van der Waals forces in density functional theory: Perturbational long-range electron-interaction corrections

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Long-range exchange and correlation effects, responsible for the failure of currently used approximate density functionals in describing van der Waals forces, are taken into account explicitly after a separation of the electron-electron interaction in the Hamiltonian into short- and long-range components. We propose a "range-separated hybrid" functional based on a local density approximation for the short-range exchange-correlation energy, combined with a long-range exact exchange energy. Long-range correlation effects are added by a second-order perturbational treatment. The resulting scheme is general and is particularly well-adapted to describe van der Waals complexes, like rare gas dimers.

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I. INTRODUCTION

Van der Waals (dispersion) interactions are universal attractive forces due to long-range correlation of electrons between weakly- or non-overlapping electron groups [1]. They play an important role in the cohesive energy of practically all kinds of materials: intermolecular complexes, extended systems, like molecular crystals, liquids or biological macromolecules. Although, in principle, density functional theory (DFT) [2] within the Kohn-Sham (KS) scheme [3] is able to provide the exact ground state energy of an electronic system, present approximate density functionals are inappropriate to describe long-range electron correlation and consequently fail for van der Waals interactions, manifested by their incapacity of reproducing the correct R^{-6} asymptotic behaviour of the intermolecular potential [4].

Several propositions have been published recently to add the missing long-range correlation contribution or to use asymptotically correct correlation energy expressions in DFT. Most of these methods require a partitioning of the system into interacting parts and are valid only for large separations [5–7]. Seamless dispersion energy functionals [8], that are valid for the whole range of possible intermolecular separations have also been proposed [9]. A general problem in schemes that use an additive correction to standard functionals is the double counting of a part of the correlation effects that are already present in the original functional.

Moreover, it is not enough to add missing correlation effects to traditional density functionals. Many of the present approximate functionals, like the local density approximation (LDA) which is well-known for its notorious overbinding tendency, and also many popular generalized gradient approximations (GGA), already predict a more-or-less pronounced bound state for simple van der Waals complexes, like rare gas dimers [10]. As it has been pointed out by Harris twenty years ago [11], this behaviour is related to the erroneous distance dependence of approximate exchange functionals. In effect, in self-interaction corrected calculations the minimum on the potential curve disappears [5]. Therefore, in order to describe correctly both the minimum and the asymptotic region of van der Waals potential energy surfaces it is mandatory to remove the unphysical bonding by appropriately correcting the exchange functional.

Here, we propose a scheme based on a long-range/short-range decomposition of the electron interaction which meets the above requirements and remedies the description of van der Waals forces in the framework of a first-principles approach, which takes into account simultaneously long-range correlation and exchange effects, avoids double counting and is size-extensive.

Our scheme is based on the hypothesis that for the description of van der Waals (London) dispersion forces one should improve the representation of long-range electron interaction (exchange and correlation) effects. At a first level of approximation, we treat the long-range exchange energy explicitly while maintaining a density functional approximation for the short-range exchange-correlation energy. This step defines a "range-separated hybrid" (RSH) scheme, which is corrected in a second step for the long-range correlation effects by a second-order perturbation theory, leading to size extensive Møller-Plesset (MP2)-like correction. This method will be referred to as RSH+MP2.

The idea of a long-range/short-range decomposition of the electron interaction is not new (see, e.g., Refs. 12–16). In the context of DFT, this approach has been used to construct multi-determinantal extensions of the KS scheme [17–24]. A density functional scheme with correct asymptotic behaviour has been proposed along these lines very recently by Baer and

Neuhauser [25] and the correct $1/r$ asymptotic behaviour of the long-range exact exchange has been also exploited in time-dependent DFT calculations of polarizabilities [26, 27], constituting the major motivation of the recent development of "Coulomb attenuated" hybrid functionals [28]. Heyd, Scuseria and Ernzerhof applied an inverse range-separation in order to get rid of the convergence problems of the exact exchange in solid-state calculations [29, 30]. Their HSE03 functional is a generalization of the PBE0 hybrid functional [31] where the long-range portion of the exact exchange is replaced by the long-range component of the PBE exchange functional [32].

In the context of the calculation of van der Waals energies, the idea of separating the electron interaction operator to short- and long-range components has already been explored by the work of Kohn, Meier and Makarov, who applied the adiabatic connection – fluctuation-dissipation approach for long-range electron interactions [33], leading to an asymptotically correct expression of the dispersion forces. It has also been shown [34] that the artificial minimum of the rare gas dimer potential curves can be removed by an exact treatment of the long-range exchange.

The second order perturbational treatment of the *full* Coulomb interaction has already been used by several authors for the van der Waals problem [5, 35, 36], and it was shown that the resulting asymptotic potential has the qualitatively correct $1/R^6$ form. As shown very recently, quantitatively reliable asymptotic form of the potential energy curve can be expected from adiabatic connection – fluctuation-dissipation theory calculations [37].

The general theoretical framework is outlined in Section II, describing the RSH scheme and the second-order perturbational treatment of long-range correlation effects. As described in Section III, our approach has been tested on rare gas dimers. These systems are typical van der Waals complexes, where the attractive interactions are exclusively due to London dispersion forces. They constitute a stringent test of the method, since the potential curves have very shallow minima of the order of about 100 μH.

Unless otherwise stated, atomic units is assumed throughout this work.

II. THEORY

A. Multi-determinantal extension of the Kohn-Sham scheme

We first recall the principle of the multi-determinantal extension of the KS scheme based on a long-range/short-range decomposition (see, e.g., Ref. 24 and references therein).

The starting point is the decomposition the Coulomb electron-electron interaction $w_{ee}(r) = 1/r$ as

$$w_{ee}(r) = w_{ee}^{\mathrm{lr},\mu}(r) + w_{ee}^{\mathrm{sr},\mu}(r), \tag{1}$$

where $w_{ee}^{\mathrm{lr},\mu}(r) = \mathrm{erf}(\mu r)/r$ is a long-range interaction and $w_{ee}^{\mathrm{sr},\mu}(r)$ is the complement short-range interaction. This decomposition is controlled by a single parameter μ. For $\mu = 0$, the long-range interaction vanishes, $w_{ee}^{\mathrm{lr},\mu=0}(r) = 0$, and the short-range interaction reduces to the Coulomb interaction, $w_{ee}^{\mathrm{sr},\mu=0}(r) = w_{ee}(r)$. Symmetrically, for $\mu \to \infty$, the short-range interaction vanishes, $w_{ee}^{\mathrm{sr},\mu\to\infty}(r) = 0$, and the long-range interaction reduces to the Coulomb interaction, $w_{ee}^{\mathrm{lr},\mu\to\infty}(r) = w_{ee}(r)$. Physically, $1/\mu$ represents the distance at which the separation is made.

