Properties of short-range and long-range correlation energy density functionals from electron-electron coalescence

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The combination of density functional theory with other approaches to the many-electron problem through the separation of the electron-electron interaction into a short-range and a long-range contribution is a promising method, which is raising more and more interest in recent years. In this work some properties of the corresponding correlation energy functionals are derived by studying the electron-electron coalescence condition for a modified (long-range-only) interaction. A general relation for the on-top (zero electron-electron distance) pair density is derived, and its usefulness is discussed with some examples. For the special case of the uniform electron gas, a simple parameterization of the on-top pair density for a long-range only interaction is presented and supported by calculations within the “extended Overhauser model”. The results of this work can be used to build self-interaction corrected short-range correlation energy functionals.

I. INTRODUCTION

In recent years, there has been a growing interest in approaches that combine density functional theory (DFT) with other approximate methods to treat the many-electron problem. In most cases, this combination is achieved by splitting the Coulomb electron-electron interaction $1/r_{12}$ into a short-range (SR) and a long-range (LR) part (see, e.g., Refs. 1, 2, 3, 4, 5, 6, 7, 8, 9).

The idea is to use different, appropriate approximations for the long-range and the short-range contributions to the exchange and/or correlation energy density functionals of the Kohn-Sham (KS) scheme, to treat, e.g., near-degeneracy effects or van der Waals forces. These approaches are often inspired by the observation that long-range correlations are not well treated by local or semilocal density functionals, but can be dealt with by other techniques, like the standard wavefunction methods of quantum chemistry. Conversely, correlation effects due to the short-range part of the electron-electron interaction can be well described by local or semilocal functionals (appropriately modified).

The error function and its complement (see Fig. 1),

$$\frac{1}{r_{12}} = v_{SR}^\mu(r_{12}) + v_{LR}^\mu(r_{12}) = \frac{\text{erfc}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}, \quad (1)$$

are often used 3, 4, 5, 10, 11 for the splitting of the Coulomb interaction, since they yield analytic matrix elements for both Gaussians and plane waves, i.e., the most common basis functions in quantum chemistry and solid state physics, respectively. The parameter $\mu$ controls the range of the decomposition. Correspondingly, the universal Coulombic functional of the electron density $n(\mathbf{r})$, $F[n]$, as defined in the constrained search formalism 3, 5,

$$F[n] = \min_{\Psi \to n} \langle \Psi | T + V_{\text{ext}} | \Psi \rangle \quad (2)$$

can be divided into a long-range part and a complementary short-range part, $F[n] = F_{LR}^\mu[n] + F_{SR}^\mu[n]$,

$$F_{LR}^\mu[n] = \min_{\Psi^\mu \to n} \langle \Psi^\mu | T + V_{LR}^\mu | \Psi^\mu \rangle$$

or, alternatively, into a short-range part and a complementary long-range part

$$F_{SR}^\mu[n] = F[n] - F_{LR}^\mu[n], \quad (3)$$

$$F_{SR}^\mu[n] = \min_{\Psi^\mu \to n} \langle \Psi^\mu | T + V_{SR}^\mu | \Psi^\mu \rangle$$

or, alternatively, into a short-range part and a complementary long-range part

$$F_{LR}^\mu[n] = F[n] - F_{SR}^\mu[n], \quad (4)$$

These two decompositions lead to different exchange-correlation energy functionals that need to be approximated; they are compared in Ref. 14, where their advantages and disadvantages are discussed.

In the present work we focus on the properties of the long-range and short-range correlation functionals that come from the modification of the electron-electron interaction at short distances, i.e., those properties that are due to the change in the electron-electron coalescence.
conditions. This means that we are only concerned with the functionals of the decomposition of Eq. (3), which involve a many-body wavefunction $\Psi^\mu$ of a system with an electron-electron interaction that is softer than $1/r_{12}$ for small $r_{12}$ (see Fig. 1). This decomposition is the one used in the approaches of Refs. 3, 8, 9, 10.

