous electron-electron interaction $w^{\rm lr}_{ee}(1,3) = \delta(t_1 - t_3)w^{\rm lr}_{ee}(r_{13})$ and the density extracted from the Green's function $n(\mathbf{r}_3) = -i\sum_{s_3} G(3,3^+)$ (where 3^+ stands for $\mathbf{x}_3t_3^+$ with $t_3^+ = t_3 + \eta$ and η is an infinitesimal positive shift), and a long-range exchange self-energy,

$$\begin{aligned}\Sigma^{\rm lr}_{\rm x}[G](1,2) &= i\int d3\, d4\, w^{\rm lr}_{ee}(1,3)\delta(1,4)\delta(2,3)G(4,3^+)\\ &= i\, w^{\rm lr}_{ee}(1,2)G(1,2^+)\\ &= -\delta(t_1 - t_2)w^{\rm lr}_{ee}(r_{12})n_1(\mathbf{x}_1,\mathbf{x}_2)\\ &= \delta(t_1 - t_2)v^{\rm lr}_{\rm x}[n_1](\mathbf{x}_1,\mathbf{x}_2),\end{aligned} \tag{16}$$

with the one-particle density matrix extracted from the Green's function $n_1(\mathbf{x}_1,\mathbf{x}_2) = -iG(\mathbf{x}_1t_1,\mathbf{x}_2t_1^+)$. The short-range self-energy correction corresponding to the operator $\hat{V}^{\rm sr}_{\rm Hxc}[n_{\Psi^{\rm lr}_\lambda}] - \hat{V}^{\rm sr}_{\rm Hxc}[n_{\Phi_0}]$ is written as

$$\Delta\Sigma^{\rm sr}_\lambda(1,2) = \Sigma^{\rm sr}_{\rm Hxc}\big[G^{\rm lr}_\lambda\big](1,2) - \Sigma^{\rm sr}_{\rm Hxc}[G_0](1,2), \tag{17}$$

where $\Sigma^{\rm sr}_{\rm Hxc}[G](1,2) = \delta(1,2)v^{\rm sr}_{\rm Hxc}[n](\mathbf{r}_1)$ is the local short-range Hxc self-energy.

The long-range four-point polarization propagator $\chi^{\rm lr}_\lambda(1,2;1',2')$ along the adiabatic connection is given by the solution of the following Bethe-Salpeter-type equation, which can be derived from the Dyson equation (13) by considering variations with respect to $G^{\rm lr}_\lambda$ [see Appendix A, Eq. (A13)],

$$\begin{aligned}\big(\chi^{\rm lr}_\lambda\big)^{-1}(1,2;1',2') &= \big(\chi^{\rm lr}_{{\rm IP},\lambda}\big)^{-1}(1,2;1',2') - \lambda f^{\rm lr}_{\rm Hx}(1,2;1',2')\\ &\quad - f^{\rm lr}_{c,\lambda}(1,2;1',2'),\end{aligned} \tag{18}$$

where $\chi^{\rm lr}_{{\rm IP},\lambda}(1,2;1',2') = -iG^{\rm lr}_\lambda(1,2')G^{\rm lr}_\lambda(2,1')$ is an independent-particle (IP) polarization propagator and $\lambda f^{\rm lr}_{\rm Hx}(1,2;1',2') = i\lambda\,\delta\Sigma^{\rm lr}_{\rm Hx}[G^{\rm lr}_\lambda](1,1')/\delta G^{\rm lr}_\lambda(2',2)$ and $f^{\rm lr}_{c,\lambda}(1,2;1',2') = i\,\delta\Sigma^{\rm lr}_{c,\lambda}[G^{\rm lr}_\lambda](1,1')/\delta G^{\rm lr}_\lambda(2',2)$ are long-range Hartree-exchange and correlation kernels. Note that these kernels only stem from the self-energy term $\Sigma^{\rm lr}_{{\rm Hx}c,\lambda}[G^{\rm lr}_\lambda]$ in Eq. (13) that corresponds to the two-electron interaction $\lambda\hat{W}^{\rm lr}_{ee}$; the other self-energy contributions which come from the one-electron terms are absorbed in the definition of $\chi^{\rm lr}_\lambda(1,2;1',2')$. The Hartree kernel is obtained from Eq. (15),

$$\begin{aligned}f^{\rm lr}_{\rm H}(1,2;1',2') &= w^{\rm lr}_{ee}(1,2)\delta(1,1')\delta(2,2')\\ &= w^{\rm lr}_{ee}(r_{12})\delta(t_1 - t_2)\delta(1,1')\delta(2,2'),\end{aligned} \tag{19}$$

while the HF-like exchange kernel is obtained from Eq. (16):

$$\begin{aligned}f^{\rm lr}_{\rm x}(1,2;1',2') &= -w^{\rm lr}_{ee}(1,2)\delta(1,2')\delta(1',2)\\ &= -w^{\rm lr}_{ee}(r_{12})\delta(t_1 - t_2)\delta(1,2')\delta(1',2).\end{aligned} \tag{20}$$

The fluctuation-dissipation theorem is then used to express $P^{\rm lr}_{c,\lambda}$ as [see Appendix A, Eq. (A24)]

$$\begin{aligned}&P^{\rm lr}_{c,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)\\ &\quad = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}e^{i\omega 0^+}\big[\chi^{\rm lr}_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2;\omega)\\ &\qquad - \chi_0(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2;\omega)\big] + \Delta^{\rm lr}_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2),\end{aligned} \tag{21}$$

where $\chi^{\rm lr}_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2;\omega)$ is the frequency-dependent Fourier transform of the one-time-interval polarization propagator $\chi^{\rm lr}_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2;\tau = t_1 - t_2) = \chi^{\rm lr}_\lambda(\mathbf{x}_1t_1,\mathbf{x}_2t_2;\mathbf{x}'_1t_1^+,\mathbf{x}'_2t_2^+)$, $\chi_0(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2;\omega)$ is the equivalent quantity for the RSH reference Hamiltonian (at $\lambda = 0$), and $\Delta^{\rm lr}_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)$ is the contribution coming from the variation of the one-particle density matrix along the adiabatic connection. The expression of $\Delta^{\rm lr}_\lambda$ in terms of the Green's functions $G^{\rm lr}_\lambda$ and G_0 is straightforward but it is sufficient to write it as $\Delta^{\rm lr}_\lambda = \Gamma[G^{\rm lr}_\lambda] - \Gamma[G_0]$, where Γ is a known functional given in Appendix A [Eq. (A22)].

So far, the theory is, in principle, *exact*. In the following we consider two possible approximations. The RPA approximation,

$$\Sigma^{\rm lr}_{{\rm xc},\lambda} = 0, \tag{22}$$

corresponds to neglecting long-range exchange and correlation in all one-electron properties. Indeed, with this approximation, one can check that $G^{\rm lr}_\lambda = G_0$ is a solution of the Dyson equation (13); that is, the Green's function remains unchanged along the adiabatic connection. It follows that $\Delta^{\rm lr}_\lambda = 0$, $f^{\rm lr}_{{\rm xc},\lambda} = 0$ and $\chi^{\rm lr}_{{\rm IP},\lambda}(1,2;1',2') = -iG_0(1,2')G_0(2,1') = \chi_0(1,2;1',2')$. Similarly, the RPAx approximation,

$$\Sigma^{\rm lr}_{c,\lambda} = 0, \tag{23}$$

corresponds to neglecting long-range correlation only in all one-electron properties. Again, this approximation implies that the Green's function remains unchanged along the adiabatic connection; that is, $G^{\rm lr}_\lambda = G_0$ and it follows that $\Delta^{\rm lr}_\lambda = 0$, $f^{\rm lr}_{c,\lambda} = 0$ and $\chi^{\rm lr}_{{\rm IP},\lambda} = \chi_0$. As different terminologies are used in the quantum chemistry and condensed-matter physics literature, let us stress that what we call RPA here corresponds to a response Eq. (18) with no exchange-correlation kernel (and it is also sometimes called linear-response time-dependent Hartree theory or *direct* RPA), and what we call RPAx corresponds to a response equation with an additional HF-like exchange kernel (and it is also sometimes called linear-response time-dependent Hartree-Fock theory or *full* RPA).

C. Expressions in an orbital basis

The RPA or RPAx equations in an orbital basis are derived in detail in Appendix B. In the basis of RSH spin orbitals, the long-range RPA or RPAx correlation energy is written

$$E_c^{\mathrm{lr}} = \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb} \langle ib|\hat{w}_{ee}^{\mathrm{lr}}|aj\rangle \left(\mathbf{P}_{c,\lambda}^{\mathrm{lr}}\right)_{ia,jb}, \qquad (24)$$

where i and j refer to occupied spin orbitals and a and b to virtual spin orbitals, $\langle ib|\hat{w}_{ee}^{\mathrm{lr}}|aj\rangle$ are the two-electron integrals with long-range interaction, and $(\mathbf{P}_{c,\lambda}^{\mathrm{lr}})_{ia,jb}$ are the matrix elements of the correlation two-particle density matrix. The one-electron terms $v_{\mathrm{H}}^{\mathrm{lr}}$ and $v_{\mathrm{x}}^{\mathrm{lr}}$ in the perturbation operator in Eq. (12) do not contribute to E_c^{lr} because of the occupied-virtual-occupied-virtual structure of the two-particle density matrix in RPA or RPAx. Following the technique proposed by Furche [26], $\mathbf{P}_{c,\lambda}^{\mathrm{lr}}$ can be obtained as

$$\mathbf{P}_{c,\lambda}^{\mathrm{lr}} = \left(\mathbf{A}_\lambda^{\mathrm{lr}} - \mathbf{B}_\lambda^{\mathrm{lr}}\right)^{1/2}\left(\mathbf{M}_\lambda^{\mathrm{lr}}\right)^{-1/2}\left(\mathbf{A}_\lambda^{\mathrm{lr}} - \mathbf{B}_\lambda^{\mathrm{lr}}\right)^{1/2} - \mathbf{1}, \qquad (25)$$