The Coulombic universal density functional $F[n] = \min_{\Psi\to n}\langle\Psi|\hat{T} + \hat{W}_{ee}|\Psi\rangle$ [38], where $\hat{T}$ is the kinetic energy operator, $\hat{W}_{ee} = (1/2)\iint d\mathbf{r}_1 d\mathbf{r}_2 w_{ee}(r_{12})\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)$ is the Coulomb electron-electron interaction operator expressed with the pair-density operator $\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)$, is then decomposed as

$$F[n] = F^{\mathrm{lr},\mu}[n] + E_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n], \tag{2}$$

where $F^{\mathrm{lr},\mu}[n] = \min_{\Psi\to n}\langle\Psi|\hat{T} + \hat{W}_{ee}^{\mathrm{lr},\mu}|\Psi\rangle$ is a long-range universal density functional associated to the interaction operator $\hat{W}_{ee}^{\mathrm{lr},\mu} = (1/2)\iint d\mathbf{r}_1 d\mathbf{r}_2 w_{ee}^{\mathrm{lr},\mu}(r_{12})\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)$, and $E_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n] = E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] + E_{xc}^{\mathrm{sr},\mu}[n]$ is by definition the corresponding complement short-range energy functional, composed by a trivial short-range Hartree contribution $E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] = (1/2)\iint d\mathbf{r}_1 d\mathbf{r}_2 w_{ee}^{\mathrm{sr},\mu}(r_{12})n(\mathbf{r}_1)n(\mathbf{r}_2)$ and an unknown short-range exchange-correlation contribution $E_{xc}^{\mathrm{sr},\mu}[n]$. At $\mu = 0$, the long-range functional reduces to the usual KS kinetic energy functional, $F^{\mathrm{lr},\mu=0}[n] = T_s[n]$, and the short-range functional to the usual Hartree-exchange-correlation functional, $E_{\mathrm{H}xc}^{\mathrm{sr},\mu=0}[n] = E_{\mathrm{H}xc}[n]$. In the limit $\mu \to \infty$, the long-range functional reduces to the Coulombic universal functional, $F^{\mathrm{lr},\mu\to\infty}[n] = F[n]$, and the short-range functional vanishes, $E_{\mathrm{H}xc}^{\mathrm{sr},\mu\to\infty}[n] = 0$.

The exact ground-state energy of a N-electron system in an external nuclei-electron potential $v_{ne}(\mathbf{r})$, $E = \min_{n\to N}\Big\{F[n] + \int d\mathbf{r} v_{ne}(\mathbf{r})n(\mathbf{r})\Big\}$ where the search is over all N-representable densities, can be re-expressed using the long-range/short-range decomposition of $F[n]$

$$\begin{aligned} E &= \min_{n\to N}\Big\{F^{\mathrm{lr},\mu}[n] + E_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n] + \int d\mathbf{r} v_{ne}(\mathbf{r})n(\mathbf{r})\Big\} \\ &= \min_{\Psi\to N}\Big\{\langle\Psi|\hat{T} + \hat{W}_{ee}^{\mathrm{lr},\mu}|\Psi\rangle \\ &\qquad + \int d\mathbf{r} v_{ne}(\mathbf{r})n_\Psi(\mathbf{r}) + E_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n_\Psi]\Big\}, \end{aligned} \tag{3}$$

where the last search is carried out over all N-electron normalized (multi-determinantal) wave functions Ψ. In Eq. (3), $n_\Psi(\mathbf{r})$ is the density coming from the wave function Ψ, i.e. $n_\Psi(\mathbf{r}) = \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle$ where $\hat{n}(\mathbf{r})$ is the density operator.

The minimizing wave function Ψ^μ in Eq. (3) is given by the corresponding Euler-Lagrange equation

$$\Big(\hat{T} + \hat{W}_{ee}^{\mathrm{lr},\mu} + \hat{V}_{ne} + \hat{V}_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n_{\Psi^\mu}]\Big)|\Psi^\mu\rangle = \mathcal{E}^\mu|\Psi^\mu\rangle, \tag{4}$$

where $\hat{V}_{ne} = \int d\mathbf{r} v_{ne}(\mathbf{r})\hat{n}(\mathbf{r})$, $\hat{V}_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n] = \int d\mathbf{r} v_{\mathrm{H}xc}^{\mathrm{sr},\mu}(\mathbf{r})\hat{n}(\mathbf{r})$ with the short-range Hartree-exchange-correlation potential $v_{\mathrm{H}xc}^{\mathrm{sr},\mu}(\mathbf{r}) = \delta E_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n]/\delta n(\mathbf{r})$, and $\mathcal{E}^\mu$ is the Lagrange multiplier associated to the constraint of the normalization of the wave function. Eq. (4) defines a long-range interacting effective Hamiltonian $\hat{H}^\mu = \hat{T} + \hat{W}_{ee}^{\mathrm{lr},\mu} + \hat{V}_{ne} + \hat{V}_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n_{\Psi^\mu}]$ that must

be solved iteratively for its multi-determinantal ground-state wave function Ψ^μ which gives, in principle, the exact physical ground-state density $n(\mathbf{r}) = n_{\Psi^\mu}(\mathbf{r}) = \langle\Psi^\mu|\hat{n}(\mathbf{r})|\Psi^\mu\rangle$, independently of μ. Finally, the exact ground-state energy expression is thus

$$E = \langle\Psi^\mu|\hat{T} + \hat{W}_{ee}^{\rm lr,\mu} + \hat{V}_{ne}|\Psi^\mu\rangle + E_{\rm Hxc}^{\rm sr,\mu}[n_{\Psi^\mu}]. \quad (5)$$

This exact formalism enables to combine a long-range wave function calculation with a short-range density functional. In the special case of $\mu = 0$, the KS scheme is recovered, while the limit $\mu \to \infty$ corresponds to the usual wave function formulation of the electronic problem.

