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Long-range density-matrix-functional theory: Application to a modified homogeneous electron gas

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We propose a method that employs functionals of the one-electron reduced density matrix (density matrix) to capture long-range effects of electron correlation. The complementary short-range regime is treated with density functionals. In an effort to find approximations for the long-range density-matrix functional, a modified power functional is applied to the homogeneous electron gas with Coulomb interactions replaced by their corresponding long-range counterparts. For the power $\beta = 1/2$ and the range-separation parameter $\omega = 1/r_s$, the functional reproduces the correlation and the kinetic correlation energies with a remarkable accuracy for intermediate and large values of r_s. Analysis of the Euler equation corresponding to this functional reveals correct r_s expansion of the correlation energy in the limit of large r_s. The first expansion coefficient is in very good agreement with that obtained from the modified Wigner-Seitz model.

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I. INTRODUCTION

Recently a plethora of hybrid schemes based on splitting of interelectronic interaction into short- and long-range parts have been formulated and tested. The main idea, originally proposed by Savin and Stoll [1,2], consists in describing the short-range component of the electron interaction by density functionals (DF) and combining them with *ab initio* methods that employ Hamiltonians with the long-range part of the electronic interaction. Almost any wave-function-based method can be coupled with short-range functionals after the Hamiltonian is properly modified. Thus, the hybrid schemes employ both Hartree-Fock (HF) wave functions [3–5] as well as multideterminantal functions like configuration interaction (CI) [6], multiconfiguration self-consistent field (MCSCF) [7], or coupled-cluster singles doubles with perturbative triples CCSD(T) [8,9] calculations. The hybrid scheme has a number of advantages over the standard (full-range) DF theory (DFT) or *ab initio* methods used separately. On one hand, density functionals are usually not capable of capturing long-range correlation effects. Consequently, they fail to accurately describe van der Waals interactions or bond breaking. Supplementing short-range density functionals (SRDFs) with the long-range wave-function functionals allows one to treat such phenomena with much greater accuracy [8–11]. On the other hand, *ab initio* methods need large basis sets to describe the electronic cusp. Treatment of this short-range effect with SRDFs allows smaller basis sets for the one-electron functions. Despite this reduction of computational cost, hybrid schemes employing multideterminantal wave functions inherit the unfavorable scaling from their *ab initio* counterparts. Consequently, they are limited to relatively small systems. A number of procedures propose coupling SRDFs with a single-determinantal long-range (LR) wave function. Such methods are as efficient as commonly used DFT schemes that include a contribution from the exact (Hartree-Fock) exchange. However, they are less successful in curing the flaws of standard DFT [12].

It is evident that a different long-range functional is needed, that combines computational efficiency with accuracy. Density-matrix-functional theory (DMFT) is a suitable candidate for this purpose. DMFT has been enjoying a rapid development in recent years. A number of functionals have been proposed [13–23] and their properties thoroughly analyzed [24–35]. Apart from obtaining ground-state energies, the recent formulation of the time-dependent variant of DMFT allows for computing excited-state energies [36–38]. A density-matrix functional (DMF) employs the one-electron reduced density matrix (density matrix) as its main variable. For a given N-electron wave function, the density matrix is defined as

$$\Gamma(\mathbf{x},\mathbf{x}') = N\int\cdots\int \Psi^*(\mathbf{x}',\ldots,\mathbf{x}_N)\Psi(\mathbf{x},\ldots,\mathbf{x}_N)d\mathbf{x}_2\cdots d\mathbf{x}_N, \tag{1}$$

where $\mathbf{x}$ stands for the combined spatial and spin coordinates, $\mathbf{x} = (\mathbf{r},s)$. The immediate advantage of density-matrix functionals over their density counterparts is that the explicit kinetic energy functional of Γ is known. The only component of the energy functional that needs to be approximated is the electron-electron repulsion term. Density-matrix functionals are often defined in terms of natural occupation numbers $\{n_p\}$ and natural spin orbitals $\{\varphi_p(\mathbf{x})\}$ that are, respectively, the eigenvalues and eigenfunctions of the corresponding Γ,

$$\Gamma(\mathbf{x},\mathbf{x}') = \sum_p n_p\varphi_p^*(\mathbf{x}')\varphi_p(\mathbf{x}). \tag{2}$$

Natural occupation numbers are allowed to be fractional, that is, they are not restricted to 0 and 1. Hence static correlation effects (requiring multideterminantal wave functions and thus fractional occupancies of orbitals) can be taken into account by DMFT more easily than by DFT. Recently proposed density-matrix functionals successfully describe the dissociation of simple molecules [19,20] and the properties of strongly correlated extended systems [21]. Since almost all available density-matrix functionals are simple extensions of the Hartree-Fock energy functional, they can be straightforwardly adopted for the range-separated hybrid method (see next sections of the paper).

Similarly to the correlated-wave-function methods, DMFT-based approaches suffer from strong dependency on the size of the basis sets employed in calculations. Therefore, they would benefit from a shifting of the burden of describing short-range effects to density functionals that are more capable in this respect. The computational efficiency of the density matrix methods still lags behind that of the Kohn-Sham implementation of DFT; however, an important step forward has been made recently. An optimization procedure for density-matrix functionals based on the projected-gradient algorithm has been formulated [39]. It is very efficient for some classes of functionals with the scaling being only M^4, where M is the number of basis set functions.