The paper is organized as follows. In Sec. III we define the long-range and short-range correlation functionals that are the object of the present study. In Sec. IV we analyze the short-range properties of the pair density of a general many-electron system with interaction $\text{erf}(\mu r_{12})/r_{12}$ when $\mu$ gets larger and larger: we derive an expansion for $\mu \rightarrow \infty$ of the on-top (zero electron-electron distance) pair density, and, following (and partly correcting) the work of Ref. 10, an expansion for $\mu \rightarrow \infty$ of the correlation energy functionals. Section V is devoted to the special case of the uniform electron gas: starting from the exact high-density limit, a simple paramaterization of the on-top pair density as a function of $\mu$ is proposed, and is favorably compared with the results obtained from the “extended Overhauser model” 15, 16 for the same quantity. The last Sec. VI explains, with some examples, how the results of this work can be used to build self-interaction corrected approximations for short-range correlation functionals.

Hartree atomic units are used throughout this work.

II. DEFINITIONS AND BASIC EQUATIONS

When the universal functional $F[n]$ is decomposed as in Eq. (3), we have a model system, whose wavefunction is denoted $\Psi^\mu$, which has the same density $n(\mathbf{r})$ of the physical system and electron-electron interaction $\text{erf}(\mu r_{12})/r_{12}$. When $\mu \rightarrow 0$ this model system becomes the Kohn-Sham system, with no electron-electron interaction, while when $\mu \rightarrow \infty$ the model system approaches the physical one, with interaction $1/r_{12}$. By definition, the density is the same for all values of $\mu$. In the approach of Refs. 3, 8, 9, 10 the model system at a fixed $\mu$ is treated with a multideterminantal wavefunction. In general, if $\mu$ is not too large, few determinants describe $\Psi^\mu$ quite accurately (because of the smaller interaction, and also because of the absence of the electron-electron cusp); the larger is the chosen value of $\mu$, the larger is the needed configuration space and thus the computational cost. The remaining part of the energy is provided by the complementary functional $\mathcal{E}_{\text{SR}}[n] = F[n] - F^\mu_{\text{SR}}[n]$ of Eq. (3), which can be divided into Hartree, exchange, and correlation contributions in the usual way for an alternative separation of exchange and correlation, see Ref. 11,

$$
\mathcal{E}^\mu_{\text{H,SR}}[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') V_{\text{SR}}^\mu(\mathbf{r} - \mathbf{r}')
$$

(5)

$$
\mathcal{E}^\mu_{x,\text{SR}}[n] = \langle \Phi \rangle V_{\text{SR}}^\mu \Phi - \mathcal{E}^\mu_{\text{H,SR}}[n]
$$

(6)

$$
\mathcal{E}^\mu_{c,\text{SR}}[n] = \mathcal{E}^\mu_{\text{SR}}[n] - \mathcal{E}^\mu_{\text{H,SR}}[n] - \mathcal{E}^\mu_{x,\text{SR}}[n],
$$

(7)

where $\Phi$ is the Kohn-Sham determinant. Notice that the Hartree and the exchange functional are linear in the interaction, so that $\mathcal{E}^\mu_{\text{H,SR}}[n] = E^\mu_{\text{H,SR}}[n]$ and $\mathcal{E}^\mu_{x,\text{SR}}[n] = E^\mu_{x,\text{SR}}[n]$, where $E^\mu_{\text{H,SR}}[n]$ and $E^\mu_{x,\text{SR}}[n]$ are the short-range functionals of the decomposition of Eq. (1). The correlation energy, instead, depends on the wavefunction $\Psi^\mu$ and we thus have $\mathcal{E}^\mu_{c,\text{SR}}[n] \neq E^\mu_{c,\text{SR}}[n]$. The complementary correlation functional $\mathcal{E}^\mu_{c,\text{SR}}[n]$ is the difference between the usual Coulombic correlation energy $E_{c}[n]$, and the long-range correlation energy functional $E^\mu_{c,\text{LR}}[n]$,

$$
E^\mu_{c,\text{LR}}[n] = \langle \Psi^\mu | T + V_{\text{LR}}^\mu | \Psi^\mu \rangle - \langle \Phi | T + V_{\text{LR}}^\mu | \Phi \rangle
$$