A short-range LDA [39] and other beyond-LDA [24, 40] approximations have been constructed to successfully describe the functional $E_{xc}^{\rm sr,\mu}[n]$. In previous applications of the method, the long-range part of the calculation has been handled by configuration interaction [21] or multi-configurational self-consistent field (MCSCF) [23] methods. We propose in this work to use instead perturbation theory.

B. Range-separated hybrid

At a first level of approximation, we introduce the RSH scheme by restricting the search in Eq. (3) to N-electron normalized one-determinant wave functions Φ

$$E^{\mu,\rm RSH} = \min_{\Phi\to N}\Big\{\langle\Phi|\hat{T} + \hat{W}_{ee}^{\rm lr,\mu}|\Phi\rangle + \int d\mathbf{r} v_{ne}(\mathbf{r}) n_\Phi(\mathbf{r}) + E_{\rm Hxc}^{\rm sr,\mu}[n_\Phi]\Big\}. \quad (6)$$

The associated minimizing one-determinant wave function Φ^μ satisfies the Euler-Lagrange equation

$$\left(\hat{T} + \hat{V}_{ne} + \hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi^\mu] + \hat{V}_{\rm Hxc}^{\rm sr,\mu}[n_{\Phi^\mu}]\right)|\Phi^\mu\rangle = \mathcal{E}_0^\mu|\Phi^\mu\rangle, \quad (7)$$

where $\hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi]$ is a long-range potential operator appearing due to the restriction to one-determinant wave functions as in Hartree-Fock (HF) theory, and $\mathcal{E}_0^\mu$ is the Lagrange multiplier associated to the normalization constraint. As usual, $\hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi]$ is the sum of a Hartree contribution, $\hat{V}_{\rm H,HF}^{\rm lr,\mu}[\Phi] = \iint d\mathbf{r}_1 d\mathbf{r}_2 w_{ee}^{\rm lr,\mu}(r_{12})\langle\Phi|\hat{n}(\mathbf{r}_1)|\Phi\rangle\hat{n}(\mathbf{r}_2)$, and a non-local exchange contribution, $\hat{V}_{x,{\rm HF}}^{\rm lr,\mu}[\Phi] = -(1/2)\iint d\mathbf{r}_1 d\mathbf{r}_2 w_{ee}^{\rm lr,\mu}(r_{12})\langle\Phi|\hat{n}_1(\mathbf{r}_2,\mathbf{r}_1)|\Phi\rangle\hat{n}_1(\mathbf{r}_1,\mathbf{r}_2)$, where $\hat{n}_1(\mathbf{r}_1,\mathbf{r}_2)$ is the first-order density matrix operator. Eq. (7) defines the RSH non-interacting effective Hamiltonian $\hat{H}_0^\mu = \hat{T} + \hat{V}_{ne} + \hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi^\mu] + \hat{V}_{\rm Hxc}^{\rm sr,\mu}[n_{\Phi^\mu}]$ that must be solved iteratively for its one-determinant ground-state wave function Φ^μ. Of course, Φ^μ does not give the exact physical density: $n_{\Phi^\mu} \neq n$.

The RSH energy expression is finally

$$E^{\mu,\rm RSH} = \langle\Phi^\mu|\hat{T} + \hat{V}_{ne}|\Phi^\mu\rangle + E_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi^\mu] + E_{\rm Hxc}^{\rm sr,\mu}[n_{\Phi^\mu}], \quad (8)$$

where $E_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi] = \langle\Phi|\hat{W}_{ee}^{\rm lr,\mu}|\Phi\rangle$ is the HF-like long-range Hartree-exchange energy. Eq. (8) defines a single-parameter hybrid scheme combining a long-range HF calculation with a short-range density functional. The case $\mu = 0$ still corresponds to the KS scheme while the method reduces now to a standard HF calculation in the limit $\mu \to \infty$.

We note that an equivalent to the RSH scheme has been investigated recently by Pedersen and Jensen [23] as a special case of the combination of a long-range MCSCF calculation with a short-range density functional.

C. Long-range correlation corrections by perturbation theory

We develop now a long-range perturbation theory, using the RSH determinant Φ^μ as the reference. To do so, we introduce the following energy expression with a formal coupling constant λ

$$E^{\mu,\lambda} = \min_{\Psi\to N}\Big\{\langle\Psi|\hat{T} + \hat{V}_{ne} + \hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi^\mu] + \lambda\hat{\mathcal{W}}^{\rm lr,\mu}|\Psi\rangle + E_{\rm Hxc}^{\rm sr,\mu}[n_\Psi]\Big\}, \quad (9)$$

where the search is carried out over all N-electron normalized (multi-determinantal) wave functions Ψ and $\hat{\mathcal{W}}^{\rm lr,\mu}$ is the long-range fluctuation potential operator

$$\hat{\mathcal{W}}^{\rm lr,\mu} = \hat{W}_{ee}^{\rm lr,\mu} - \hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi^\mu]. \quad (10)$$

The minimizing wave function $\Psi^{\mu,\lambda}$ in Eq. (9) is given by the Euler-Lagrange equation

$$\left(\hat{T} + \hat{V}_{ne} + \hat{V}_{{\rm H}x,{\rm HF}}^{\rm lr,\mu}[\Phi^\mu] + \lambda\hat{\mathcal{W}}^{\rm lr,\mu} + \hat{V}_{\rm Hxc}^{\rm sr,\mu}[n_{\Psi^{\mu,\lambda}}]\right)|\Psi^{\mu,\lambda}\rangle = \mathcal{E}^{\mu,\lambda}|\Psi^{\mu,\lambda}\rangle, \quad (11)$$

where $\mathcal{E}^{\mu,\lambda}$ is the Lagrange multiplier associated to the normalization constraint. For $\lambda = 1$, the physical energy is recovered, $E = E^{\mu,\lambda=1}$, in principle independently of μ, and Eq. (11) reduces to Eq. (4): $\Psi^{\mu,\lambda=1} = \Psi^\mu$, $\mathcal{E}^{\mu,\lambda=1} = \mathcal{E}^\mu$. For $\lambda = 0$, Eq. (11) reduces to the RSH effective Schrödinger equation of Eq. (7): $\Psi^{\mu,\lambda=0} = \Phi^\mu$, $\mathcal{E}^{\mu,\lambda=0} = \mathcal{E}_0^\mu$.