We propose a range-separated method, SRDF-LRDMF, in which the short- and the long-range parts of the interelectronic Coulomb interaction are taken into account by, respectively, short-range density functionals and long-range density-matrix functionals (LRDMFs). Such an approach is potentially superior to both standard DFT (in treating static correlation effects) and DMFT (by describing accurately and more efficiently dynamic correlation) methods. Its development requires the design and testing of long-range density-matrix functionals. As a first step of this task, we investigate the performance of some LRDMFs for the homogeneous electron gas with long-range Coulomb interactions.

The organization of the paper is as follows. In Sec. II a general formalism leading to the formulation of the range-separation scheme is provided. The modification of the simple power density-matrix functional and its application to the electron gas system is presented in Sec. III. Section IV contains an analysis of the $\beta = 1/2$ power functional with the range-separation parameter being the inverse of the Wigner-Seitz radius of the electron gas that accurately reproduces the correlation energy. The paper ends with conclusions.

II. GENERAL FORMALISM

Assume a spin-independent Hamiltonian $\hat{H}$ for an N-electron system described by the external potential $\upsilon_{\text{ext}}(\mathbf{r})$,

$$\hat{H} = \hat{T} + \sum_{i<j}^{N} r_{ij}^{-1} + \sum_{i=1}^{N} \upsilon_{\text{ext}}(\mathbf{r}_i) \tag{3}$$

(note that atomic units are used throughout the text). If we employ the concept of a universal density functional $F[\rho]$, the ground-state energy corresponding to $\hat{H}$ reads

$$E = \min_{\rho} \left\{ F[\rho] + \int \rho(\mathbf{r}) \upsilon_{\text{ext}}(\mathbf{r})\, d\mathbf{r} \right\}, \tag{4}$$

where the universal functional is defined as

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \, \hat{T} + \sum_{i<j}^{N} r_{ij}^{-1} \, | \Psi \rangle \, . \tag{5}$$

In an effort to describe the long-range part of the electronic interaction with a density-matrix functional, one splits the Coulomb operator $1/r$ into the long- and short-range parts $\upsilon_{ee}^{\text{LR}}(r)$ and $\upsilon_{ee}^{\text{SR}}(r)$, respectively,

$$\frac{1}{r} = \upsilon_{ee}^{\text{SR}}(r) + \upsilon_{ee}^{\text{LR}}(r). \tag{6}$$

Consequently, $F[\rho]$ can be divided into the long-range

$$F^{\text{LR}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \, \hat{T} + \sum_{i<j}^{N} \upsilon_{ee}^{\text{LR}}(r_{ij}) \, | \Psi \rangle \tag{7}$$

and the short-range

$$F^{\text{SR}}[\rho] = F[\rho] - F^{\text{LR}}[\rho] \tag{8}$$

components [40]. The long-range density functional $F^{\text{LR}}[\rho]$ can be defined as a minimum of a density-matrix functional, namely,

$$F^{\text{LR}}[\rho] = \min_{\Gamma \to \rho} \left\{ T[\Gamma] + E_{ee}^{\text{LR}}[\Gamma] \right\}, \tag{9}$$

where the symbol $\Gamma \to \rho$ indicates that the diagonal part of the density matrix coincides with the electron density ρ, that is, $\Gamma(\mathbf{x},\mathbf{x}) = \rho(\mathbf{x})$. The kinetic energy functional present in Eq. (9) is given explicitly in terms of the density matrix as

$$T[\Gamma] = -\frac{1}{2} \iint \delta(\mathbf{x} - \mathbf{x}') \, \nabla_{\mathbf{r}}^2 \, \Gamma(\mathbf{x},\mathbf{x}') \, d\mathbf{x} \, d\mathbf{x}'. \tag{10}$$

The long-range electron-electron interaction functional is defined via the constrained-search procedure and reads (cf. Ref. [41])

$$E_{ee}^{\text{LR}}[\Gamma] = \min_{\Psi \to \Gamma} \langle \Psi | \sum_{i<j}^{N} \upsilon_{ee}^{\text{LR}}(r_{ij}) \, | \Psi \rangle \, , \tag{11}$$

where $\Psi \to \Gamma$ stands for wave functions related to a given density matrix by Eq. (1). Equations (7), (8) and (9) lead to the conclusion that the ground-state energy (4) is also a minimum of the density-matrix functional, namely,

$$\begin{aligned} E &= \min_{\rho} \left\{ \min_{\Gamma \to \rho} \left(T[\Gamma] + E_{ee}^{\text{LR}}[\Gamma] \right) \right. \\ &\quad \left. + F^{\text{SR}}[\rho] + \int \rho(\mathbf{r}) \upsilon_{\text{ext}}(\mathbf{r}) \, d\mathbf{r} \right\} \\ &= \min_{\Gamma} \left\{ T[\Gamma] + E_{ee}^{\text{LR}}[\Gamma] + F^{\text{SR}}[\rho_\Gamma] + \int \rho_\Gamma(\mathbf{r}) \upsilon_{\text{ext}}(\mathbf{r}) \, d\mathbf{r} \right\} \end{aligned} \tag{12}$$

$[\rho_\Gamma(\mathbf{x}) = \Gamma(\mathbf{x},\mathbf{x})]$. The expression in the curly brackets in the second equality of Eq. (12) defines the range-separated density-matrix energy functional

$$E[\Gamma] = T[\Gamma] + E_{ee}^{\text{LR}}[\Gamma] + F^{\text{SR}}[\rho_\Gamma] + \int \rho_\Gamma(\mathbf{r}) \upsilon_{\text{ext}}(\mathbf{r}) \, d\mathbf{r}. \tag{13}$$