with $\mathbf{M}_\lambda^{\mathrm{lr}} = (\mathbf{A}_\lambda^{\mathrm{lr}} - \mathbf{B}_\lambda^{\mathrm{lr}})^{1/2}(\mathbf{A}_\lambda^{\mathrm{lr}} + \mathbf{B}_\lambda^{\mathrm{lr}})(\mathbf{A}_\lambda^{\mathrm{lr}} - \mathbf{B}_\lambda^{\mathrm{lr}})^{1/2}$, and the orbital rotation Hessians

$$\left(\mathbf{A}_\lambda^{\mathrm{lr}}\right)_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \lambda\left[\langle ib|\hat{w}_{ee}^{\mathrm{lr}}|aj\rangle - \xi\langle ib|\hat{w}_{ee}^{\mathrm{lr}}|ja\rangle\right], \qquad (26a)$$

$$\left(\mathbf{B}_\lambda^{\mathrm{lr}}\right)_{ia,jb} = \lambda\left[\langle ab|\hat{w}_{ee}^{\mathrm{lr}}|ij\rangle - \xi\langle ab|\hat{w}_{ee}^{\mathrm{lr}}|ji\rangle\right], \qquad (26b)$$

where ϵ_i are the RSH orbital eigenvalues and $\xi = 0$ or $\xi = 1$ for RPA or RPAx, respectively. For spin-restricted closed-shell calculations, the correlation energy is written, in terms of spatial orbitals,

$$E_c^{\mathrm{lr}} = \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb} \langle ib|\hat{w}_{ee}^{\mathrm{lr}}|aj\rangle \left({}^1\mathbf{P}_{c,\lambda}^{\mathrm{lr}}\right)_{ia,jb}, \qquad (27)$$

where i and j now refer to occupied spatial orbitals, a and b refer to virtual spatial orbitals, and ${}^1\mathbf{P}_{c,\lambda}^{\mathrm{lr}}$ is the spin-singlet-adapted correlation two-particle density matrix obtained as

$${}^1\mathbf{P}_{c,\lambda}^{\mathrm{lr}} = 2\left[\left({}^1\mathbf{A}_\lambda^{\mathrm{lr}} - {}^1\mathbf{B}_\lambda^{\mathrm{lr}}\right)^{1/2}\left({}^1\mathbf{M}_\lambda^{\mathrm{lr}}\right)^{-1/2}\left({}^1\mathbf{A}_\lambda^{\mathrm{lr}} - {}^1\mathbf{B}_\lambda^{\mathrm{lr}}\right)^{1/2} - \mathbf{1}\right], \qquad (28)$$

with ${}^1\mathbf{M}_\lambda^{\mathrm{lr}} = ({}^1\mathbf{A}_\lambda^{\mathrm{lr}} - {}^1\mathbf{B}_\lambda^{\mathrm{lr}})^{1/2}({}^1\mathbf{A}_\lambda^{\mathrm{lr}} + {}^1\mathbf{B}_\lambda^{\mathrm{lr}})({}^1\mathbf{A}_\lambda^{\mathrm{lr}} - {}^1\mathbf{B}_\lambda^{\mathrm{lr}})^{1/2}$, and the singlet orbital rotation Hessians

$$\left({}^1\mathbf{A}_\lambda^{\mathrm{lr}}\right)_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \lambda\left[2\langle ib|\hat{w}_{ee}^{\mathrm{lr}}|aj\rangle - \xi\langle ib|\hat{w}_{ee}^{\mathrm{lr}}|ja\rangle\right], \qquad (29a)$$

$$\left({}^1\mathbf{B}_\lambda^{\mathrm{lr}}\right)_{ia,jb} = \lambda\left[2\langle ab|\hat{w}_{ee}^{\mathrm{lr}}|ij\rangle - \xi\langle ab|\hat{w}_{ee}^{\mathrm{lr}}|ji\rangle\right]. \qquad (29b)$$

Only singlet excitations contribute to Eq. (27), since the two-electron integrals involved vanish for triplet excitations.

In Eq. (25), it is assumed that $\mathbf{A}_\lambda^{\mathrm{lr}} + \mathbf{B}_\lambda^{\mathrm{lr}}$ and $\mathbf{A}_\lambda^{\mathrm{lr}} - \mathbf{B}_\lambda^{\mathrm{lr}}$ are positive definite. In RPA, this is always the case. On the contrary, in RPAx, this is not always the case; that is, instabilities can be encountered, and Eq. (25) can fail. In spin-restricted closed-shell formalism, one may encounter singlet instabilities in the RPAx theory defined here, for example, when dissociating a bond, but not triplet instabilities since triplet excitations do not contribute at all. In practice, singlet instabilities are usually not encountered for weakly interacting closed-shell systems. Note that other variants of RPA-type correlation energy expressions using a HF exchange response kernel, such as the plasmon formula [38,53,54] or the equivalent ring coupled-cluster-doubles theory [38], require contributions from both singlet and triplet excitations and are thus subject to triplet instabilities (e.g., in a system such as $\mathrm{Be_2}$).

Similarly to the notation used in Ref. [20], the range-separated method obtained by adding to the RSH energy the long-range RPAx correlation energy [$\xi = 1$ in Eqs. (26) or (29)] is referred to as RSH + lrRPAx. For consistency, the range-separated method obtained by adding to the RSH energy the long-range RPA correlation energy [$\xi = 0$ in Eqs. (26) or (29)] is referred to as RSH + lrRPA, although it is equivalent to the method called "LC-ωLDA + dRPA" in Refs. [21–24] in the special case of the short-range LDA functional. At second order in the electron-electron interaction, the RSH + lrRPAx method reduces to the range-separated method of Ref. [9] based on long-range second-order Møller-Plesset perturbation theory, to which we refer as RSH + lrMP2. Since RPA approaches can be seen as simple approximations to coupled-cluster theory [38], the RSH + lrRPA and RSH + lrRPAx methods bear some resemblance to the range-separated method of Ref. [14], where the long-range correlation energy is evaluated by coupled-cluster theory (with single, double, and perturbative triple excitations), to which we refer as RSH + lrCCSD(T).

We note that one can develop long-range many-body perturbation theories starting from references other than the RSH reference. For example, starting from the usual (approximate) KS reference could be appropriate for solid-state systems. For the finite systems considered here, RSH is a good reference, as confirmed by other authors [23].

III. COMPUTATIONAL DETAILS

All calculations have been performed with a development version of MOLPRO 2008 [55], implementing Eqs. (27)–(29). We first perform a self-consistent RSH calculation with the short-range PBE xc functional of Ref. [14] (this RSH calculation could also be referred to as "lrHF + srPBE," a notation closer to the one used by other authors [14]) and add the long-range MP2, RPA, RPAx, or CCSD(T) correlation energy calculated with RSH orbitals. For RPA or RPAx, the λ integration in Eq. (27) is done by a seven-point Gauss-Legendre quadrature [26]. The range separation parameter is taken at $\mu = 0.5$ bohr^{-1}, in agreement with previous studies [56], without trying to adjust it for each system. To show the dependence on the orbitals, the full-range RPA calculations have been done with PBE [57] and HF orbitals, which are denoted as PBE + RPA and HF + RPA, respectively [58]. The full-range MP2, RPAx, and CCSD(T) calculations have been done with HF orbitals, and thus, for notation consistency, are denoted as HF + MP2, HF + RPAx, and HF + CCSD(T), respectively. We use large Dunning basis sets [59–65]. Core electrons are kept frozen in all the full-range and range-separated MP2, RPA, RPAx, and CCSD(T) calculations (i.e., only excitations of valence electrons are considered). The basis-set superposition error (BSSE) is removed using the counterpoise method. For the alkaline-earth-metal dimers, it has been checked that adding diffuse basis functions or core excitations does not change significantly the results. Extrapolations to the complete basis-set (CBS) limit have also been considered for some systems. For the full-range methods, the standard three-point exponential formula for the HF (or KS) reference $E_{\text{HF}}(n) = E_{\text{HF}}(\text{CBS}) + Ae^{-Bn}$ with the cardinal number $n = 3,4,5$ and two-point formula for the correlation energy $E_c(n) = E_c(\text{CBS}) + C/n^3$ with $n = 4,5$ have been used. For the range-separated methods, we have also used these two formulas for the RSH reference and the long-range correlation energy, even though in this case the dependence on the cardinal number would deserve a detailed study.

For each dimer interaction energy curve, we choose 16–20 intermolecular distances, with denser sampling around the equilibrium distance. A third-order polynomial is used for interpolation. The hard-core radius is taken as the distance where the interaction energy is 0 and the equilibrium distance and binding energy are from the minimum of the interpolated interaction energy curve. The harmonic vibrational frequency is obtained from the second-order derivative of the energy curve at the equilibrium distance. For C_6 dispersion coefficients, the interaction energy E_{int} is calculated at seven extra distances R_i from 30 to 60 bohr, and the coefficient is estimated by averaging with the following formula:

$$C_6 = \exp\left(\frac{1}{7}\sum_{i=1}^{7}[\ln|E_{\text{int}}(R_i)| + 6\ln(R_i)]\right), \tag{30}$$

similar to what has been done in Ref. [22].

IV. APPLICATIONS

A. Basis-set dependence

The convergence of the equilibrium binding energy of Ar_2 with respect to the basis-set size up to the CBS limit for the full-range methods HF + MP2, PBE + RPA, HF + RPA, and HF + CCSD(T) and for the range-separated methods RSH + lrMP2, RSH + lrRPA, RSH + lrRPAx, and RSH + lrCCSD(T) is represented in Fig. 1. Full-range RPA with PBE orbitals has a very strong dependence on the basis size, as already noted (e.g., Refs. [20,26]). Full-range RPA with HF orbitals has a bit weaker basis dependence, similar to full-range HF + MP2, HF + RPAx, and HF + CCSD(T). All the range-separated methods have essentially identical, very favorable basis-set convergence. Since the slow convergence of full-range methods is related to the explicit description of short-range correlation, it is not surprising that range-separated methods have a faster convergence because they leave the description of short-range correlation to the short-range density functional. These results are consistent with other studies (e.g., Refs. [22,24]). Note that, with the aug-cc-pV5Z basis set, all the range-separated methods are essentially converged (98%–99% of the CBS binding energy); therefore, we do not use CBS extrapolations in the following. However, one should keep in mind that with this basis set the full-range methods are not yet fully converged, with about 90% of the CBS binding energy.