We expand $E^{\mu,\lambda}$ in powers of λ, $E^{\mu,\lambda} = \sum_{k=0}^\infty E^{\mu,(k)}\lambda^k$, and apply the general results of the non-linear Rayleigh-Schrödinger perturbation theory [41–43] outlined in the Appendix. It is easy to verify that the sum of zeroth- and first-order energy contributions gives back the RSH total energy

$$E^{\mu,(0)} + E^{\mu,(1)} = E^{\mu,\rm RSH}. \quad (12)$$

The second-order correction can be written as

$$E^{\mu,(2)} = -\langle\Phi^\mu|\hat{\mathcal{W}}^{\rm lr,\mu}\left(1 + \hat{R}_0^\mu\hat{G}_0^\mu\right)^{-1}\hat{R}_0^\mu\hat{\mathcal{W}}^{\rm lr,\mu}|\Phi^\mu\rangle, \quad (13)$$

where $\hat{R}_0^\mu$ is the reduced resolvent

$$\hat{R}_0^\mu = \sum_I \frac{|\Phi_I^\mu\rangle\langle\Phi_I^\mu|}{\mathcal{E}_{0,I}^\mu - \mathcal{E}_0^\mu}, \quad (14)$$

in terms of the excited eigenfunctions Φ_I^μ and eigenvalues $\mathcal{E}_{0,I}^\mu$ of the RSH effective Hamiltonian $\hat{H}_0^\mu$, and $\hat{G}_0^\mu$ is a short-range screening operator

$$\hat{G}_0^{\mathrm{sr},\mu} = 2 \iint d\mathbf{r} d\mathbf{r}' \hat{n}(\mathbf{r}) |\Phi^\mu\rangle f_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n_{\Phi^\mu}](\mathbf{r},\mathbf{r}') \langle\Phi^\mu| \hat{n}(\mathbf{r}'), \tag{15}$$

with the short-range Hartree-exchange-correlation kernel $f_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n](\mathbf{r},\mathbf{r}') = \delta^2 E_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n]/\delta n(\mathbf{r}) \delta n(\mathbf{r}')$.

Let insert the spectral resolution of Eq. (14) in Eq. (13). Since $\hat{\mathcal{W}}^{\mathrm{lr}}$ is a two-electron operator only singly and doubly excited determinants, $\Phi_{i\to a}^\mu$ and $\Phi_{ij\to ab}^\mu$ where i, j refer to occupied spin-orbitals and a, b to virtual spin-orbitals of Φ^μ, can *a priori* contribute to $E^{\mu,(2)}$. Actually, singly excited determinants gives vanishing matrix elements, $\langle\Phi_{i\to a}^\mu|\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi^\mu\rangle = 0$, since it can be easily verified that $\langle\Phi_{i\to a}^\mu|\hat{W}_{ee}^{\mathrm{lr}}|\Phi^\mu\rangle = \langle\Phi_{i\to a}^\mu|\hat{V}_{\mathrm{H}x,\mathrm{HF}}^{\mathrm{lr},\mu}[\Phi^\mu]|\Phi^\mu\rangle$, as in standard HF theory. Consequently, the product $\hat{R}_0^\mu \hat{G}_0^\mu$ in Eq. (13) involves vanishing matrix elements, $\langle\Phi^\mu|\hat{n}(\mathbf{r})|\Phi_{ij\to ab}^\mu\rangle = 0$, i.e. the non-linear terms are zero with the present choice of the perturbation operator $\hat{\mathcal{W}}^{\mathrm{lr}}$. The second-order energy correction is thus

$$\begin{aligned} E^{\mu,(2)} &= -\langle\Phi^\mu|\hat{\mathcal{W}}^{\mathrm{lr},\mu}\hat{R}_0^\mu\hat{\mathcal{W}}^{\mathrm{lr},\mu}|\Phi^\mu\rangle \\ &= \sum_{\substack{i<j \\ a<b}} \frac{|\langle\Phi_{ij\to ab}^\mu|\hat{W}_{ee}^{\mathrm{lr},\mu}|\Phi^\mu\rangle|^2}{\mathcal{E}_0^\mu - \mathcal{E}_{0,ij\to ab}^\mu} \\ &= \sum_{\substack{i<j \\ a<b}} \frac{|\langle\phi_i^\mu\phi_j^\mu|\hat{w}_{ee}^{\mathrm{lr},\mu}|\phi_a^\mu\phi_b^\mu\rangle - \langle\phi_i^\mu\phi_j^\mu|\hat{w}_{ee}^{\mathrm{lr},\mu}|\phi_b^\mu\phi_a^\mu\rangle|^2}{\varepsilon_i^\mu + \varepsilon_j^\mu - \varepsilon_a^\mu - \varepsilon_b^\mu}, \end{aligned} \tag{16}$$

where ϕ_k^μ is a spin-orbital of Φ^μ and ε_k^μ is its associated eigenvalue, $\langle\phi_i^\mu\phi_j^\mu|\hat{w}_{ee}^{\mathrm{lr},\mu}|\phi_a^\mu\phi_b^\mu\rangle$ are the two-electron integrals associated to the long-range interaction $w_{ee}^{\mathrm{lr},\mu}(r_{12})$, and we recall that the indexes i, j refer to occupied spin-orbitals and a, b to virtual spin-orbitals. Eq. (16) is fully analogous to the conventional MP2 energy correction. The total RSH+MP2 energy is $E^{\mu,\mathrm{RSH+MP2}} = E^{\mu,\mathrm{RSH}} + E^{\mu,(2)}$.

¿From a practical point of view, once the RSH orbitals and one-electron eigenvalues are available, any standard MP2 implementation can be used, provided that the long-range electron repulsion integrals corresponding to the RSH orbitals are plugged in. Due to the long-range nature of these integrals one can take advantage of efficient modern algorithms, like the local MP2 [44], multipolar integral approximations, which have particularly favorable convergence properties for long-range part of the split Coulomb interaction [45], or the resolution of identity approach [46]. It means that in appropriate implementations the extra cost of the MP2 corrections can be made negligible for large systems with respect to the resolution of the self-consistent RSH equations, similar to a usual KS calculations with a hybrid functional. Solid state applications for semi-conductors can also be envisaged on Wannier orbital-based MP2 implementations [47].