Its minimization, carried out over N-representable density matrices, yields the ground-state energy. As required, the long-range part of the electron-electron repulsion is described by the density-matrix functional ($E_{ee}^{\text{LR}}[\Gamma]$) whereas the density functional ($F^{\text{SR}}[\rho_\Gamma]$) treats the short-range complement. The functionals can be further decomposed into the Hartree and the exchange-correlation parts, that is,

$$E_{ee}^{\text{LR}}[\Gamma] = \frac{1}{2} \iint \rho_\Gamma(\mathbf{r}_1) \rho_\Gamma(\mathbf{r}_2) \, \upsilon_{ee}^{\text{LR}}(r_{12}) \, d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}^{\text{LR}}[\Gamma] \tag{14}$$

and

$$F^{\text{SR}}[\rho_\Gamma] = \frac{1}{2} \iint \rho_\Gamma(\mathbf{r}_1) \rho_\Gamma(\mathbf{r}_2) \, \upsilon_{ee}^{\text{SR}}(r_{12}) \, d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}^{\text{SR}}[\rho_\Gamma], \tag{15}$$

which results in the following form of the density-matrix functional:

$$E[\Gamma] = T[\Gamma] + E_H[\rho_\Gamma] + E_{\mathrm{xc}}^{\mathrm{LR}}[\Gamma] + E_{\mathrm{xc}}^{\mathrm{SR}}[\rho_\Gamma] + \int \rho_\Gamma(\mathbf{r})\upsilon_{\mathrm{ext}}(\mathbf{r})\, d\mathbf{r}. \tag{16}$$

The Hartree functional $E_H[\rho]$ includes the full-range Coulomb electron-electron interaction and reads

$$E_H[\rho] = \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\, r_{12}^{-1}\, d\mathbf{r}_1 d\mathbf{r}_2. \tag{17}$$

Note that the short-range exchange-correlation density functional $E_{\mathrm{xc}}^{\mathrm{SR}}[\rho_\Gamma]$ present in Eq. (16) is defined exactly in the same way as in the literature, and a number of local or nonlocal approximations are available [8,9,42–44]. The long-range exchange-correlation density-matrix functional $E_{\mathrm{xc}}^{\mathrm{LR}}[\Gamma]$ is an additional quantity. Even though its formal definition is known [cf. Eqs. (11) and (14)], it is of no practical value and approximations must be developed.

Given $E_{\mathrm{xc}}^{\mathrm{LR}}[\Gamma]$ and $E_{\mathrm{xc}}^{\mathrm{SR}}[\rho]$, the ground-state energy is found by minimizing the functional (16) with respect to N-representable density matrices. It is important to realize that, even for the exact functional $E[\Gamma]$, its minimizer $\Gamma_{\mathrm{min}}^{\mathrm{LR}}(\mathbf{x},\mathbf{x}')$ is not the same as the density matrix $\Gamma(\mathbf{x},\mathbf{x}')$ corresponding to the full Hamiltonian (3) and related by Eq. (1) to the ground-state wave function. Only the diagonal parts of $\Gamma_{\mathrm{min}}^{\mathrm{LR}}$ and Γ coincide, that is, $\Gamma_{\mathrm{min}}^{\mathrm{LR}}(\mathbf{x},\mathbf{x}) = \Gamma(\mathbf{x},\mathbf{x})$, and correspond to the exact density of a given system.

III. DENSITY-MATRIX FUNCTIONAL FOR A HOMOGENEOUS ELECTRON GAS WITH LONG-RANGE COULOMB INTERACTIONS

Since most short-range density functionals have been proposed based on conventional local or nonlocal functionals, one may wonder if the currently available density-matrix functionals are a good starting point for the development of the long-range density-matrix functional Eq. (14). We will investigate this issue in the context of the homogeneous electron gas (HEG). To this end, consider a modified homogeneous electron gas of density ρ with full Coulomb interactions replaced by their long-range counterparts. For simplicity we call this system a long-range homogeneous electron gas (LRHEG). As for the standard HEG (with full Coulomb interactions), a sum of the background-background, background-electron, and the Hartree part of the electron-electron interactions vanishes. Consequently, the total energy expression includes only the kinetic and the long-range exchange-correlation terms. Employing the spectral representation of the density matrix, Eq. (2), and using Eq. (16), we obtain the total energy functional for the LRHEG:

$$E^{\mathrm{LR}}[\Gamma] = -\frac{1}{2}\sum_p n(\mathbf{k}_p)\langle\varphi_{\mathbf{k}_p}|\nabla^2|\varphi_{\mathbf{k}_p}\rangle + E_{\mathrm{xc}}^{\mathrm{LR}}[\{n(\mathbf{k}_p)\},\{\varphi_{\mathbf{k}_p}(\mathbf{x})\}]. \tag{18}$$

The momentum distribution function $n(\mathbf{k})$, where $\mathbf{k}$ is a wave vector, present in Eq. (18) is an analog of the natural occupation numbers for extended systems. Since we consider a rotationally invariant system, the momentum distribution is a function of $|\mathbf{k}|$ and $n(\mathbf{k}) = n(k)$.