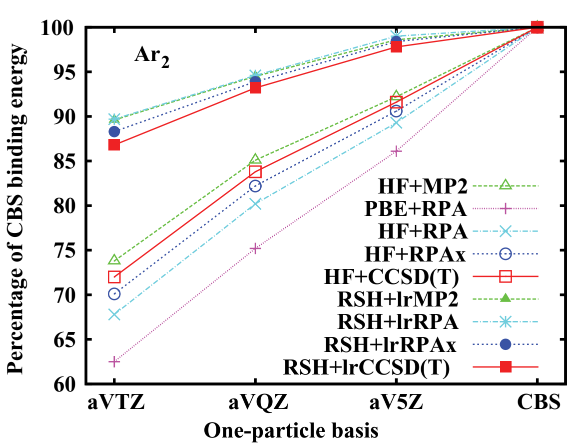

FIG. 1. (Color online) Basis-set dependence of the equilibrium binding energy of Ar_2 for different full-range and range-separated methods, presented as the percentage of the binding energy recovered with respect to the CBS limit (aVTZ, aVQZ, and aV5Z stand for aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z, respectively).

B. Rare-gas dimers

In Fig. 2, the interaction energy curves of He_2, Ne_2, Ar_2, and Kr_2, obtained with the full-range and range-separated methods, are compared. As already known, full-range HF + MP2 underestimates the interaction energy for the smallest systems He_2 and Ne_2 and overestimates it for the largest systems Ar_2 and Kr_2. Full-range PBE + RPA gives an almost dissociative curve for He_2 and largely underestimates the interaction energy for Ne_2, Ar_2, and Kr_2. Using HF orbitals in full-range RPA drastically improves the interaction energy curve for He_2, and to a least extend for Ne_2, but gives less binding for Ar_2 and Kr_2. Full-range HF + RPAx significantly improves over full-range HF + RPA but still gives underestimated interaction energies. It can be noted that full-range HF + RPAx yields interaction energy curves almost identical to the full-range HF + MP2 curves for He_2 and Ne_2 and almost identical to the full-range PBE + RPA curves for Ar_2 and Kr_2. Full-range HF + CCSD(T) gives systematically quite accurate interaction energies. Quite similarly to full-range HF + MP2, the range-separated RSH + lrMP2 underestimates the interaction energy for He_2 and Ne_2 and overestimates it for Ar_2 and Kr_2. RSH + lrRPA tends to improve over both full-range PBE + RPA and HF + RPA but still leads to significantly underestimated interaction energies. RSH + lrRPAx improves over both RSH + lrRPA and full-range HF + RPAx; it still systematically underestimates the interaction energy at equilibrium but appears quite accurate at medium and large distances. On the contrary, RSH + lrCCSD(T) systematically overestimates the interaction energy at medium and large distances.

The hard-core radii, equilibrium distances, equilibrium binding energies, harmonic vibrational frequencies, and dispersion coefficients C_6 for ten homonuclear and heteronuclear rare-gas dimers calculated with the full-range and range-separated methods are given in Table I. The trends seen in Fig. 2 are confirmed. Full-range RPA (with PBE or HF orbitals) yields very inaccurate equilibrium properties. Full-range HF + RPAx improves over full-range HF + RPA (with the exception of C_6 coefficients, which turn out to be quite good in PBE + RPA for these systems), but the

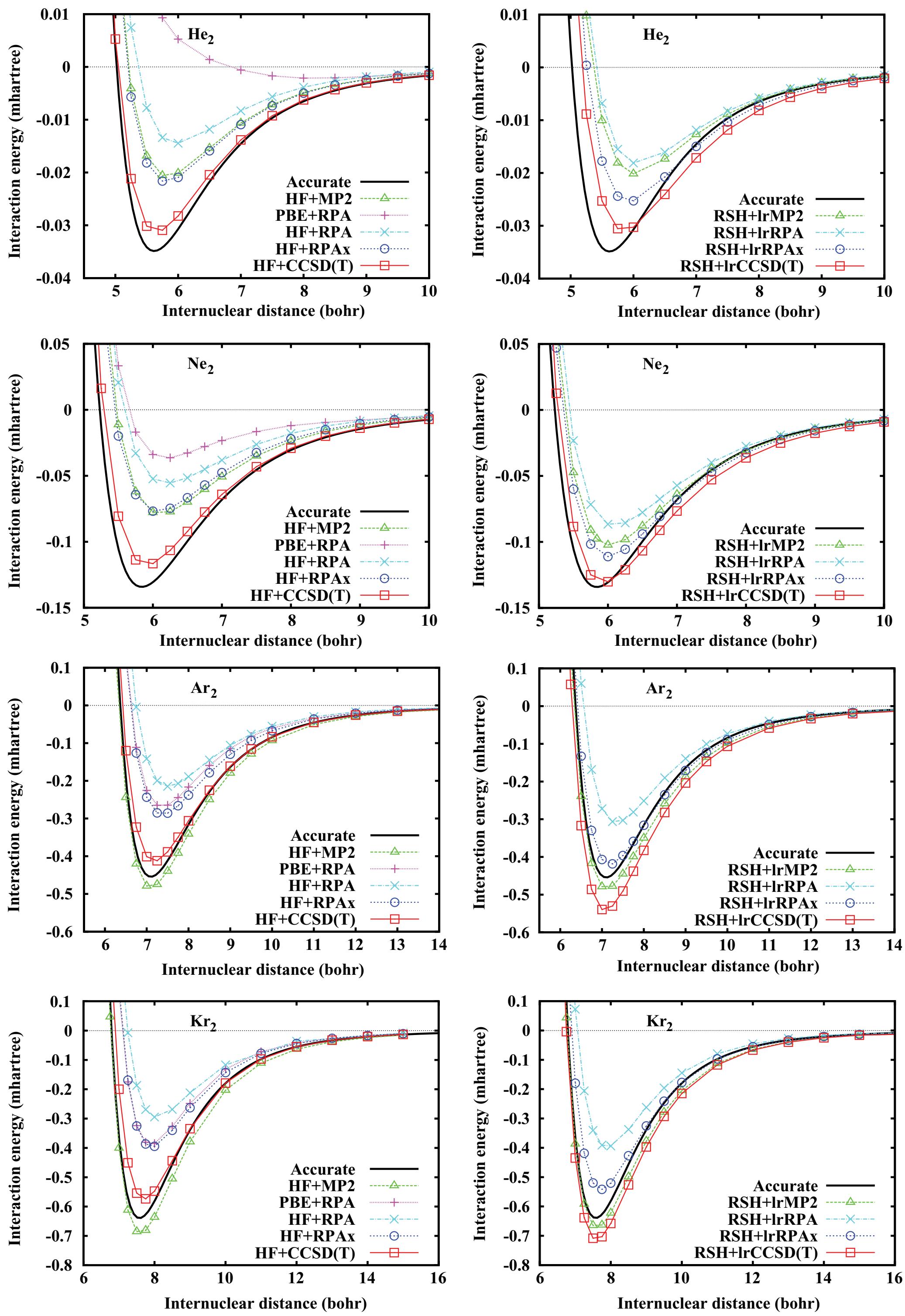

FIG. 2. (Color online) Interaction energy curves of He_2, Ne_2, Ar_2, and Kr_2 calculated using different full-range (left) and range-separated (right) methods. The basis is aug-cc-pV5Z. The accurate curves are from Ref. [66].

errors remain large. Range separation largely improves RPA and RPAx. RSH + lrRPAx gives much better equilibrium properties than RSH + lrRPA, with mean absolute percentage errors smaller by more than a factor of two, while these two methods give similar accuracy for C_6 coefficients. Full-range HF + MP2 is reasonably accurate, and range separation has a much smaller impact on it. For these systems, RSH + lrMP2 gives an overall similar accuracy than RSH + RPAx, although the C_6 coefficients tend to be globally more accurate in RSH + lrRPAx. Full-range HF + CCSD(T) gives the best results. Surprisingly, range separation tends to deteriorate the accuracy of CCSD(T), especially for