System	d_m (a.u.)	ε_m (μH)	C_6^{fit}(a.u.)	C_6^{exp}(a.u.)
He_2	5.62	34.87	1.534	1.461
Ne_2	5.84	134.18	6.860	6.282
Ar_2	7.10	454.50	73.19	63.75
Kr_2	7.58	639.42	153. 1	129.6

TABLE I: Absolute parameters of the reference potential curves determined from Ref. 52. The C_6^{fit} coefficients were obtained from a logarithmic fit in the same conditions as explained for the calculated potentials.

III. RESULTS AND CONCLUSIONS

The above described RSH+MP2 approach has been applied to rare gas dimers, using a LDA-based short-range exchange-correlation functional with a range-separation parameter of $\mu = 0.5$. This latter value corresponds to the smallest mean average error of the atomization energies calculated by the RSH scheme for the G2-1 set (a subset of 55 molecules of the G3 set [48, 49]) of small molecules [50]. This value is in agreement with the intuitive picture predicting that $1/\mu$ should be close to the physical dimensions of a valence electron pair. The interaction energies were calculated with a modified version of the MOLPRO package [51]. The basis set superposition error (BSSE) has been removed by the counterpoise method.

The results are presented as reduced potentials, $U^*(r^*) = U(r^* \cdot d_m)/\varepsilon_m$, where the reduced variables $U^* = U/\varepsilon_m$ and $r^* = r/d_m$, are defined with respect to the equilibrium distance d_m and the well-depth ε_m of accurate "experimental" potential curves [52] (cf. Table I). The calculated potentials are characterized by the hard core radius, σ^* defined by $U^*(\sigma^*) = 0$ (experimentally $\sigma^* \approx 0.89$), the reduced well depth, U_m^*, and the equilibrium distance, r_m^*, (experimentally, by construction, $U_m^* = -1$ and $r_m^* = 1$). The minimum region is also characterized by the harmonic vibrational frequencies, ω, related to the second derivative of the potential at the minimum.

The long-range behaviour of the potential energy curves can be appreciated from the C_6 coefficients. Experimental C_6 coefficients are usually obtained from optical data (dipole oscillator strength distributions) [53] and characterize the purely dipolar contribution to the long-range interaction energy. Since we had no access to such a decomposition of the interaction energy, we have determined an effective C_6 coefficient by a logarithmic fit of the interaction energies between 30 and 60 Bohrs. This quantity, which includes higher order multipolar effects too, is presented in the form of a reduced variable, $C_6^* = C_6/C_6^{\mathrm{fit}}$. Here C_6^{fit} has been obtained from an analogous fit to the points of the reference potential reported in Table I. For the sake of comparison, the experimental C_6^{exp} (purely dipolar) values are also reported.

The RSH and RSH+MP2 potential curves, as well as the HF, the standard MP2 and the coupled-cluster CCSD(T) ones, calculated with the aug-cc-pVTZ basis set are represented for the four dimers in Figure 1, and compared to the experimental curves. Note that the reduced representations of the ex-

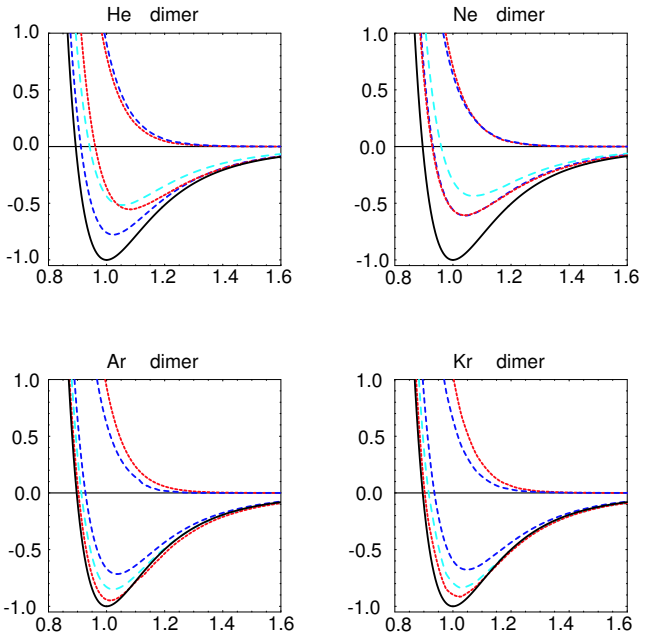

FIG. 1: Reduced HF (dotted repulsive), RSH (dashed repulsive), MP2 (long dashed), CCSD(T) (dashed), RSH+MP2 (dotted) and Tang-Toennis reference (full) potential curves for He_2, Ne_2, Ar_2 and Kr_2 dimers.

perimental potentials of different rare gas dimers are practically indistinguishable. The calculated RSH potentials are always repulsive, like the HF ones. The RSH+MP2 potentials are slightly too repulsive at short interatomic distances, as reflected by the values of the hard core radii, systematically higher than the experiment (around 0.89). The RSH+MP2 and CCSD(T) curves are almost the same for Ne_2 with a well depth of around $U_m^* = 0.6$, while the RSH+MP2 minima of the Ar_2 and Kr_2 systems are even better ($U_m^* > 0.9$) than the CCSD(T) ones ($U_m^* \approx 0.7$). The position of the minimum is predicted within 1–4% in the RSH+MP2 approximation. The 6–8% deviation found for the He_2 RSH+MP2 minimum can be explained by an exaggerated repulsion, reflected by the highest σ^* found in this case. In comparison with the usual MP2 potential curves, the RSH+MP2 follow similar trends, being systematically more stabilizing and closer to the experimental curve.

The main quantitative features of the RSH+MP2 potentials obtained by the aug-cc-pVTZ and aug-cc-pV5Z basis sets [54–57] are summarized in Table II and compared to the results of standard MP2 and CCSD(T) supermolecule calculations with the same basis sets. The basis set has a non-negligible effect on the calculated parameters of the potential curves, which converge systematically towards the experimental values for all the properties. For He_2 the double augmented d-aug-cc-pV5Z basis set results are also included, representing a further improvement of the well depth, but having practically no effect on the equilibrium distance.