The most successful exchange-correlation functionals in DMFT can be seen as extensions of the Hartree-Fock exchange functional, which reads $E_x^{\mathrm{HF}}[\Gamma] = -\frac{1}{2}\sum_{pq} n_p n_q K_{pq}$ (the two-electron integrals $\{K_{pq}\}$ are of the exchange type). In DMFs the product of two occupation numbers, $n_p n_q$, is replaced by a two-variable function $G(n_p,n_q)$. It is straightforward to modify such density-matrix functionals to account only for the long-range exchange-correlation effects. One proceeds in the same manner as in the case of the Hartree-Fock functional and replaces the exchange integrals with their LR counterparts. We assume then the following form of the long-range density matrix exchange-correlation functional:

$$E_{\mathrm{xc}}^{\mathrm{LR}}[\Gamma] = -\frac{1}{2}\sum_{pq} G(n_p,n_q)\, K_{pq}^{\mathrm{LR}}, \tag{19}$$

where $\{K_{pq}^{\mathrm{LR}}\}$ is the set of long-range exchange integrals expressed in terms of the natural orbitals,

$$K_{pq}^{\mathrm{LR}} = \iint \varphi_p^*(\mathbf{x}_1)\varphi_q^*(\mathbf{x}_2)\upsilon_{ee}^{\mathrm{LR}}(r_{12})\, \varphi_q(\mathbf{x}_1)\varphi_p(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2. \tag{20}$$

The function G is symmetric, $G(x,y) = G(y,x)$, and satisfies two other conditions:

$$\begin{aligned} G(x,0) &= 0, \\ G(1,1) &= 1. \end{aligned} \tag{21}$$

These result from the requirement that the Hartree-Fock functional should be recovered by $E_{\mathrm{xc}}^{\mathrm{LR}}$ for integer (0 or 1) occupation numbers. After replacing summations with integrations in Eqs. (18) and (19), $\sum_p \to (8\pi^3)^{-1} V \int d\mathbf{k}$ (V is the volume of the system), and using plane waves for the natural spin orbitals $\varphi_{\mathbf{k}}(\mathbf{x}) = V^{-1/2}\exp(i\mathbf{k}\mathbf{r})\sigma(s)$, one is led to the following total energy functional for the LRHEG:

$$E^{\mathrm{LR}}[n] = (8\pi^3)^{-1} V \int n(k) k^2 d\mathbf{k} - (8\pi^3)^{-2} V^2 \times \iint G[n(k_1),n(k_2)] K_{\mathbf{k}_1\mathbf{k}_2}^{\mathrm{LR}} d\mathbf{k}_1 d\mathbf{k}_2. \tag{22}$$

Equation (22) is spin-summed for the spin-unpolarized electron gas assumed in the paper. The momentum distributions for both spins are identical and equal to $n(k)$. This function is normalized to half of the density, that is,

$$(4\pi^3)^{-1}\int n(k) d\mathbf{k} = \rho. \tag{23}$$

In practical calculations one has to make a particular choice for the long-range interaction function $\upsilon_{ee}^{\mathrm{LR}}(r)$. The standard error function (erf) seems to be the most reasonable choice for two reasons. First of all, most of the available short-range density functionals $E_{\mathrm{xc}}^{\mathrm{SR}}[\rho]$ that are to be combined with $E_{xc}^{\mathrm{LR}}[\Gamma]$ [cf. Eq.(16)] do employ the error function. Moreover, the error function allows for analytic calculation of the two-electron integrals for Gaussian-type and plane-wave basis set functions (the most often used basis set functions for molecular and extended system calculations) which is of great computational advantage. Therefore we assume

$$v_{ee}^{\mathrm{LR}}(r) = \frac{\mathrm{erf}(\omega r)}{r}. \quad (24)$$

The parameter ω is a nonnegative number governing the range of decomposition of the Coulomb interaction. Note that for $\omega \to \infty$ standard density-matrix functionals are recovered. For a LRHEG the integrals (20) can be computed analytically and read

$$K_{\mathbf{k}_1\mathbf{k}_2}^{\mathrm{LR}} = \frac{4\pi}{V}\frac{\exp[-(k_{12}/2\omega)^2]}{k_{12}^2}, \quad (25)$$

where $k_{12} = |\mathbf{k}_1 - \mathbf{k}_2|$. Finally, the expression for the energy per electron, $E^{\mathrm{LR}}[n]/N$, Eq. (22), takes the form

$$\varepsilon[n] = (8\pi^3\rho)^{-1}\int n(k)k^2 d\mathbf{k} - (16\pi^5\rho)^{-1} \times \iint G[n(k_1),n(k_2)]k_{12}^{-2}\exp[-(k_{12}/2\omega)^2]d\mathbf{k}_1 d\mathbf{k}_2. \quad (26)$$

Note that, since the following considerations refer to the LRHEG, from now on the upper index LR is skipped in all pertinent quantities.

The energy of the electron gas and the corresponding momentum distribution result from minimizing the energy functional (26) with respect to $n(k)$ under the condition that the density is constant and corresponds to a given value ρ, Eq. (23). This leads to the Euler-Lagrange equation

$$\frac{\delta\{\varepsilon[n] - \mu[(4\pi^3)^{-1}\int n(k)d\mathbf{k} - \rho]\}}{\delta n(\mathbf{k})} = 0, \quad (27)$$

where μ is a Lagrange multiplier. Note that the momentum distribution is physically admissible if it complies with the condition

$$\forall\, \mathbf{k},\ 0 \leqslant n(k) \leqslant 1. \quad (28)$$

It is well known that most approximate density-matrix functionals produce inadmissible momentum distributions unless the condition (28) is additionally imposed in the minimization process [29,30,45]. It is usually done by some form of parametrization of $n(k)$. Consequently, the resulting momentum distributions achieve the value 1 for a certain range of k where the Euler-Lagrange equation is not satisfied. The necessity of parametrizing the momentum distribution in order to satisfy the condition (28) should be understood as a deficiency of the approximate functionals. The exact functional will result in a physically admissible function $n(k)$ without imposing this condition [24,46,47]. It will be shown in the next section that the long-range functional adopted in this paper inherits the deficiency of its full-range counterpart and may produce momentum distributions that happen to be integer for a certain range of k.