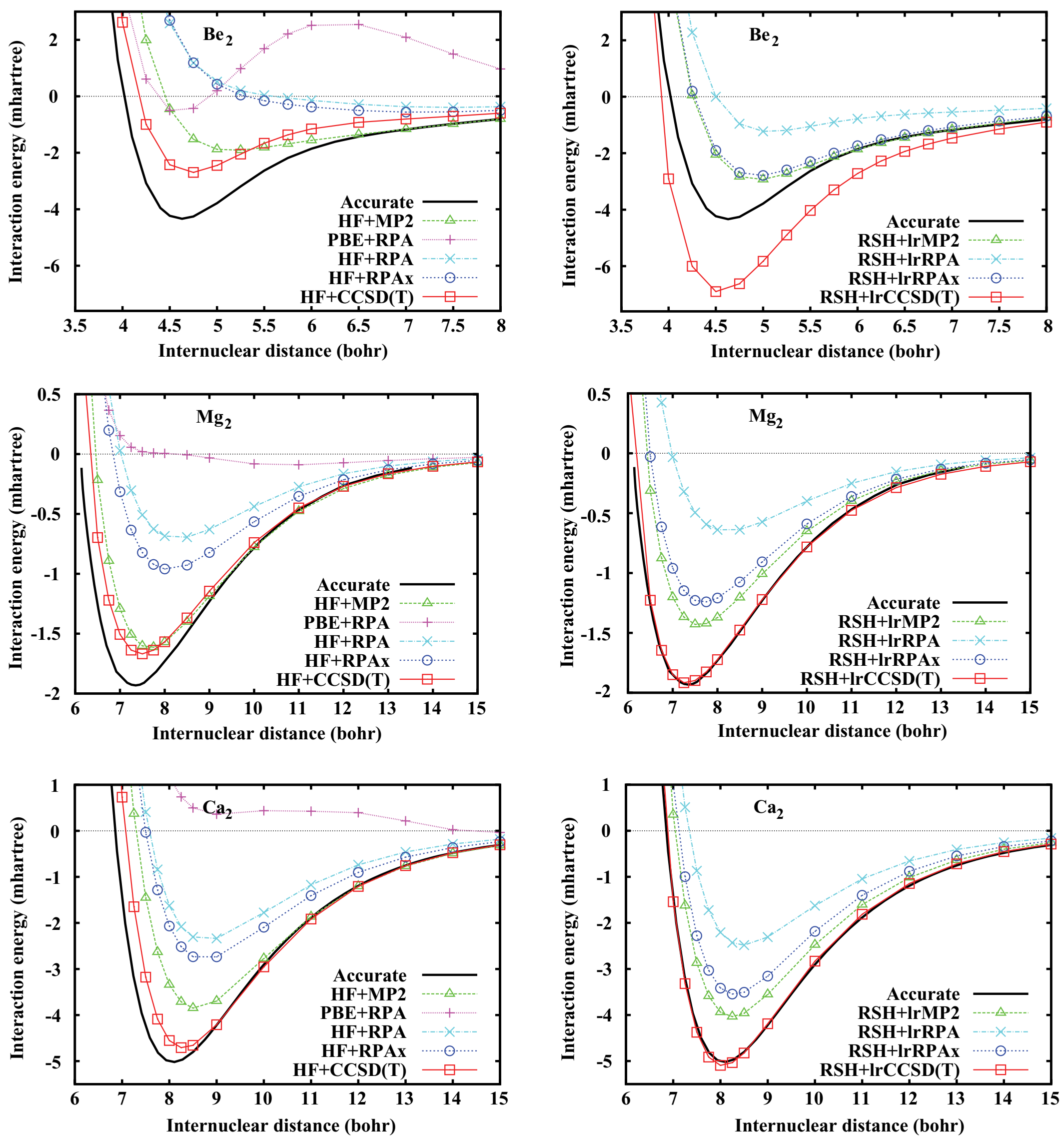

FIG. 3. (Color online) Interaction energy curves of Be_2, Mg_2, and Ca_2 calculated by full-range (left) and range-separated (right) methods. The basis is cc-pV5Z. The accurate curves are from Refs. [67–69].

C_6 coefficients. Nevertheless, among the range-separated methods, RSH + lrCCSD(T) still gives the best equilibrium properties.

C. Alkaline-earth-metal dimers

In Fig. 3, the interaction energy curves of Be_2, Mg_2, and Ca_2, obtained with the full-range and range-separated methods, are compared. These systems have static correlation effects, especially Be_2, and are thus more challenging for the single-reference methods tested here. Full-range PBE + RPA gives unphysical interaction energy curves, with a large bump for Be_2, and with essentially no bond for Mg_2 and Ca_2. Full-range HF + RPA yields an almost dissociative curve for Be_2 with no bump (which is consistent with that seen in Ref. [43]) and physically reasonable curves for Mg_2 and Ca_2. Full-range HF + RPAx moderately improves over full-range HF + RPA. Among the full-range methods, HF + MP2 and HF + CCSD(T) clearly give the best interaction energy curves. As for rare-gas dimers, RSH + lrRPA always largely underestimates the interaction energy. RSH + lrMP2 and RSH + lrRPAx give much less underestimated interaction energies, with RSH + lrMP2 being a bit more accurate for Mg_2 and Ca_2. While RSH + lrCCSD(T) largely overestimates the interaction energy for Be_2, it is remarkably accurate for Mg_2 and Ca_2. We note that RSH + lrCCSD(T) could be made more accurate for Be_2 by choosing a larger range-separation parameter μ [71].

The hard-core radii, equilibrium distances, equilibrium binding energies, harmonic vibrational frequencies, and dispersion coefficients C_6 for Be_2, Mg_2, and Ca_2 are given in Table II. It is confirmed that range separation largely improves the equilibrium properties of RPA and RPAx. Again, RSH + lrRPAx is much more accurate than RSH + lrRPA, with mean absolute percentage errors smaller by about a factor of two. Range separation also overall brings a significant improvement in MP2. Among the range-separated methods, RSH + lrCCSD(T) gives the best equilibrium properties.

TABLE I. Hard-core radii σ (bohr), equilibrium distances R_e (bohr), equilibrium binding energies D_e (mhartree), harmonic vibrational frequencies ω_e (cm^{-1}), and dispersion coefficients C_6 for ten homonuclear and heteronuclear rare-gas dimers from different full-range and range-separated methods with aug-cc-pV5Z basis. Mean absolute percentage errors (MA%E) are also given.

	HF + MP2	PBE + RPA	HF + RPA	HF + RPAx	HF + CCSD(T)	RSH + lrMP2	RSH + lrRPA	RSH + lrRPAx	RSH + lrCCSD(T)	Estimated exact[a]
He_2										
σ	5.20	6.81	5.34	5.18	5.03	5.35	5.39	5.25	5.17	5.02
R_e	5.83	8.16	5.95	5.82	5.65	6.00	6.10	5.92	5.85	5.62
D_e	0.0208	0.0021	0.0145	0.0218	0.0313	0.0202	0.0183	0.0255	0.0309	0.0348
ω_e	26.9	4.5	24.1	27.4	33.6	26.2	22.3	28.6	30.4	34.3
C_6	1.13	1.36	0.88	1.14	1.46	1.42	1.34	1.67	1.91	1.461
He-Ne										
σ	5.32	5.81	5.44	5.29	5.13	5.33	5.38	5.27	5.19	5.16
R_e	5.95	6.37	6.08	5.91	5.77	5.99	6.07	5.93	5.87	5.76
D_e	0.0401	0.0064	0.0284	0.0410	0.0609	0.0458	0.0401	0.0533	0.0638	0.0660
ω_e	28.8	13.0	23.8	29.5	34.3	28.4	26.2	30.9	33.5	36.1
C_6	2.43	2.77	1.84	2.32	3.07	3.12	2.84	3.44	4.04	3.029
He-Ar										
σ	6.02	6.31	6.27	6.11	5.92	6.01	6.14	5.99	5.87	5.92
R_e	6.73	6.96	6.97	6.83	6.64	6.77	6.89	6.73	6.63	6.61
D_e	0.0736	0.0307	0.0424	0.0608	0.0874	0.0808	0.0616	0.0854	0.1071	0.0937
ω_e	32.3	24.1	25.9	29.4	35.7	31.5	29.0	33.3	37.4	36.0
C_6	9.1	9.1	6.1	7.6	11.6	10.6	8.7	10.8	12.6	9.538
He-Kr										
σ	6.38	6.67	6.67	6.50	6.28	6.35	6.52	6.34	6.22	6.25
R_e	7.15	7.37	7.42	7.26	7.05	7.14	7.31	7.13	7.03	6.98
D_e	0.0747	0.0337	0.0423	0.0606	0.0881	0.0833	0.0613	0.0857	0.1084	0.0996
ω_e	30.1	22.3	23.4	26.3	32.4	30.7	25.9	31.2	34.2	33.7
C_6	12.9	12.5	8.5	10.7	14.0	14.9	12.0	14.7	17.3	13.40
Ne_2										
σ	5.47	5.63	5.57	5.43	5.28	5.36	5.43	5.33	5.27	5.23
R_e	6.11	6.18	6.19	6.07	5.90	6.03	6.10	5.98	5.93	5.84
D_e	0.079	0.037	0.056	0.077	0.118	0.102	0.088	0.111	0.131	0.134
ω_e	22.8	18.7	19.7	22.6	28.8	23.8	22.9	25.9	28.3	29.4
C_6	5.24	6.84	3.91	4.77	6.35	6.80	6.10	7.03	8.08	6.383
Ne-Ar										
σ	6.02	6.21	6.28	6.13	5.94	5.92	6.06	5.93	5.84	5.89
R_e	6.72	6.87	7.01	6.85	6.65	6.66	6.80	6.67	6.59	6.57
D_e	0.163	0.095	0.092	0.126	0.189	0.196	0.147	0.192	0.235	0.211
ω_e	25.3	21.6	17.4	22.6	27.7	27.2	23.0	26.9	29.3	28.7
C_6	19.2	18.9	12.5	15.2	18.2	22.6	18.3	21.8	25.3	19.50
Ne-Kr										
σ	6.31	6.53	6.61	6.46	6.24	6.20	6.36	6.23	6.14	6.17
R_e	7.08	7.21	7.36	7.20	6.98	6.97	7.13	7.01	6.91	6.89
D_e	0.174	0.104	0.096	0.131	0.201	0.212	0.153	0.201	0.248	0.224
ω_e	22.4	19.0	17.0	19.8	24.5	24.4	20.7	23.1	26.5	25.3
C_6	27.0	26.2	17.4	21.1	27.4	31.5	24.8	29.5	34.0	27.30
Ar_2										
σ	6.32	6.61	6.74	6.60	6.41	6.32	6.55	6.40	6.28	6.37
R_e	7.10	7.36	7.52	7.37	7.17	7.11	7.34	7.18	7.07	7.10
D_e	0.483	0.269	0.215	0.289	0.414	0.484	0.308	0.420	0.542	0.454
ω_e	32.7	25.5	21.4	25.5	30.7	32.1	25.5	30.0	33.5	32.1
C_6	76.3	58.6	42.9	52.0	64.5	80.7	57.4	69.6	85.0	64.30
Ar-Kr										
σ	6.55	6.85	7.00	6.85	6.65	6.55	6.80	6.64	6.52	6.59
R_e	7.36	7.64	7.81	7.66	7.45	7.37	7.62	7.46	7.34	7.35
D_e	0.570	0.319	0.248	0.334	0.481	0.563	0.346	0.472	0.615	0.531
ω_e	29.5	22.9	19.4	22.7	27.3	28.7	22.5	26.3	29.8	28.6
C_6	109.9	82.1	60.7	73.6	94.8	114.1	80.0	97.4	117.1	91.13

TABLE I. *(Continued.)*

	HF + MP2	PBE + RPA	HF + RPA	HF + RPAx	HF + CCSD(T)	RSH + lrMP2	RSH + lrRPA	RSH + lrRPAx	RSH + lrCCSD(T)	Estimated exact[a]
Kr_2										
σ	6.77	7.09	7.24	7.10	6.88	6.77	7.05	6.88	6.75	6.79
R_e	7.60	7.90	8.08	7.92	7.70	7.61	7.89	7.72	7.60	7.58
D_e	0.691	0.388	0.296	0.396	0.575	0.671	0.397	0.542	0.713	0.638
ω_e	25.1	19.8	16.2	19.7	23.2	24.4	19.2	21.9	25.0	24.4
C_6	159	116	86	105	132	162	109	134	163	129.6
MA%E (%)										
σ	2.1	9.3	6.3	3.8	0.7	1.8	3.9	1.5	1.0	0.0
R_e	2.1	9.4	6.1	3.9	1.0	2.2	4.5	2.2	1.0	0.0
D_e	23	62	56	39	10	16	36	14	11	0.0
ω_e	12	36	33	21	3.4	9.5	23	10	4.6	0.0
C_6	13	7.0	36	22	4.1	14	9.2	10	29	0.0

[a]From Ref. [66].