The basis set superposition error of the equilibrium distances and of the interaction energies are reported in Table III, as the difference in the parameters of the BSSE-contaminated and BSSE-free reduced potential energy curves. The BSSE corrections on the bond lengths and on the interaction energies are always negative, i.e. the BSSE-contaminated distances are too short and the energies are too low. In some case, like the Ne_2 dimer with aug-cc-pVTZ basis, the binding energy correction may attain 55 or 67% of the well depth at the MP2 and CCSD(T) level of approximation. The corresponding RSH+MP2 BSSE effect is considerably smaller, but it is still 34%. The BSSE effect on the bond lengths are much less spectacular, but still more pronounced in the MP2 and CCSD(T) methods than in the RSH+MP2 approach. As a general trend we can conclude that the RSH+MP2 has usually less than the half of the MP2 or CCSD(T) basis set superposition errors. This is a considerable advantage for an efficient and reliable exploration of potential energy surfaces, especially when the lack of well-defined subsystems make impossible to perform a counterpoise correction.

Effective C_6^* coefficients obtained from the RSH+MP2 approach agree with the experiment within 5% for He_2 and Ne_2, and are overestimated by 15–20% for Ar_2 and Kr_2. It means that the asymptotic behaviour of the RSH+MP2 potential curves is reasonable. We recall that the exact C_6 coefficient is given by the Casimir-Polder relation [1]

$$C_6 = \frac{3\hbar}{\pi} \int_0^\infty d\omega \alpha_1(i\omega)\alpha_2(i\omega) \qquad (17)$$

where $\alpha_1(i\omega)$ and $\alpha_2(i\omega)$ are the exact dynamical polarizabilities of the monomers. It is known that the asymptotic form of the MP2 energy expression corresponds to an uncoupled HF-type, non-interacting approximation of the monomer polarizabilities. This means that MP2 calculations do not reproduce the *exact* C_6^* coefficients: usually they tend to overestimate them. For instance, in the case of the benzene dimer, this overestimation in the complete basis limit may reach a factor of 2; for less polarizable systems the situation is less critical. An analogous behaviour is expected for RSH+MP2. Note however, that in this case one-electron excitations are obtained from the self-consistent RSH one-electron states, which include, in addition to the long-range exact exchange, short-range exchange-correlation effects too. A more reliable approximation can be developed on the basis of the adiabatic connection – fluctuation-dissipation approach [33, 37] which would ensure, in principle, the exact asymptotic limit of the potential energy curves. The development of a range-separated version of this method is under progress.

In conclusion, the RSH+MP2 approach provides an efficient DFT-based description of weak intermolecular complexes bound by dispersion forces. Even in its simplest, LDA-based implementation, it represents a huge improvement over KS calculations, which lead to unreliable potential curves in the minimum region with a qualitatively wrong asymptotic behaviour. Range-separated extensions of other density functionals, like the gradient-corrected PBE functional, are in progress. By removing systematic errors of currently used approximate DFT functionals and introducing corrections which grasp the essential physics of van der Waals interactions, the RSH+MP2 approach extends the applicability of density functional calculations to weak intermolecular forces. Further

Method	MP2					CCSD(T)					RSH+MP2				
System	r_m^*	U_m^*	ω/ω_m	σ^*	C_6^*	r_m^*	U_m^*	ω/ω_m	σ^*	C_6^*	r_m^*	U_m^*	ω/ω_m	σ^*	C_6^*
He_2	1.000	-1.000	1.000	0.894	1.000	1.000	-1.000	1.000	0.894	1.000	1.000	-1.000	1.000	0.894	1.000
AVTZ	1.052	-0.516	1.058	0.941	0.754	1.023	-0.777	1.047	0.912	0.966	1.080	-0.553	1.141	0.961	1.008
AV5Z	1.036	-0.594	1.032	0.926	0.760	1.007	-0.896	1.019	0.896	0.980	1.078	-0.593	1.135	0.957	1.028
d-AV5Z	1.032	-0.629	1.032	0.923	0.763	1.003	-0.946	1.020	0.893	0.958	1.077	-0.613	1.135	0.955	1.038
Ne_2	1.000	-1.000	1.000	0.896	1.000	1.000	-1.000	1.000	0.896	1.000	1.000	-1.000	1.000	0.896	1.000
AVTZ	1.073	-0.435	1.004	0.960	0.766	1.041	-0.609	0.983	0.931	0.914	1.040	-0.605	0.965	0.928	0.950
AV5Z	1.043	-0.588	0.977	0.936	0.816	1.009	-0.877	0.950	0.904	0.990	1.036	-0.751	0.965	0.923	1.036
Ar_2	1.000	-1.000	1.000	0.897	1.000	1.000	-1.000	1.000	0.897	1.000	1.000	-1.000	1.000	0.897	1.000
AVTZ	1.023	-0.850	1.033	0.913	1.095	1.037	-0.715	1.051	0.927	0.958	1.012	-0.948	1.013	0.903	1.154
AV5Z	0.998	-1.062	0.996	0.891	1.136	1.011	-0.910	1.013	0.903	1.175	1.007	-1.040	1.003	0.896	1.215
Kr_2	1.000	-1.000	1.000	0.896	1.000	1.000	-1.000	1.000	0.896	1.000	1.000	-1.000	1.000	0.896	1.000
AVTZ	1.029	-0.840	1.049	0.918	1.124	1.048	-0.677	1.069	0.936	0.960	1.016	-0.919	1.011	0.905	1.136
AV5Z	1.002	-1.080	1.021	0.893	1.153	1.016	-0.898	1.038	0.908	0.980	1.007	-1.023	1.008	0.897	1.154

TABLE II: Reduced parameters of the calculated MP2, CCSD(T) and RSH+MP2 (μ =0.5) potential energy curves obtained by the aug-cc-pVTZ (AVTZ), aug-cc-pV5Z (AV5Z) and d-aug-cc-pV5Z (d-AV5Z) basis sets. Reduced experimental parameters are listed in the first line for each dimer. Absolute reference values are given in Table I.