For the long-range density-matrix functionals, a definition of the correlation energy is naturally introduced as the difference between the energies of correlated and uncorrelated LRHEGs of the same density ρ. For the uncorrelated electron gas, the momentum distribution is given by a step function, namely,

$$n(k) = \begin{cases} 1, & k < k_{F,} \\ 0, & k \geqslant k_{F,} \end{cases} \quad (29)$$

where the Fermi wave vector reads $k_F = \rho^{1/3}3^{1/3}\pi^{2/3}$. For such a function, the first term of Eq. (26), that is, the kinetic energy per particle, yields

$$t_s[\rho] = \frac{3}{10}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{r_s^2}. \quad (30)$$

The Wigner-Seitz radius r_s is given as $r_s = (9\pi/4)^{1/3}k_F^{-1}$. Because of the condition (21) the second term of the energy functional (26), the exchange-correlation energy, reduces to the exact exchange energy expression [2]

$$\varepsilon_x[\rho] = -\pi^{-1}\omega\left[(2x - 4x^3)e^{-1/4x^2} - 3x + 4x^3 + \pi^{1/2}\mathrm{erf}\left(\frac{1}{2x}\right)\right], \quad (31)$$

where $x = \omega/2k_F$. The correlation energy per particle is then defined as

$$\varepsilon_{\mathrm{corr}}[n] = \varepsilon[n] - \varepsilon_x[\rho] - t_s[\rho] \quad (32)$$

[$n(k)$ is normalized to ρ]. This definition of the correlation energy coincides with that commonly adopted in the literature (cf. Ref. [42]).

We restrict the form of the function that enters the exchange-correlation functional (19) to the power function

$$G(x,y) = (xy)^\beta, \quad (33)$$

β being a real, positive number. Originally, the power functional with $\beta = 1/2$ was proposed by Müller [48] and independently by Buijse and Baerends [13] (in the literature this functional is also known as the corrected Hartree functional). Numerous studies have shown that this functional strongly overestimates the correlation energy for both finite and extended systems with the full-range Coulomb interactions [19,26,27,45]. Studies of the power functional applied to the electron gas revealed that it is incapable of reproducing the correct high-density limit of the correlation energy [25]. For $\beta = 1/2$ it was shown that $\varepsilon_{\mathrm{corr}}$ is much too low in the entire range of r_s [29,45]. For $r_s > 5.77$ the total energy per particle predicted by the functional is constant and equal to $-1/8$ hartree [35,46]. The optimal value of the power β for reproducing the correlation energy of a HEG with the smallest error was found to be $\beta = 0.55$ [32]. Recent studies have shown that for certain values of β it is possible to describe correctly the energy gaps of semiconductors and strongly correlated Mott insulators as well as spectra of strongly correlated transition-metal oxide series [21,49].

To investigate the performance of the power functional for the LRHEG, we numerically minimized the functional given by Eqs. (26) and (33) for a number of powers β and a series of values of densities ρ and parameters ω. To assure that the momentum distributions are physically admissible, the condition (28) was imposed by substituting $n(k)$ with

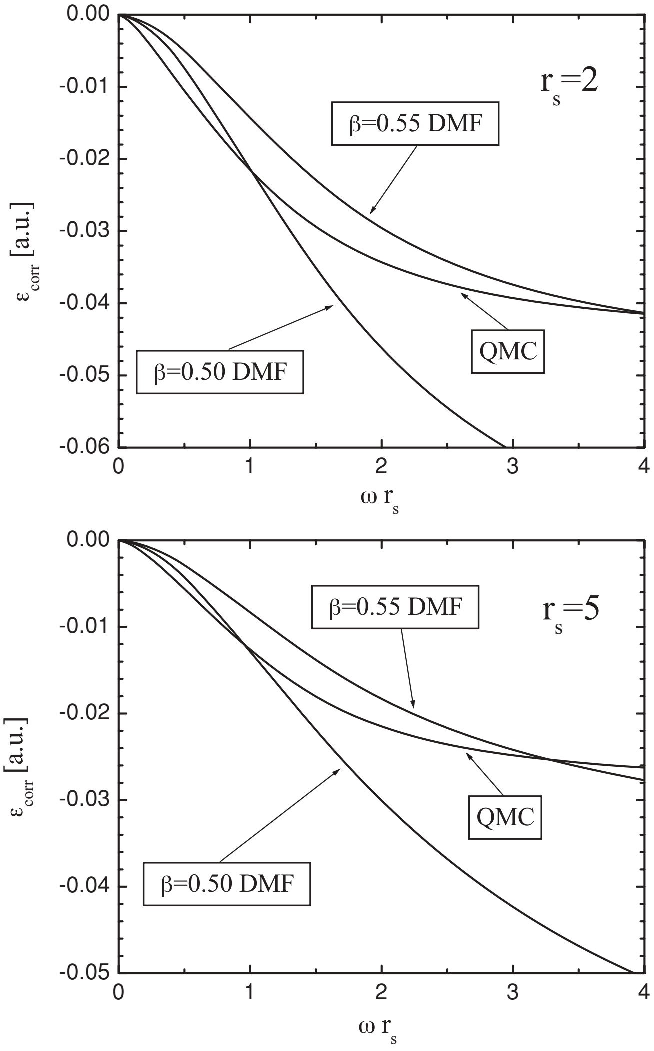

FIG. 1. Correlation energy (in atomic units) of the long-range homogeneous electron gas obtained from the density-matrix power functional with $\beta = 0.50$ and 0.55 [cf. Eqs. (26) and (33)]. The results are compared with the accurate fit to the quantum Monte Carlo (QMC) data of Paziani *et al.* [42]. The upper and lower panels correspond to $r_s = 2$ and 5, respectively.