TABLE II. Hard-core radii σ (bohr), equilibrium distances R_e (bohr), equilibrium binding energies D_e (mhartree), harmonic vibrational frequencies ω_e (cm^{-1}), and dispersion coefficients C_6 for Be_2, Mg_2, and Ca_2 from different full-range and range-separated methods with cc-pV5Z basis. Mean absolute percentage errors (MA%E) are also given.

	HF + MP2	PBE + RPA	HF + RPA	HF + RPAx	HF + CCSD(T)	RSH + lrMP2	RSH + lrRPA	RSH + lrRPAx	RSH + lrCCSD(T)	Estimated exact
Be_2										
σ	4.44	4.34	5.59	5.30	4.16	4.25	4.50	4.27	3.87	4.01[a]
R_e	5.15	4.60	7.48	7.17	4.71	4.92	5.08	4.92	4.54	4.63[a]
D_e	1.92	0.58	0.39	0.56	2.70	2.95	1.24	2.81	6.92	4.31[a]
ω_e	139	297	34	37	242	199	152	198	315	267[a]
C_6	256	164	138	180	195	232	149	213	274	214[d]
Mg_2										
σ	6.44	8.30	7.02	6.83	6.29	6.40	6.98	6.49	6.13	6.10[b]
R_e	7.66	10.72	8.28	8.11	7.48	7.59	8.23	7.68	7.31	7.35[b]
D_e	1.62	0.09	0.70	0.96	1.67	1.43	0.65	1.24	1.92	1.93[b]
ω_e	47	7.9	31	35	48	45	30	42	52	51.1[b]
C_6	686	405	364	485	616	571	349	494	671	627[d]
Ca_2										
σ	7.29	–	7.57	7.49	7.07	7.04	7.33	7.11	6.85	6.88[c]
R_e	8.57	–	8.76	8.72	8.30	8.25	8.47	8.30	8.05	8.09[c]
D_e	3.85	–	2.37	2.78	4.71	4.03	2.48	3.55	5.10	5.02[c]
ω_e	56	–	44	47	64	60	50	57	68	63.7[c]
C_6	2574	1335	1301	1710	2311	2090	1173	1617	2224	2221[d]
MA%E (%)										
σ	7.4	–	22	18	3.2	4.4	11	5.4	1.5	0.0
R_e	7.1	–	28	24	2.0	3.8	8.7	4.5	1.0	0.0
D_e	32	–	69	61	19	26	63	33	21	0.0
ω_e	23	–	53	48	5.3	14	35	18	9.1	0.0
C_6	15	33	40	21	5.0	7.7	41	16	12	0.0

[a]From Ref. [67].
[b]From Ref. [68].
[c]From Ref. [69].
[d]From Ref. [70].

V. CONCLUSIONS

We have expounded the details of a formally exact adiabatic-connection fluctuation-dissipation density-functional theory based on range separation. Range-separated density-functional theory with RPAs including or not the long-range Hartree-Fock exchange response kernel (referred to as RSH + lrRPA and RSH + lrRPAx, respectively) are then obtained as well-identified approximations on the long-range Green's-function self-energy [Eqs. (22) and (23)]. The long-range Green's function does not vary along the adiabatic connection at the RSH + lrRPA and RSH + lrRPAx levels, which makes these schemes relatively simple compared to the exact theory. In practice, RSH + lrRPA and RSH + lrRPAx have been applied in a spin-restricted closed-shell formalism, in which both schemes only include spin-singlet orbital excitations, and thus are not subject to triplet instabilities.

These range-separated RPA-type schemes have been tested on rare-gas and alkaline-earth-metal dimers, featuring challenging weak (van der Waals) interactions. Both range separation and inclusion of the exact Hartree-Fock response kernel largely improve the accuracy of RPA. The RSH + lrRPAx method appears as a reasonably accurate method for weak interactions but globally less accurate for equilibrium properties than the more intensive range-separated coupled-cluster method. Although for the small systems considered here, range-separated second-order perturbation theory (RSH + lrMP2) turns out to yield results similar in accuracy to those from RSH + lrRPAx (and in fact more accurate for Mg_2 and Ca_2), a recent investigation [72] shows that RSH + lrRPAx corrects the overestimation of the binding energy in RSH + lrMP2 for larger weakly interacting stacked complexes, such as the benzene dimer.

ACKNOWLEDGMENTS

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APPENDIX A: ADIABATIC-CONNECTION FLUCTUATION-DISSIPATION DENSITY-FUNCTIONAL THEORY

In this appendix, we outline a general, formally exact adiabatic-connection fluctuation-dissipation density-functional theory, using Green's-function many-body theory. For further details on standard Green's function theory, see, for example, Refs. [73–76].

A. Adiabatic connection

We consider the following adiabatic connection defined by the λ-dependent energy:

$$E_\lambda = \min_\Psi\{\langle\Psi|\hat{K}_0 + \lambda\hat{W}|\Psi\rangle + F[n_\Psi]\}, \tag{A1}$$

where $\hat{K}_0$ is an arbitrary one-particle Hamiltonian, $\hat{W}$ is a perturbation operator (generally, the sum of a two-particle operator $\hat{W}_{ee}$ and an one-particle operator), and $F[n]$ is a λ-independent density functional. The minimizing multideterminant wave function Ψ_λ satisfies the Euler-Lagrange equation,

$$\hat{H}_\lambda|\Psi_\lambda\rangle = \mathcal{E}_\lambda|\Psi_\lambda\rangle, \tag{A2}$$

where $\mathcal{E}_\lambda$ is the Lagrange multiplier for the normalization constraint and $\hat{H}_\lambda$ is the effective Hamiltonian along the adiabatic connection,

$$\hat{H}_\lambda = \hat{K}_0 + \lambda\hat{W} + \hat{V}_\lambda, \tag{A3}$$

where $\hat{V}_\lambda = \int d\mathbf{r}\,\delta F[n_{\Psi_\lambda}]/\delta n(\mathbf{r})\,\hat{n}(\mathbf{r})$ is a self-consistent one-particle potential operator. Note that $\hat{H}_{\lambda=1}$ is not necessarily the physical Hamiltonian. This adiabatic connection links the energy of interest $E_{\lambda=1}$ to the reference energy $E_{\lambda=0} = \langle\Phi_0|\hat{K}_0|\Phi_0\rangle + F[n_{\Phi_0}]$ calculated with the single-determinant wave function $\Phi_0 = \Psi_{\lambda=0}$ of the reference Hamiltonian $\hat{H}_0 = \hat{K}_0 + \hat{V}_0$. The one-particle density is not kept constant with respect to λ.

An adiabatic connection formula for $E_{\lambda=1}$ is found by taking the derivative of E_λ with respect to λ, noting that E_λ is stationary with respect to Ψ_λ, and reintegrating between $\lambda = 0$ and $\lambda = 1$:

$$E_{\lambda=1} = E_{\lambda=0} + \int_0^1 d\lambda\,\langle\Psi_\lambda|\hat{W}|\Psi_\lambda\rangle. \tag{A4}$$

The correlation energy, defined as $E_c = E_{\lambda=1} - E_{\lambda=0} - (dE_\lambda/d\lambda)_{\lambda=0}$, where $(dE_\lambda/d\lambda)_{\lambda=0} = \langle\Phi_0|\hat{W}|\Phi_0\rangle$ is the first-order energy correction, is thus given by

$$E_c = \int_0^1 d\lambda[\langle\Psi_\lambda|\hat{W}|\Psi_\lambda\rangle - \langle\Phi_0|\hat{W}|\Phi_0\rangle], \tag{A5}$$

or, equivalently, in the representation of space-spin coordinates $\mathbf{x} = (\mathbf{r},s)$,

$$E_c = \frac{1}{2}\int_0^1 d\lambda \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' w(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') \times P_{c,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2'), \tag{A6}$$

where $w(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')$ is the interaction potential corresponding to the operator $\hat{W}$ and $P_{c,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')$ is the correlation part of the two-particle density matrix along the adiabatic connection.

This exposition encompasses both standard full-range many-body theory and range-separated density-functional theory. Indeed, if $\hat{K}_0$ is the Hartree-Fock Hamiltonian (i.e., $\hat{K}_0 = \hat{T} + \hat{V}_{ne} + \hat{V}_{\text{Hx,HF}}$), $\hat{W}$ is the standard Møller-Plesset fluctuation perturbation operator (i.e., $\hat{W} = \hat{W}_{ee} - \hat{V}_{\text{Hx,HF}}$) and $F[n] = 0$, then Eq. (A6) yields the full-range many-body correlation energy, defined with respect to the Hartree-Fock energy. Similarly, with the corresponding long-range operators $\hat{K}_0 = \hat{T} + \hat{V}_{ne} + \hat{V}^{\text{lr}}_{\text{Hx,HF}}$ and $\hat{W} = \hat{W}^{\text{lr}}_{ee} - \hat{V}^{\text{lr}}_{\text{Hx,HF}}$ and the short-range density functional $F[n] = E^{\text{sr}}_{\text{Hxc}}[n]$, Eq. (A6) yields now the long-range correlation energy, defined with respect to the RSH energy [Eq. (5)].