Method	MP2		CCSD(T)		RSH+MP2	
System	r_m^*	U_m^*	r_m^*	U_m^*	r_m^*	U_m^*
He_2						
AVTZ	-0.007	-0.125	-0.008	-0.121	-0.000	-0.063
AV5Z	-0.004	-0.048	-0.002	-0.037	-0.001	-0.015
d-AV5Z	-0.008	-0.160	-0.007	-0.113	-0.001	-0.031
Ne_2						
AVTZ	-0.049	-0.547	-0.035	-0.674	-0.031	-0.335
AV5Z	-0.011	-0.150	-0.006	-0.148	-0.001	-0.025
Ar_2						
AVTZ	-0.020	-0.263	-0.023	-0.239	-0.007	-0.101
AV5Z	-0.005	-0.138	-0.004	-0.103	-0.002	-0.022
Kr_2						
AVTZ	-0.013	-0.191	-0.017	-0.174	-0.007	-0.126
AV5Z	-0.003	-0.073	-0.002	-0.049	-0.002	-0.039

TABLE III: BSSE correction for the reduced parameters r_m^* and U_m^*.

tests should decide whether this method is generally applicable to the important domains of the physisorption, or cohesion in molecular crystals and in layered semi-conductors.

Appendix A: Nonlinear Rayleigh-Schrödinger perturbation theory

Let us consider the following general total energy expression, involving a Hamiltonian $\hat{H}^{(0)}$, a perturbation operator $\hat{W}$ and a density functional $F[n]$,

$$E^\lambda = \min_{\Psi\to N}\Big\{\langle\Psi|\hat{H}^{(0)}+\lambda\hat{W}|\Psi\rangle + F[n_\Psi]\Big\}, \qquad \text{(A1)}$$

where the search is carried out over all N-electron normalized wave functions Ψ, $\langle\Psi|\Psi\rangle = 1$, and n_Ψ is the density coming from Ψ, $n_\Psi(\mathbf{r}) = \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle$, where $\hat{n}(\mathbf{r})$ is the density operator. In Eq. (A1), λ is a formal coupling constant; we are ultimately interested in the case $\lambda = 1$. The minimizing wave function Ψ^λ satisfies the Euler-Lagrange equation

$$\left(\hat{H}^{(0)}+\lambda\hat{W}+\hat{\Omega}^\lambda\right)|\Psi^\lambda\rangle = \mathcal{E}^\lambda|\Psi^\lambda\rangle, \qquad \text{(A2)}$$

where the eigenvalue $\mathcal{E}^\lambda$ comes from the normalization condition and $\hat{\Omega}^\lambda$ is a potential operator coming from the variation of $F[n]$, non linear in λ,

$$\hat{\Omega}^\lambda = \int d\mathbf{r}\frac{\delta F[n^\lambda]}{\delta n(\mathbf{r})}\hat{n}(\mathbf{r}), \qquad \text{(A3)}$$

where n^λ is the density coming from Ψ^λ, $n_\lambda(\mathbf{r}) = \langle\Psi^\lambda|\hat{n}(\mathbf{r})|\Psi^\lambda\rangle$.

Starting from the reference $\lambda = 0$, we develop a perturbation theory in λ. We introduce the intermediate normalized wave function $\tilde{\Psi}^\lambda$

$$|\tilde{\Psi}^\lambda\rangle = \frac{|\Psi^\lambda\rangle}{\langle\Psi^{\lambda=0}|\Psi^\lambda\rangle}, \qquad \text{(A4)}$$

and expand $\tilde{\Psi}^\lambda$, n^λ, $\hat{\Omega}^\lambda$ and $\mathcal{E}^\lambda$ in powers of λ: $\tilde{\Psi}^\lambda = \sum_{k=0}^\infty \tilde{\Psi}^{(k)}\lambda^k$, $n^\lambda = \sum_{k=0}^\infty n^{(k)}\lambda^k$, $\hat{\Omega}^\lambda = \sum_{k=0}^\infty \hat{\Omega}^{(k)}\lambda^k$ and $\mathcal{E}^\lambda = \sum_{k=0}^\infty \mathcal{E}^{(k)}\lambda^k$. The coefficients $n^{(k)}$ are obtained from the expansion of $\tilde{\Psi}^\lambda$ through

$$n^\lambda(\mathbf{r}) = \frac{\langle\tilde{\Psi}^\lambda|\hat{n}(\mathbf{r})|\tilde{\Psi}^\lambda\rangle}{\langle\tilde{\Psi}^\lambda|\tilde{\Psi}^\lambda\rangle}, \qquad \text{(A5)}$$

and the coefficients $\hat{\Omega}^{(k)}$ are found from the expansion of n^λ,

after expanding $\hat{\Omega}^\lambda$ around $n^{(0)}$,

$$\hat{\Omega}^\lambda = \int d\mathbf{r}\frac{\delta F[n^{(0)}]}{\delta n(\mathbf{r})}\hat{n}(\mathbf{r}) + \iint d\mathbf{r}d\mathbf{r}'\frac{\delta^2 F[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\Delta n^\lambda(\mathbf{r}')\hat{n}(\mathbf{r}) + \cdots . \tag{A6}$$

where $\Delta n^\lambda = n^\lambda - n^{(0)}$. The zeroth-order equation is

$$\left(\hat{H}^{(0)} + \hat{\Omega}^{(0)}\right)|\tilde{\Psi}^{(0)}\rangle = \mathcal{E}^{(0)}|\tilde{\Psi}^{(0)}\rangle, \tag{A7}$$

and of course $\tilde{\Psi}^{(0)} = \Psi^{\lambda=0}$. For the general order $k \geq 1$,

$$\left(\hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)}\right)|\tilde{\Psi}^{(k)}\rangle + \hat{W}|\tilde{\Psi}^{(k-1)}\rangle + \sum_{i=1}^{k}\hat{\Omega}^{(i)}|\tilde{\Psi}^{(k-i)}\rangle = \sum_{i=0}^{k}\mathcal{E}^{(i)}|\tilde{\Psi}^{(k-i)}\rangle. \tag{A8}$$