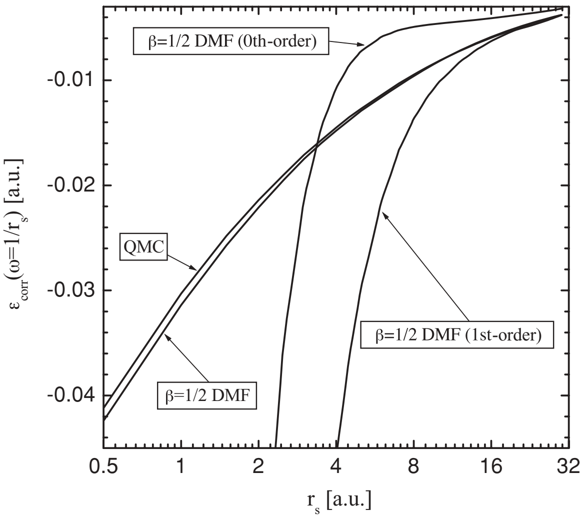

FIG. 2. Correlation energy (in atomic units) of the long-range homogeneous electron gas obtained for the range parameter $\omega = 1/r_s$. The "$\beta = 1/2$ DMF" curve was obtained by numerical minimization of the $\beta = 1/2$ density-matrix power functional. The other DMF curves are the zeroth-order and the first three terms from the first-order approximations, Eqs. (43) and (45), respectively. The DMF results are compared with the accurate fit to the quantum Monte Carlo (QMC) data of Paziani *et al.* [42].

$\cos^2[p(k)]$ and searching for the optimal $p(k)$ functions. The normalization condition Eq. (23) was taken into account by means of the undetermined Lagrange multiplier method. The minimization was performed on a Gaussian grid using the conjugate-gradient algorithm. Because of the integrable logarithmic singularity present for $k_1 = k_2$ in the second integral of Eq. (26), the quadrature of integrands with a logarithmic singularity was employed. For all other integrals, the Gaussian quadrature was used.

The resulting correlation energies, defined in Eq. (32), corresponding to $r_s = 2$ and 5, as functions of ωr_s are presented in Fig. 1. The results were obtained for the powers $\beta = 0.5$ and 0.55. The reference curves (denoted as QMC) come from a very accurate fitting function of Paziani *et al.* [42]. The fitting function reproduces very closely the results of quantum Monte Carlo (QMC) simulations. It incorporates known asymptotics of the correlation energy when $\omega, r_s \to 0$ (the limit of a noninteracting gas) and $\omega \to \infty$ (full Coulomb interactions). It is evident from the figure that neither density-matrix power functional reproduces the correlation energy with a uniform accuracy for the whole range of ω. For $\beta = 0.55$ the agreement with the reference curve is better for larger values of ω, which is in line with findings of Lathiotakis *et al.* [32], who showed that for this value of β the overall error of the correlation energy for the ordinary HEG ($\omega \to \infty$) is the lowest. A closer look at Fig. 1 reveals a striking feature for the $\beta = 1/2$ functional. The curves pertinent to this functional intersect the reference curves in the vicinity of $\omega r_s = 1$. We investigate this behavior in detail in the next section and show that the correlation energy is indeed reproduced very accurately by this functional for $\omega = 1/r_s$ in the region of intermediate and large values of r_s.

IV. THE CASE OF $\beta = 1/2$ AND $\omega = 1/r_s$

The long-range density-matrix power functional [Eqs. (26) and (33)] corresponding to the power $\beta = 1/2$ reads

$$\varepsilon[n] = (8\pi^3\rho)^{-1}\int n(k)k^2 d\mathbf{k} - (16\pi^5\rho)^{-1} \times \iint [n(k_1)n(k_2)]^{1/2}\, k_{12}^{-2} \exp[-(k_{12}/2\omega)^2]\, d\mathbf{k}_1 d\mathbf{k}_2. \tag{34}$$

Figure 2 presents the correlation energy obtained from numerical calculations for the range-separation parameter $\omega = 1/r_s$ as a function of r_s. The agreement with the reference curve is excellent, especially in regions of intermediate and large values of r_s. In the region of r_s relevant for most atoms and molecules, the relative error of the correlation energy decreases from 4.5% for $r_s = 0.5$ to only 0.5% for $r_s = 10$. The increase in the

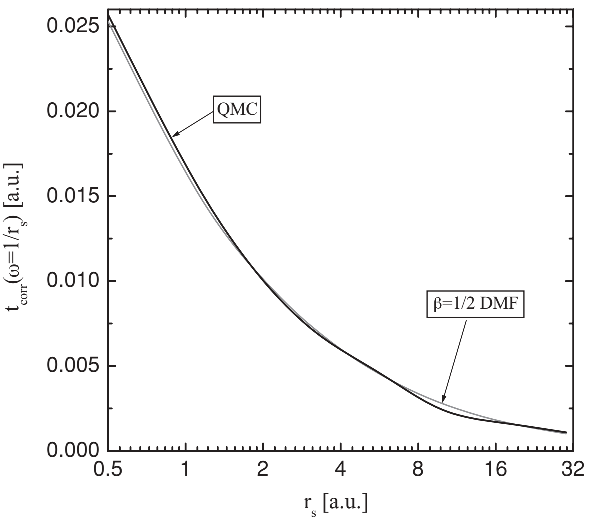

FIG. 3. Kinetic correlation energy (in atomic units) of the long-range homogeneous electron gas obtained for the range parameter $\omega = 1/r_s$. The gray curve ("$\beta = 1/2$ DMF") was obtained by numerical minimization of the $\beta = 1/2$ density-matrix power functional. It is compared with the accurate fit to the quantum Monte Carlo (QMC) data of Paziani *et al.* [42] (the black curve).