(8)

$$
\mathcal{E}^\mu_{c,\text{SR}}[n] = E_c[n] - E^\mu_{c,\text{LR}}[n].
$$

(9)

In what follows we study the short-range functional $\mathcal{E}^\mu_{c,\text{SR}}[n]$ or, equivalently the long-range functional $E^\mu_{c,\text{LR}}[n]$, in the limit of large $\mu$, i.e., when the model system described by $\Psi^\mu$ is approximating the physical system.

Following Toulouse et al. 10, we start from the Helmann-Feynmann theorem which gives

$$
\frac{\partial}{\partial \mu} \mathcal{E}^\mu_{c,\text{SR}}[n] = - \frac{2}{\sqrt{\pi}} \int_0^\infty 4\pi r_{12}^2 f^\mu_{\text{LR}}(r_{12}) e^{-r_{12}^2} dr_{12},
$$

(10)

where the spherically and system-averaged pair density (or intracule density) $f^\mu_{\text{LR}}(r_{12})$ is obtained by integrating $|\Psi^\mu|^2$ over all variables but $r_{12} = |\mathbf{r}_{\mathbf{1}} - \mathbf{r}_{\mathbf{2}}|$: we first define the spherical average of the pair density (with $\mathbf{r} = \mathbf{r}_{\mathbf{1}}$),

$$
\tilde{f}^\mu_{\text{LR}}(\mathbf{r}, r_{12}) = \frac{N(N-1)}{2} \sum_{\sigma_1 \ldots \sigma_N} \int |\Psi^\mu(\mathbf{r}, \mathbf{r}_{\mathbf{1}}, \mathbf{r}_{\mathbf{2}}, \ldots, \mathbf{r}_N)|^2 \frac{d\Omega_{r_{12}}}{4\pi} d\mathbf{r}_3 \ldots d\mathbf{r}_N,
$$

(11)

and then integrate over all reference positions $\mathbf{r}$,

$$
f^\mu_{\text{LR}}(r_{12}) = \int \tilde{f}^\mu_{\text{LR}}(\mathbf{r}, r_{12}) d\mathbf{r}.
$$

(12)

The correlated part of $f^\mu_{\text{LR}}(r_{12})$ appearing in Eq. (10) is $f^\mu_{\text{c}} = f^\mu - f_{\text{KS}}$, where $f_{\text{KS}}(r_{12})$ is obtained by replacing $\Psi^\mu$ with the Kohn-Sham determinant $\Phi$ in Eq. (11).

The correlated intracule $f^\mu_{\text{c}}(r_{12})$ can be expanded in its Taylor series around $r_{12} = 0$ up to some order $M$,

$$
f^\mu_{\text{c}}(r_{12}) = \sum_{n=0}^{M-1} c_n(\mu) r_{12}^n + O(r_{12}^M).
$$

(13)

By inserting this expansion into Eq. (10) we find

$$
\frac{\partial}{\partial \mu} \mathcal{E}^\mu_{c,\text{SR}}[n] = - \frac{4\sqrt{\pi}}{\mu} \sum_{n=0}^{M-1} c_n(\mu) \frac{n+3}{2} + O\left(\frac{1}{\mu^{M+3}}\right).
$$

(14)