B. One-particle Green's function

The one-particle Green's function along the adiabatic connection is defined as

$$G_\lambda(1,2) = -i\langle\Psi_\lambda|T[\hat{\psi}_\lambda(1)\hat{\psi}_\lambda^\dagger(2)]|\Psi_\lambda\rangle, \quad \text{(A7)}$$

where $1 = (\mathbf{x}_1,t_1)$ and $2 = (\mathbf{x}_2,t_2)$ refer to space-spin and time coordinates, $\hat{\psi}_\lambda(1) = e^{i\hat{H}_\lambda t_1}\hat{\psi}(\mathbf{x}_1)e^{-i\hat{H}_\lambda t_1}$ and $\hat{\psi}_\lambda^\dagger(2) = e^{i\hat{H}_\lambda t_2}\hat{\psi}^\dagger(\mathbf{x}_2)e^{-i\hat{H}_\lambda t_2}$ are the annihilation and creation operators in the Heisenberg picture, and T is the Wick time-ordering operator.

A Dyson-type equation connects the inverse of G_λ to the inverse of the Green's function associated with the one-electron Hamiltonian $\hat{K}_0 + \hat{V}_\lambda$, denoted by $G_{V,\lambda}$,

$$G_\lambda^{-1}(1,2) = G_{V,\lambda}^{-1}(1,2) - \Sigma_\lambda(1,2), \quad \text{(A8)}$$

which can be considered as the definition of the self-energy Σ_λ. In turn, the inverse of $G_{V,\lambda}$ can be expressed from the inverse of the Green's function G_0 of the reference Hamiltonian $\hat{H}_0 = \hat{K}_0 + \hat{V}_0$ as $G_{V,\lambda}^{-1} = G_0^{-1} - (v_\lambda - v_0)$, where v_λ and v_0 are the one-electron potentials associated with $\hat{V}_\lambda$ and $\hat{V}_0$, respectively.

For time-independent Hamiltonians, the Green's function only depends on the time difference $\tau = t_1 - t_2$, so one defines $G_\lambda(\mathbf{x}_1,\mathbf{x}_2;\tau) = G_\lambda(\mathbf{x}_1 t_1,\mathbf{x}_2 t_2)$, which has a discontinuity at $\tau = 0$. The one-particle density matrix $n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_2) = \langle\Psi_\lambda|\hat{n}_1(\mathbf{x}_1,\mathbf{x}_2)|\Psi_\lambda\rangle$, with $\hat{n}_1(\mathbf{x}_1,\mathbf{x}_2) = \hat{\psi}^\dagger(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_1)$, can be obtained from the limit $\tau \to 0^-$,

$$n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_2) = -iG_\lambda(\mathbf{x}_1,\mathbf{x}_2;\tau = 0^-). \quad \text{(A9)}$$

C. Four-point polarization propagator

The four-point polarization propagator along the adiabatic connection is defined as

$$\chi_\lambda(1,2;1',2') = i[G_{2,\lambda}(1,2;1',2') - G_\lambda(1,1')G_\lambda(2,2')], \quad \text{(A10)}$$

where $G_{2,\lambda}$ is the two-particle Green's function,

$$G_{2,\lambda}(1,2;1',2') = -\langle\Psi_\lambda|T[\hat{\psi}_\lambda(1)\hat{\psi}_\lambda(2)\hat{\psi}_\lambda^\dagger(2')\hat{\psi}_\lambda^\dagger(1')]|\Psi_\lambda\rangle. \quad \text{(A11)}$$

Alternatively, using the Schwinger derivative technique, χ_λ can be expressed as the functional derivative of the one-particle Green's function with respect to the two-point potential v_λ (see, e.g., Refs. [73,76]):

$$\chi_\lambda(1,2;1',2') = -i\frac{\delta G_{V,\lambda}(1,1')}{\delta v_\lambda(2',2)}. \quad \text{(A12)}$$

The four-point polarization propagator satisfies a so-called Bethe-Salpeter equation that directly stems from the Dyson equation of Eq. (A8). Considering variations with respect to iG_λ (achieved through variations of v_λ) yields

$$-i\frac{\delta G_\lambda^{-1}(1,1')}{\delta G_\lambda(2',2)} = -i\frac{\delta G_{V,\lambda}^{-1}(1,1')}{\delta G_\lambda(2',2)} + i\frac{\delta\Sigma_\lambda(1,1')}{\delta G_\lambda(2',2)}. \quad \text{(A13)}$$

The term on the left-hand side of Eq. (A13) gives straightforwardly

$$-i\frac{\delta G_\lambda^{-1}(1,1')}{\delta G_\lambda(2',2)} = iG_\lambda^{-1}(1,2')G_\lambda^{-1}(2,1') = \chi_{\mathrm{IP},\lambda}^{-1}(1,2;1',2'), \quad \text{(A14)}$$

where $\chi_{\mathrm{IP},\lambda}(1,2;1',2') = -iG_\lambda(1,2')G_\lambda(2,1')$ is a so-called independent-particle (IP) polarization propagator [77]. The first term on the right-hand side of Eq. (A13) gives the inverse of the four-point polarization propagator, according to Eq. (A12),

$$-i\frac{\delta G_{V,\lambda}^{-1}(1,1')}{\delta G_\lambda(2',2)} = i\frac{\delta v_\lambda(1,1')}{\delta G_\lambda(2',2)} = \chi_\lambda^{-1}(1,2;1',2'), \quad \text{(A15)}$$

and the second term is the so-called Bethe-Salpeter four-point kernel,

$$i\frac{\delta\Sigma_\lambda(1,1')}{\delta G_\lambda(2',2)} = f_\lambda(1,2;1',2'), \quad \text{(A16)}$$

and finally, using Eqs. (A14)–(A16) in Eq. (A13), the Bethe-Salpeter equation for χ_λ is written

$$\chi_\lambda^{-1}(1,2;1',2') = \chi_{\mathrm{IP},\lambda}^{-1}(1,2;1',2') - f_\lambda(1,2;1',2'). \quad \text{(A17)}$$

D. Fluctuation-dissipation theorem

Similarly to the expression of the one-particle density matrix in terms of the one-particle Green's function [Eq. (A9)], the two-particle density matrix can be extracted from the polarization propagator. Defining $\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau) = \chi_\lambda(\mathbf{x}_1 t_1,\mathbf{x}_2 t_2;\mathbf{x}_1' t_1^+,\mathbf{x}_2' t_2^+)$, that is, the polarization propagator with times $t_1' \to t_1^+$ and $t_2' \to t_2^+$ which depends only on the time difference $\tau = t_1 - t_2$, it is easy to check that in the limit $\tau \to 0^-$, after applying the time-ordering operator in Eq. (A11) and using Eq. (A9), one has the following relation:

$$\begin{aligned} &i\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau = 0^-) \\ &= \langle\Psi_\lambda|\hat{n}_1(\mathbf{x}_2,\mathbf{x}_2')\hat{n}_1(\mathbf{x}_1,\mathbf{x}_1')|\Psi_\lambda\rangle - n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_1')n_{1,\lambda}(\mathbf{x}_2,\mathbf{x}_2'). \end{aligned} \quad \text{(A18)}$$

The two-particle density matrix $n_{2,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \langle\Psi_\lambda|\hat{\psi}^\dagger(\mathbf{x}_2')\hat{\psi}^\dagger(\mathbf{x}_1')\hat{\psi}(\mathbf{x}_1)\hat{\psi}(\mathbf{x}_2)|\Psi_\lambda\rangle$ can thus be expressed as

$$\begin{aligned} &n_{2,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') \\ &= \langle\Psi_\lambda|\hat{n}_1(\mathbf{x}_2,\mathbf{x}_2')\hat{n}_1(\mathbf{x}_1,\mathbf{x}_1')|\Psi_\lambda\rangle - \delta(\mathbf{x}_1' - \mathbf{x}_2)n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_2') \\ &= i\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau = 0^-) + n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_1')n_{1,\lambda}(\mathbf{x}_2,\mathbf{x}_2') \\ &\quad - \delta(\mathbf{x}_1' - \mathbf{x}_2)n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_2'). \end{aligned} \quad \text{(A19)}$$

The correlation part of the two-particle density matrix $P_{c,\lambda} = n_{2,\lambda} - n_{2,\lambda=0}$ is thus

$$\begin{aligned} &P_{c,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') \\ &= i\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau = 0^-) - i\chi_0(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau = 0^-) \\ &\quad + \Delta_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2'), \end{aligned} \quad \text{(A20)}$$

where χ_0 is the polarization propagator of the noninteracting reference system for $\lambda = 0$ and Δ_λ is a term coming from the variation of the one-particle density matrix along the adiabatic connection,

$$\begin{aligned} &\Delta_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') \\ &= n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_1')n_{1,\lambda}(\mathbf{x}_2,\mathbf{x}_2') - \delta(\mathbf{x}_1' - \mathbf{x}_2)n_{1,\lambda}(\mathbf{x}_1,\mathbf{x}_2') \\ &\quad - n_{1,0}(\mathbf{x}_1,\mathbf{x}_1')n_{1,0}(\mathbf{x}_2,\mathbf{x}_2') + \delta(\mathbf{x}_1' - \mathbf{x}_2)n_{1,0}(\mathbf{x}_1,\mathbf{x}_2'). \end{aligned} \quad \text{(A21)}$$

Using Eq. (A9), one can also express this term with the Green's function as $\Delta_\lambda = \Gamma[G_\lambda] - \Gamma[G_0]$, where we define the functional Γ as

$$\Gamma[G] = -G(\mathbf{x}_1,\mathbf{x}_1';\tau=0^-)G(\mathbf{x}_2,\mathbf{x}_2';\tau=0^-) + \delta(\mathbf{x}_1'-\mathbf{x}_2)iG(\mathbf{x}_1,\mathbf{x}_2';\tau=0^-). \tag{A22}$$

Finally, introducing the Fourier transform of $\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau)$ in terms of the frequency ω,

$$i\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\tau=0^-) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}e^{i\omega 0^+} \times \chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\omega), \tag{A23}$$

we arrive at the form of the fluctuation dissipation that we use:

$$\begin{aligned}P_{c,\lambda}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') &= -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}e^{i\omega 0^+}[\chi_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\omega) \\ &\quad - \chi_0(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\omega)] + \Delta_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2').\end{aligned} \tag{A24}$$

APPENDIX B: RANDOM-PHASE APPROXIMATION IN AN ORBITAL BASIS

In this appendix, we give the working equations in an orbital basis resulting from the many-body theory outlined in Appendix A in the special case of a RPA-type simplification. For further details, see, for example, Refs. [26,53,78,79].