accuracy for the correlation energy is dramatic comparing to the performance of the $\beta = 1/2$ power functional for standard HEG [45]. In the latter case the correlation energy is overestimated by 66% and 350% for $r_s = 0.5$ and 10, respectively. Another quantity the accuracy of which can be estimated is the kinetic correlation energy $t_{\text{corr}} = t - t_s$. The kinetic energy t predicted by the density-matrix functional is given explicitly as the first term of the expression (34). Note that t_{corr} introduced above for the electron gas coincides with a definition of the kinetic correlation energy in density-functional theory. Therefore, the reference values of t_{corr} could be obtained by applying the virial theorem [50] to the results from Ref. [42]. Since the exact form of the functional $t_{\text{corr}}[n]$ is known, the error in reproducing this quantity must originate solely from the inaccuracy of the momentum distribution function. The results for t_{corr} presented in Fig. 3 reveal a very good agreement between the reference and the DMF data. In the vicinity of $r_s = 12$, the reference curve exhibits a bump. We believe that in this case the reference curve is inaccurate since it was obtained from the virial theorem.

In the reminder of this section we derive the large-r_s limit of the correlation energy for the $\beta = 1/2$ power functional and show that it compares surprisingly well with the reference results. In an effort to find $\varepsilon(\omega = 1/r_s, r_s \gg 1)$, consider the Euler-Lagrange equation (27) which turns into

$$\begin{aligned}&(1/2)n(k_1)^{1/2}k_1^2 - (4\pi^2)^{-1}\\&\quad\times\int n(k_2)^{1/2}k_{12}^{-2}\exp[-(k_{12}/2\omega)^2]d\mathbf{k}_2 = \mu\rho n(k_1)^{1/2},\end{aligned} \tag{35}$$

where μ is a Lagrange multiplier. Multiplying both sides of Eq. (35) by $n(k_1)^{1/2}$ and integrating the result with respect to $\mathbf{k}$, we obtain a simple relation between the total energy (34) and μ:

$$\varepsilon = \mu\rho. \tag{36}$$

Notice that this relation is unique to the power $\beta = 1/2$ and it holds only when $\forall\, \mathbf{k}$, $0 < n(k) < 1$ [see the comment below Eq. (27)].

As shown in Ref. [46], the integral equation of the form of Eq. (27) can be turned into the Schrödinger equation by introducing an auxiliary function $\eta(k)$ such that

$$n(k) = 4\pi^3\rho\eta^2(k) \tag{37}$$

and taking the Fourier transform. The resulting equation reads

$$-\frac{1}{2}\nabla^2\eta(\mathbf{r}) - \frac{1}{2}\frac{\text{erf}(\omega r)}{r}\eta(\mathbf{r}) = \varepsilon\eta(\mathbf{r}), \tag{38}$$

where the relation (36) has been employed and $\eta(\mathbf{r})$ results from the inverse Fourier transform of $\eta(k)$. Equation (38) cannot be solved analytically for an arbitrary value of ω. Since small-ω solutions are of interest (for $\omega = 1/r_s$, this would correspond to the large-r_s limit), it is justified to assume a harmonic approximation for the potential $-(1/2)\text{erf}(\omega r)/r$ and write it as

$$-\frac{1}{2}\frac{\text{erf}(\omega r)}{r} \approx -\frac{\omega}{\pi^{1/2}} + \frac{\omega^3}{3\pi^{1/2}}r^2. \tag{39}$$

In this approximation, $\eta(r)$ is simply the wave function of the isotropic harmonic oscillator corresponding to the lowest eigenvalue, namely,

$$\eta(r) = \frac{2^{3/8}\omega^{9/8}}{3^{3/8}\pi^{15/16}}\exp\left(-\frac{\omega^{3/2}}{6^{1/2}\pi^{1/4}}r^2\right), \tag{40}$$

and the corresponding zeroth-order eigenvalue reads

$$\varepsilon^{(0)} = -\frac{\omega}{\pi^{1/2}} + \frac{3^{1/2}\omega^{3/2}}{2^{1/2}\pi^{1/4}}. \tag{41}$$

The pertinent zeroth-order momentum distribution normalized to $4\pi^3\rho$ is given by a Gaussian-type function of the form

$$n^{(0)}(k) = \frac{3^{7/4}\pi^{7/8}}{2^{3/4}\omega^{9/4}r_s^3}\exp\left(-\frac{3^{1/2}\pi^{1/4}k^2}{2^{1/2}\omega^{3/2}}\right). \tag{42}$$

We now turn to the case when ω is taken as the inverse of r_s. The condition $n(k) \leqslant 1$ for physically admissible momentum distributions imposes a lower bound on r_s. In the zeroth-order approximation, Eq. (42), one obtains $r_{\text{crit}} = 2^{-1}3^{7/3}\pi^{7/6} \approx 25$. This means that for $r_s < r_{\text{crit}}$ the optimal momentum distribution corresponding to the $\beta = 1/2$ power functional is exactly equal to 1 for k smaller than a certain value. Such behavior has already been observed for density-matrix functionals applied to standard HEGs [29,45]. From Eqs. (32) and (41) taken for $\omega = 1/r_s$, the zeroth-order approximation to the correlation energy per particle follows immediately as

$$\varepsilon_{\text{corr}}^{(0)} = -\frac{0.226}{r_s} + \frac{0.920}{r_s^{3/2}} - \frac{1.105}{r_s^2}. \tag{43}$$