This means that when $\mu \rightarrow \infty$, i.e., when we are approaching the full interaction $1/r_{12}$, the correlation energy functional $\mathcal{E}^\mu_{c,\text{SR}}[n]$ has an expansion in powers of
\(\mu^{-1}\) whose coefficients are determined by the short-range behavior of \(f_{\mu}\). In order to determine as many coefficients as possible in the expansion of Eq. (14), we must have to know how the \(c_i(\mu)\) behave in the limit of large \(\mu\). In Ref. 10 the same expansion was considered, and the first two terms were obtained by simply inserting in Eq. (14) the values of \(c_0\) and \(c_1\) for the physical system (with Coulomb interaction). In the next Sec. III we study \(\mu\), explain why. Moreover, we obtain the first-order (in \(\mu^{-1}\)) result of Ref. 10 for the first term (\(\times \mu^{-3}\)), and switch to variables \(r_{12} = r_1 - r_2\) and \(R = (r_1 + r_2)/2\). In the limit \(r_{12} = |r_{12}| \to 0\) there must be a term H\(\mu\) that compensates the divergence (or, more precisely, the very large value) of \(\text{erf}(\mu r_{12})/r_{12}\). As for the Coulombic system, this compensation comes from the relative kinetic energy term, and to determine the small \(r_{12}\) behavior of the spherical average of \(|\Psi_{\mu}|^2\) we only need to look at the Schrödinger equation for the relative motion of two electrons 18, 19, 20 approximation each other with relative angular momentum \(\ell = 0\). Higher \(\ell\), in fact, will contribute to \(|\Psi_{\mu}|^2\) to orders \(r_{12}^\ell\) in the limit of small \(r_{12}\). Only in the case of a fully polarized system the case \(\ell = 1\) must be considered to determine the \(r_{12} \to 0\) behavior of \(|\Psi_{\mu}|^2\), since only odd \(\ell\) are allowed 19 (triplet symmetry): this case is considered in Appendix 19. The rare case of unnatural parity singlet states 20 (which needs \(\ell = 2\)) is not considered in this work.

As it was done for the Coulomb electron-electron interaction 18, 19, 20, we thus focus on the relative wavefunction \(\psi_{\mu}(r_{12})\) for two electrons in the \(\ell = 0\) state. By defining \(x = r_{12}\) and \(u_{\mu}(x) = \sqrt{\mu} \psi_{\mu}(x)\), the relevant Schrödinger-like equation reads

\[
\left[-\frac{d^2}{dx^2} + \frac{\text{erf}(x)}{x}\right] u_{\mu}(x) = \mathcal{E}_{\mu}(x, R, r_3, ..., r_N) u_{\mu}(x),
\]

where \(\mathcal{E}_{\mu}\) is a complicated operator that does not affect the result as long as it remains bounded when \(\mu \to \infty\) and \(x \to 0\), as it is reasonable to assume from the hamiltonian of Eq. (15) 19, 18, 20. We change variable \(y = \mu x\), and divide both members of Eq. (19) by \(\mu^2\) to obtain

\[
\left[-\frac{d^2}{dy^2} + \frac{\text{erf}(y)}{\mu y}\right] u_{\mu}(y) = \frac{1}{\mu^2} \mathcal{E}_{\mu}(y, R, r_3, ..., r_N) u_{\mu}(y).
\]

We then expand \(u_{\mu}(y)\) for large \(\mu\),

\[
u_{\mu}(y) = u(\infty)(y) + \frac{1}{\mu} u^{(-1)}(y) + O\left(\frac{1}{\mu^3}\right),
\]

insert this expansion into Eq. (17), and impose that the left-hand-side be of order \(\mu^0\) as the right-hand side. With the boundary condition that \(\psi_{\mu}(x)\) is finite at \(x = 0\), we obtain

\[
\nu_{\mu}(y) = ay
\]

\[
\frac{d^2u^{(-1)}(y)}{dy^2} = a \text{ erf}(y),
\]

and we find that the final solution for \(\psi_{\mu}(x)\) from Eqs. (19) - (20) is

\[
\psi_{\mu}(x) = a \left[1 + x p_1(\mu x) + \frac{1}{\sqrt{\pi} \mu} + \frac{A_1}{\mu} + ...\right],
\]

where \(A_1\) is a constant coming from the integration of Eq. (20) that is not determined by the condition that \(\psi_{\mu}(x)\) is finite in \(x = 0\), and \(a\) determines the value \(\psi(0)\) for the Coulombic system (\(\mu = \infty\)). The function \(p_1(y)\) is given by

\[
p_1(y) = \frac{e^{-y^2} - 2}{2\sqrt{\pi} y} + \left[\frac{1}{2} + \frac{1}{4} y^2\right] \text{ erf}(y),
\]

and has the following asymptotic behaviors

\[
p_1(y \to 0) = \frac{y}{\sqrt{\pi}} + O(y^3)
\]

\[
p_1(y \to \infty) = \frac{1}{2} - \frac{1}{\sqrt{\pi} y} + O\left(\frac{1}{y^2}\right).
\]