The corresponding eigenvalue correction of order k is

$$\mathcal{E}^{(k)} = \langle\tilde{\Psi}^{(0)}|\hat{W}|\tilde{\Psi}^{(k-1)}\rangle + \sum_{i=1}^{k}\langle\tilde{\Psi}^{(0)}|\hat{\Omega}^{(i)}|\tilde{\Psi}^{(k-i)}\rangle, \tag{A9}$$

containing, besides the usual first term, a "non-linearity" term as well. Introducing the reduced resolvent, $\hat{R}_0$,

$$\hat{R}_0 = \sum_I \frac{|\tilde{\Psi}_I^{(0)}\rangle\langle\tilde{\Psi}_I^{(0)}|}{\mathcal{E}_I^{(0)} - \mathcal{E}^{(0)}}, \tag{A10}$$

where $\tilde{\Psi}_I^{(0)}$ and $\mathcal{E}_I^{(0)}$ are the excited eigenfunctions and eigenvalues of $\hat{H}^{(0)}$, the wave function correction of order k writes

$$|\tilde{\Psi}^{(k)}\rangle = -\hat{R}_0\hat{W}|\tilde{\Psi}^{(k-1)}\rangle - \hat{R}_0\hat{\Omega}^{(k)}|\tilde{\Psi}^{(0)}\rangle - \hat{R}_0\sum_{i=1}^{k-1}\left(\hat{\Omega}^{(i)} - \mathcal{E}^{(i)}\right)|\tilde{\Psi}^{(k-i)}\rangle. \tag{A11}$$

The total energy can be re-expressed in terms of the eigenvalue $\mathcal{E}^\lambda$ and the "double counting correction" D^λ

$$E^\lambda = \mathcal{E}^\lambda + D^\lambda, \tag{A12}$$

where

$$D^\lambda = F[n^\lambda] - \int d\mathbf{r}\frac{\delta F[n^\lambda]}{\delta n(\mathbf{r})}n^\lambda(\mathbf{r}). \tag{A13}$$

We expand E^λ and D^λ in powers of λ: $E^\lambda = \sum_{k=0}^{\infty}E^{(k)}\lambda^k$ and $D^\lambda = \sum_{k=0}^{\infty}D^{(k)}\lambda^k$. The coefficients $D^{(k)}$ are found from the expansion of n^λ, after expanding D^λ around $n^{(0)}$,

$$\begin{aligned} D^\lambda &= F[n^{(0)}] + \int d\mathbf{r}\frac{\delta F[n^{(0)}]}{\delta n(\mathbf{r})}\Delta n^\lambda(\mathbf{r}) \\ &+\frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{\delta^2 F[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\Delta n^\lambda(\mathbf{r}')\Delta n^\lambda(\mathbf{r}) + \cdots \\ &- \int d\mathbf{r}\frac{\delta F[n^{(0)}]}{\delta n(\mathbf{r})}n^\lambda(\mathbf{r}) \\ &- \iint d\mathbf{r}d\mathbf{r}'\frac{\delta^2 F[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\Delta n^\lambda(\mathbf{r}')n^\lambda(\mathbf{r}) - \cdots . \end{aligned} \tag{A14}$$

The zeroth-order total energy is simply

$$E^{(0)} = \mathcal{E}^{(0)} + F[n^{(0)}] - \int d\mathbf{r}\frac{\delta F[n^{(0)}]}{\delta n(\mathbf{r})}n^{(0)}(\mathbf{r}), \tag{A15}$$

The general correction of order $k \geq 1$ writes

$$E^{(k)} = \langle\tilde{\Psi}^{(0)}|\hat{W}|\tilde{\Psi}^{(k-1)}\rangle + \Delta^{(k)} \tag{A16}$$

where $\Delta^{(k)}$ is

$$\Delta^{(k)} = \sum_{i=1}^{k}\langle\tilde{\Psi}^{(0)}|\hat{\Omega}^{(i)}|\tilde{\Psi}^{(k-i)}\rangle + D^{(k)}. \tag{A17}$$

At first order, it can be verified that the nonlinearity term of the eigenvalue and the double counting correction cancel each other, i.e. $\Delta^{(1)} = 0$, and we obtain the conventional first-order energy correction

$$E^{(1)} = \langle\tilde{\Psi}^{(0)}|\hat{W}|\tilde{\Psi}^{(0)}\rangle. \tag{A18}$$

At second order, the situation is analogous, i.e. $\Delta^{(2)} = 0$, and again the conventional form of the energy correction is retrieved

$$E^{(2)} = \langle\tilde{\Psi}^{(0)}|\hat{W}|\tilde{\Psi}^{(1)}\rangle. \tag{A19}$$

The nonlinearity effects are "hidden" in the first-order wave function correction, which can be obtained from the self-consistent equation:

$$|\tilde{\Psi}^{(1)}\rangle = -\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle - \hat{R}_0\hat{\Omega}^{(1)}|\tilde{\Psi}^{(0)}\rangle \tag{A20}$$

Since the first-order potential operator is, for real wave functions,

$$\hat{\Omega}^{(1)} = 2\iint d\mathbf{r}d\mathbf{r}'\frac{\delta^2 F[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\langle\tilde{\Psi}^{(0)}|\hat{n}(\mathbf{r}')|\tilde{\Psi}^{(1)}\rangle\hat{n}(\mathbf{r}), \tag{A21}$$

Eq. (A20) can be re-expressed as

$$|\tilde{\Psi}^{(1)}\rangle = -\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle - \hat{R}_0\hat{G}_0|\tilde{\Psi}^{(1)}\rangle, \tag{A22}$$

where

$$\hat{G}_0 = 2\iint d\mathbf{r}d\mathbf{r}'\hat{n}(\mathbf{r})|\tilde{\Psi}^{(0)}\rangle\frac{\delta^2 F[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\langle\tilde{\Psi}^{(0)}|\hat{n}(\mathbf{r}'). \tag{A23}$$

The final expression of the second-order energy correction can be written as the series

$$\begin{aligned} E^{(2)} &= -\langle\tilde{\Psi}^{(0)}|\hat{W}\left(1 + \hat{R}_0\hat{G}_0\right)^{-1}\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle \\ &= -\langle\tilde{\Psi}^{(0)}|\hat{W}\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle \\ &\quad +\langle\tilde{\Psi}^{(0)}|\hat{W}\hat{R}_0\hat{G}_0\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle \\ &\quad -\cdots . \end{aligned} \tag{A24}$$

Further details and higher-order expressions will be given in a forthcoming publication.

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