A. Expressions in a spin-orbital basis

In the RPA and RPAx approximations, the Green's function does not vary along the adiabatic connection, that is, $G_\lambda = G_0$, which implies that the IP polarization propagator [Eq. (A14)] is just the noninteracting reference polarization propagator, $\chi_{\text{IP},\lambda}(1,2;1',2') = -iG_0(1,2')G_0(2,1') = \chi_0(1,2;1',2')$, and in the fluctuation-dissipation theorem of Eq. (A24) the term coming from the variation of the one-particle density matrix vanishes, $\Delta_\lambda = 0$.

The frequency-dependent noninteracting polarization propagator has the following well-known Lehmann representation:

$$\chi_0(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\omega) = \sum_{ia}\frac{\phi_i^*(\mathbf{x}_1')\phi_a(\mathbf{x}_1)\phi_a^*(\mathbf{x}_2')\phi_i(\mathbf{x}_2)}{\omega-(\epsilon_a-\epsilon_i)+i0^+} - \sum_{ia}\frac{\phi_i^*(\mathbf{x}_2')\phi_a(\mathbf{x}_2)\phi_a^*(\mathbf{x}_1')\phi_i(\mathbf{x}_1)}{\omega+(\epsilon_a-\epsilon_i)-i0^+}, \tag{B1}$$

where $\phi_p(\mathbf{x})$ and ϵ_p are the spin orbitals and corresponding eigenvalues of the reference system, and i and a run over occupied and virtual spin orbitals, respectively. Hence, χ_0 can be completely represented in the basis of spin-orbital products, $\phi_p^*(\mathbf{x}_1')\phi_q(\mathbf{x}_1)$, where p refers to an occupied orbital and q to a virtual orbital, and vice versa, with matrix elements

$$[\Pi_0(\omega)]_{pq,rs} = \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' \phi_p(\mathbf{x}_1')\phi_q^*(\mathbf{x}_1) \times \chi_0(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';\omega)\phi_r^*(\mathbf{x}_2)\phi_s(\mathbf{x}_2'). \tag{B2}$$

Assuming orthonormality of the spin orbitals, the matrix elements are easily calculated,

$$[\Pi_0(\omega)]_{ia,jb} = \frac{\delta_{ij}\delta_{ab}}{\omega-(\epsilon_a-\epsilon_i)+i0^+}, \tag{B3a}$$

$$[\Pi_0(\omega)]_{ai,bj} = -\frac{\delta_{ij}\delta_{ab}}{\omega+(\epsilon_a-\epsilon_i)-i0^+}, \tag{B3b}$$

$$[\Pi_0(\omega)]_{ai,jb} = [\Pi_0(\omega)]_{ia,bj} = 0, \tag{B3c}$$

where both i and j refer to occupied orbitals and both a and b to virtual orbitals. The matrix is thus diagonal, and the inverse of χ_0 has the following 2×2 supermatrix representation:

$$\Pi_0(\omega)^{-1} = -\left[\begin{pmatrix}\boldsymbol{\Delta\epsilon} & \mathbf{0}\\ \mathbf{0} & \boldsymbol{\Delta\epsilon}\end{pmatrix} - \omega\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{pmatrix}\right], \tag{B4}$$

where $\boldsymbol{\Delta\epsilon}_{ia,jb} = (\epsilon_a-\epsilon_i)\delta_{ij}\delta_{ab}$, each block matrix being reindexed with the composite indices ia and jb.

In the RPA and RPAx approximations, the Bethe-Salpeter kernel of Eq. (A16) is approximated as the frequency-independent Hartree(-Fock) form [Eqs. (19) and (20)],

$$f_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \lambda w_{ee}(r_{12})[\delta(\mathbf{x}_1-\mathbf{x}_1')\delta(\mathbf{x}_2-\mathbf{x}_2') - \xi\delta(\mathbf{x}_1-\mathbf{x}_2')\delta(\mathbf{x}_1'-\mathbf{x}_2)], \tag{B5}$$

where $w_{ee}(r_{12})$ is a two-particle interaction and $\xi=0$ or $\xi=1$ for RPA or RPAx, respectively. This kernel has the following supermatrix elements:

$$\begin{aligned}(\mathbb{F}_\lambda)_{pq,rs} &= \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' \phi_p(\mathbf{x}_1')\phi_q^*(\mathbf{x}_1) \\ &\quad \times f_\lambda(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')\phi_r^*(\mathbf{x}_2)\phi_s(\mathbf{x}_2') \\ &= \lambda\left[\langle qr|\hat{w}_{ee}|ps\rangle - \xi\langle qr|\hat{w}_{ee}|sp\rangle\right],\end{aligned} \tag{B6}$$

where $\langle qr|\hat{w}_{ee}|ps\rangle$ are the two-electron integrals. The supermatrix representation of the interacting polarization propagator χ_λ is then found from the Bethe-Salpeter equation [Eq. (A17)] written in the spin-orbital basis,

$$\begin{aligned}\Pi_\lambda(\omega)^{-1} &= \Pi_0(\omega)^{-1} - \mathbb{F}_\lambda \\ &= -\left[\begin{pmatrix}\mathbf{A}_\lambda & \mathbf{B}_\lambda\\ \mathbf{B}_\lambda^* & \mathbf{A}_\lambda^*\end{pmatrix} - \omega\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{pmatrix}\right],\end{aligned} \tag{B7}$$

where $\mathbf{A}_\lambda$ and $\mathbf{B}_\lambda$ are the so-called orbital rotation Hessians:

$$(\mathbf{A}_\lambda)_{ia,jb} = (\epsilon_a-\epsilon_i)\delta_{ij}\delta_{ab} + \lambda\left[\langle ib|\hat{w}_{ee}|aj\rangle - \xi\langle ib|\hat{w}_{ee}|ja\rangle\right], \tag{B8a}$$

$$(\mathbf{B}_\lambda)_{ia,jb} = \lambda\left[\langle ab|\hat{w}_{ee}|ij\rangle - \xi\langle ab|\hat{w}_{ee}|ji\rangle\right]. \tag{B8b}$$

We need to consider the linear-response non-Hermitian eigenvalue equation

$$\begin{pmatrix}\mathbf{A}_\lambda & \mathbf{B}_\lambda\\ \mathbf{B}_\lambda^* & \mathbf{A}_\lambda^*\end{pmatrix}\begin{pmatrix}\mathbf{X}_{n,\lambda}\\ \mathbf{Y}_{n,\lambda}\end{pmatrix} = \omega_{n,\lambda}\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{pmatrix}\begin{pmatrix}\mathbf{X}_{n,\lambda}\\ \mathbf{Y}_{n,\lambda}\end{pmatrix}, \tag{B9}$$

whose solutions come in pairs: positive excitation energies $\omega_{n,\lambda}$ with eigenvectors $(\mathbf{X}_{n,\lambda},\mathbf{Y}_{n,\lambda})$ and opposite (de-)excitation energies $-\omega_{n,\lambda}$ with eigenvectors $(\mathbf{Y}_{n,\lambda}^*,\mathbf{X}_{n,\lambda}^*)$. Choosing the normalization of the eigenvectors so that $\mathbf{X}_{n,\lambda}^\dagger\mathbf{X}_{m,\lambda} - \mathbf{Y}_{n,\lambda}^\dagger\mathbf{Y}_{m,\lambda} = \delta_{nm}$, the supermatrix $\Pi_\lambda(\omega)$ can be expressed as the following spectral representation (where the sum is over eigenvectors with positive excitation energies):

$$\Pi_\lambda(\omega) = \sum_n \left[\frac{1}{\omega - \omega_{n,\lambda} + i0^+} \begin{pmatrix} \mathbf{X}_{n,\lambda} \\ \mathbf{Y}_{n,\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\dagger_{n,\lambda} & \mathbf{Y}^\dagger_{n,\lambda} \end{pmatrix} \right. \quad \text{(B10)}$$

$$\left. - \frac{1}{\omega + \omega_{n,\lambda} - i0^+} \begin{pmatrix} \mathbf{Y}^*_{n,\lambda} \\ \mathbf{X}^*_{n,\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{Y}^{*\dagger}_{n,\lambda} & \mathbf{X}^{*\dagger}_{n,\lambda} \end{pmatrix} \right]. \quad \text{(B11)}$$