The first-order correlation energy may be easily computed by inserting $n^{(0)}(k)$ into Eq. (34). The resulting large-r_s expansions read

$$\varepsilon^{(1)} = -\frac{1}{\pi^{1/2} r_s} + \frac{3^{1/2}}{2^{1/2}\pi^{1/4} r_s^{3/2}} - \frac{9}{16 r_s^2} + O\left(r_s^{-5/2}\right) \tag{44}$$

and

$$\varepsilon_{\text{corr}}^{(1)} = -\frac{0.226}{r_s} + \frac{0.920}{r_s^{3/2}} - \frac{1.668}{r_s^2} + O\left(r_s^{-5/2}\right). \tag{45}$$

The zeroth-order and the first three terms of the first-order approximations, Eqs. (43) and (45), respectively, are presented in Fig. 2. The first-order approximation performs very well, not only in the large-r_s limit but also for the intermediate values. One should keep in mind, however, that only for r_s greater than the critical value r_{crit} is the underlying zeroth-order momentum distribution physically admissible.

The results for the correlation energy of the LRHEG with the range parameter $\omega = 1/r_s$ suggests that the $\beta = 1/2$ power functional is capable of reproducing very accurately the energy of the gas in the low-density limit. Let us take a closer look at the r_s expansion of the correlation energy in this limit. Analysis of the properly scaled Hamiltonian for the electron gas with the Coulomb interactions replaced by the function $\text{erf}(\omega r)/r$ reveals that for $\omega = 1/r_s$ the large-r_s expansion of $\varepsilon_{\text{corr}}$ is analogous to that of the standard HEG in the Wigner crystal limit and reads [51]

$$\varepsilon_{\text{corr}} = \frac{A}{r_s} + \frac{B}{r_s^{3/2}} + O\left(r_s^{-2}\right). \tag{46}$$

From Eq. (45) one immediately concludes that the $\beta = 1/2$ power functional exhibits correct r_s scaling in the low-density limit. The first two expansion coefficients, −0.226 and 0.920, are surprising close to those obtained from the Paziani *et al.* exchange-correlation density functional, which read −0.217 and 0.887. Note that, even though the functional includes some exact limits, the values of the $\omega = 1/r_s, r_s \to \infty$ expansion coefficients are not analytical but result from the assumed fitting parameters.

Another estimate of the value of the first expansion coefficient in Eq. (46) is furnished by the Wigner-Seitz model proposed for HEGs in the low-density limit [52]. According to the Wigner-Seitz model, a unit cell of the lattice consists of a sphere of radius r_s with one electron in the center. The sphere is filled with positive uniform charge so it is overall neutral, and the electric field outside the sphere is zero (no interaction among the spheres). As a result the total energy per electron of the lattice composed of such closely packed spheres includes only two terms: the electron-background and the background-background interactions. After replacement of the Coulomb interaction operator with its long-range counterpart, $\text{erf}(\omega r)/r$, and setting $\omega = 1/r_s$, the electron-background and the background-background potential energies read $-[6\pi^{-1/2} + 3e\,\text{erf}(1)]/(4 e r_s) \approx -0.943/r_s$ and $3[3 + e^4(9 + 6\pi^{1/2}\text{erf}2)]/(80 e^4 \pi^{1/2} r_s) \approx 0.416/r_s$, respectively ($e$ denotes the exponential constant). Consequently, the total energy per particle predicted by the Wigner-Seitz model reads $-0.528/r_s$ and compares very well with $-0.564/r_s$—the first term in the large-r_s expansion predicted by the $\beta = 1/2$ power functional [cf. Eq. (41)]. The correlation energy resulting from the Wigner-Seitz approach reads $-0.190/r_s$, which agrees within 19% and 12% with the DMF and Paziani *et al.* values, respectively.

V. CONCLUSIONS

We propose a method that employs functionals of the one-electron density matrix to capture long-range effects of electron correlation. The functionals are to be combined with short-range density functionals. As the first step in developing practical functionals, the long-range density-matrix power functionals have been applied to the long-range homogeneous electron gas. The main finding of the paper is that the functional corresponding to the power $\beta = 1/2$ and the range-separation parameter $\omega = 1/r_s$ excellently reproduces the correlation energy and the kinetic correlation energy for intermediate and large values of r_s, Figs. 2 and 3, respectively. This is in contrast to the density-matrix functionals proposed for the full-range Coulomb interactions, which yield much larger errors. The agreement of the kinetic correlation energy with the reference data proves good accuracy of the second moments of the momentum distribution functions. Unfortunately, the quality of the momentum distributions obtained from the density-matrix functional cannot be directly assessed since the exact functions (or some accurate approximations) corresponding to $\omega = 1/r_s$ are not available.

Analysis of the variational equation corresponding to the $\beta = 1/2$ power functional reveals a correct r_s expansion of the correlation energy in the limit of large r_s. The first expansion coefficient is in very good agreement with that obtained from the modified Wigner-Seitz model. A comparison with this simple model is justified because it yields the low-density correlation energy within error of less than 1% for the full Coulomb interactions [52].

The excellent performance of the investigated functional for the long-range electron gas makes this method a promising candidate for strongly correlated extended systems [21,49]. A balanced treatment of the electron correlation offered by this method should make it superior also to standard DMFT-based approaches when applied to molecular systems. Work along this line is in progress.

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