The fluctuation-dissipation theorem [Eq. (A24)] leads to the supermatrix representation of the correlation part of the two-particle density matrix $P_{c,\lambda}$ (using contour integration in the upper half of the complex plane),

$$\mathbb{P}_{c,\lambda} = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega 0^+} [\Pi_\lambda(\omega) - \Pi_0(\omega)]$$
$$= \sum_n \begin{pmatrix} \mathbf{Y}^*_{n,\lambda}\mathbf{Y}^{*\dagger}_{n,\lambda} & \mathbf{Y}^*_{n,\lambda}\mathbf{X}^{*\dagger}_{n,\lambda} \\ \mathbf{X}^*_{n,\lambda}\mathbf{Y}^{*\dagger}_{n,\lambda} & \mathbf{X}^*_{n,\lambda}\mathbf{X}^{*\dagger}_{n,\lambda} \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \quad \text{(B12)}$$

the simple contribution coming from $\Pi_0(\omega)$ resulting from its diagonal form [Eqs. (B3)], and the correlation energy [Eq. (A6)] has the following expression in spin-orbital basis:

$$E_c = \frac{1}{2}\int_0^1 d\lambda \sum_{pq,rs} \langle ps|\hat{w}|qr\rangle (\mathbb{P}_{c,\lambda})_{pq,rs}$$
$$= \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb}\sum_n \{\langle ib|\hat{w}_{ee}|aj\rangle (\mathbf{Y}_{n,\lambda})^*_{ia}(\mathbf{Y}_{n,\lambda})_{jb}$$
$$+ \langle ij|\hat{w}_{ee}|ab\rangle (\mathbf{Y}_{n,\lambda})^*_{ia}(\mathbf{X}_{n,\lambda})_{jb}$$
$$+ \langle ab|\hat{w}_{ee}|ij\rangle (\mathbf{X}_{n,\lambda})^*_{ia}(\mathbf{Y}_{n,\lambda})_{jb}$$
$$+ \langle aj|\hat{w}_{ee}|ib\rangle [(\mathbf{X}_{n,\lambda})^*_{ia}(\mathbf{X}_{n,\lambda})_{jb} - \delta_{ij}\delta_{ab}]\}, \quad \text{(B13)}$$

where out of the integrals $\langle ps|\hat{w}|qr\rangle$ associated with the general perturbation operator only the integrals of the type $\langle ib|\hat{w}_{ee}|aj\rangle$ associated with the two-electron contribution of the perturbation operator survive because of the occupied-virtual-occupied-virtual structure of the two-particle density matrix. Using now real spin orbitals, the correlation energy can be simplified to

$$E_c = \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb} \langle ib|\hat{w}_{ee}|aj\rangle (\mathbf{P}_{c,\lambda})_{ia,jb}, \quad \text{(B14)}$$

where

$$(\mathbf{P}_{c,\lambda})_{ia,jb} = \sum_n (\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})_{ia}(\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})_{jb} - \delta_{ij}\delta_{ab}, \quad \text{(B15)}$$

or, in matrix form,

$$\mathbf{P}_{c,\lambda} = \sum_n (\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})(\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})^{\mathrm{T}} - \mathbf{1}. \quad \text{(B16)}$$

Using the well-known fact that if $\mathbf{A}_\lambda + \mathbf{B}_\lambda$ and $\mathbf{A}_\lambda - \mathbf{B}_\lambda$ are positive definite, the non-Hermitian eigenvalue equation (B9) with real spin orbitals can be transformed into the half-size symmetric eigenvalue equation

$$\mathbf{M}_\lambda \mathbf{Z}_{n,\lambda} = \omega^2_{n,\lambda}\mathbf{Z}_{n,\lambda}, \quad \text{(B17)}$$

where $\mathbf{M}_\lambda = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2}(\mathbf{A}_\lambda + \mathbf{B}_\lambda)(\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2}$ and with eigenvectors $\mathbf{Z}_{n,\lambda} = \sqrt{\omega_{n,\lambda}}(\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{-1/2}(\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})$, and using the spectral decomposition $\mathbf{M}_\lambda^{-1/2} = \sum_n \omega^{-1}_{n,\lambda}\mathbf{Z}_{n,\lambda}\mathbf{Z}^{\mathrm{T}}_{n,\lambda}$, the correlation two-particle density matrix $\mathbf{P}_{c,\lambda}$ can be expressed as

$$\mathbf{P}_{c,\lambda} = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2}\,\mathbf{M}_\lambda^{-1/2}\,(\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} - \mathbf{1}. \quad \text{(B18)}$$

B. Expressions for spin-restricted closed-shell calculations

For spin-restricted closed-shell calculations, the eigenvectors $(\mathbf{X}_{n,\lambda}, \mathbf{Y}_{n,\lambda})$ can be transformed into spin-singlet excitation and diexcitation vectors,

$$({}^1\mathbf{x}_{n,\lambda})_{ia} = \frac{1}{\sqrt{2}}[(\mathbf{X}_{n,\lambda})_{i\uparrow a\uparrow} + (\mathbf{X}_{n,\lambda})_{i\downarrow a\downarrow}], \quad \text{(B19a)}$$

$$({}^1\mathbf{y}_{n,\lambda})_{ia} = \frac{1}{\sqrt{2}}[(\mathbf{Y}_{n,\lambda})_{i\uparrow a\uparrow} + (\mathbf{Y}_{n,\lambda})_{i\downarrow a\downarrow}], \quad \text{(B19b)}$$

and spin-triplet excitation and diexcitation vectors,

$$({}^{3,0}\mathbf{x}_{n,\lambda})_{ia} = \frac{1}{\sqrt{2}}[(\mathbf{X}_{n,\lambda})_{i\uparrow a\uparrow} - (\mathbf{X}_{n,\lambda})_{i\downarrow a\downarrow}], \quad \text{(B20a)}$$

$$({}^{3,0}\mathbf{y}_{n,\lambda})_{ia} = \frac{1}{\sqrt{2}}[(\mathbf{Y}_{n,\lambda})_{i\uparrow a\uparrow} - (\mathbf{Y}_{n,\lambda})_{i\downarrow a\downarrow}], \quad \text{(B20b)}$$

$$({}^{3,-1}\mathbf{x}_{n,\lambda})_{ia} = (\mathbf{X}_{n,\lambda})_{i\uparrow a\downarrow}, \quad \text{(B20c)}$$

$$({}^{3,-1}\mathbf{y}_{n,\lambda})_{ia} = (\mathbf{Y}_{n,\lambda})_{i\downarrow a\uparrow}, \quad \text{(B20d)}$$

$$({}^{3,1}\mathbf{x}_{n,\lambda})_{ia} = (\mathbf{X}_{n,\lambda})_{i\downarrow a\uparrow}, \quad \text{(B20e)}$$

$$({}^{3,1}\mathbf{y}_{n,\lambda})_{ia} = (\mathbf{Y}_{n,\lambda})_{i\uparrow a\downarrow}, \quad \text{(B20f)}$$

the indices i, a, j, b referring now to spatial orbitals. With this transformation, the linear-response eigenvalue equation (B9) decouples into a singlet eigenvalue equation,

$$\begin{pmatrix} {}^1\mathbf{A}_\lambda & {}^1\mathbf{B}_\lambda \\ {}^1\mathbf{B}^*_\lambda & {}^1\mathbf{A}^*_\lambda \end{pmatrix} \begin{pmatrix} {}^1\mathbf{x}_{n,\lambda} \\ {}^1\mathbf{y}_{n,\lambda} \end{pmatrix} = {}^1\omega_{n,\lambda} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} {}^1\mathbf{x}_{n,\lambda} \\ {}^1\mathbf{y}_{n,\lambda} \end{pmatrix}, \quad \text{(B21)}$$

with the singlet orbital rotation Hessians,

$$({}^1\mathbf{A}_\lambda)_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \lambda\,[2\langle ib|\hat{w}_{ee}|aj\rangle - \xi\langle ib|\hat{w}_{ee}|ja\rangle]\,, \quad \text{(B22a)}$$

$$({}^1\mathbf{B}_\lambda)_{ia,jb} = \lambda\,[2\langle ab|\hat{w}_{ee}|ij\rangle - \xi\langle ab|\hat{w}_{ee}|ji\rangle]\,, \quad \text{(B22b)}$$

and three identical triplet eigenvalue equations,

$$\begin{pmatrix} {}^3\mathbf{A}_\lambda & {}^3\mathbf{B}_\lambda \\ {}^3\mathbf{B}^*_\lambda & {}^3\mathbf{A}^*_\lambda \end{pmatrix} \begin{pmatrix} {}^3\mathbf{x}_{n,\lambda} \\ {}^3\mathbf{y}_{n,\lambda} \end{pmatrix} = {}^3\omega_{n,\lambda} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} {}^3\mathbf{x}_{n,\lambda} \\ {}^3\mathbf{y}_{n,\lambda} \end{pmatrix}, \quad \text{(B23)}$$

with the triplet orbital rotation Hessians,

$$({}^3\mathbf{A}_\lambda)_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \lambda\xi\langle ib|\hat{w}_{ee}|ja\rangle, \quad \text{(B24a)}$$

$$({}^3\mathbf{B}_\lambda)_{ia,jb} = -\lambda\xi\langle ab|\hat{w}_{ee}|ji\rangle. \quad \text{(B24b)}$$

Performing the sums over spins in the correlation energy expression of Eq. (B14), one gets, for real spatial orbitals,

$$E_c = \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb} \langle ib|\hat{w}_{ee}|aj\rangle ({}^1\mathbf{P}_{c,\lambda})_{ia,jb}, \quad \text{(B25)}$$

where remains only the contribution from the spin-singlet-adapted correlation two-particle density matrix $({}^1\mathbf{P}_{c,\lambda})_{ia,jb} = \sum_{\sigma_1=\uparrow,\downarrow}\sum_{\sigma_2=\uparrow,\downarrow}(\mathbf{P}_{c,\lambda})_{i\sigma_1 a\sigma_1, j\sigma_2 b\sigma_2}$, which can be calculated similarly as before,

$$\begin{aligned}{}^1\mathbf{P}_{c,\lambda} &= 2\left[\sum_n ({}^1\mathbf{x}_{n,\lambda} + {}^1\mathbf{y}_{n,\lambda})({}^1\mathbf{x}_{n,\lambda} + {}^1\mathbf{y}_{n,\lambda})^{\mathrm{T}} - \mathbf{1}\right] \\ &= 2[({}^1\mathbf{A}_\lambda - {}^1\mathbf{B}_\lambda)^{1/2}\,{}^1\mathbf{M}_\lambda^{-1/2}({}^1\mathbf{A}_\lambda - {}^1\mathbf{B}_\lambda)^{1/2} - \mathbf{1}],\end{aligned} \quad \text{(B26)}$$

where ${}^1\mathbf{M}_\lambda = ({}^1\mathbf{A}_\lambda - {}^1\mathbf{B}_\lambda)^{1/2}({}^1\mathbf{A}_\lambda + {}^1\mathbf{B}_\lambda)({}^1\mathbf{A}_\lambda - {}^1\mathbf{B}_\lambda)^{1/2}$.

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