The spherically- and system-averaged pair-density of Eq. (12) has thus, to leading orders in \(1/\mu\) for large \(\mu\), the small-\(r_{12}\) expansion

\[
f_{\mu}(r_{12}) = f(0) \left[1 + 2 r_{12} p_1(\mu r_{12}) + \frac{2}{\sqrt{\pi} \mu} + \frac{2 A_1}{\mu}\right],
\]

where \(f(0)\) is the on-top value corresponding to the full interacting system \([f(0)\text{ is proportional to } a^2\]

Equation (24) tells us...
that if in Eq. (25) we fix \( r_{12} \) equal to a small value \( r_0 \ll 1 \), and then let \( \mu \) go to \( \infty \) we recover the Coulombic cusp, \( f(r_0) = f(0)(1 + r_0 + ...). \) But for any finite large \( \mu \), Eq. (25) shows that we always obtain a constant quadratic behavior for small \( r_{12} \), \( f^{\mu}(r_{12}) = f(0)(1 + 2r_{12}^2/\mu^2 + ...). \) This is how the cuspless wavefunction corresponding to the interaction \( \text{erf}(\mu r_{12})/r_{12} \) develops the Coulombic cusp in the \( \mu \to \infty \) limit. An alternative derivation of Eq. (25), more similar to what one usually does for the Coulombic cusp \cite{18, 19, 20, 21}, is reported in Appendix A.

To obtain the complementary short-range correlation functional we can insert Eq. (25) into Eq. (14), which gives

\[
\frac{\partial}{\partial \mu} E_{c,SR}[\mu] = -2\pi f_c(0) - 4(\sqrt{2\pi} + A_1) f(0) \left( \frac{1}{\mu^2} \right) + O\left( \frac{1}{\mu^3} \right). \tag{26}
\]

We see that to fully determine the term \( \propto \mu^{-4} \) in Eq. (26) we have to know the value of the constant \( A_1 \). This constant determines how the on-top \( f^{\mu}(0) \) approaches the Coulombic value \( f(0) \) for large \( \mu \). In fact, from Eq. (26) we have

\[
f^{\mu}(0) = f(0) \left( 1 + \frac{1}{\mu} \left( \frac{2}{\sqrt{\pi}} + 2A_1 \right) \right) + O\left( \frac{1}{\mu^2} \right). \tag{27}
\]

In Ref. \cite{10} the \( \mu \to \infty \) limit of the long-range interaction was formally rewritten as the Coulomb interaction \( 1/r_{12} \) plus a perturbation \cite{10}

\[
\frac{\text{erf}(\mu r_{12})}{r_{12}} = \frac{1}{r_{12}} - \frac{\pi}{\mu^2} \delta(r_{12}) + O\left( \frac{1}{\mu^3} \right), \tag{28}
\]

where \( \delta(r) \) is the Dirac delta function. The fact that the perturbation is of order \( \mu^{-2} \) lead to the conclusion \cite{10} that the perturbation on \( \Psi^\mu \) is also of order \( \mu^{-2} \) with respect to the Coulombic case, which should correspond to \( A_1 = -1/\sqrt{\pi} \) in Eq. (28). However, because of the singular nature of the Dirac delta function, this argument does not hold at \( r_{12} = 0 \).

To determine the correction to the on-top value when \( \mu \to \infty \), here we take a large value of \( \mu \) and a small value \( r_{12} = r_0 \) such that \( \mu^{-1} \ll r_0 \ll 1 \) (take, e.g., \( r_0 = 1/\mu^{1-q} \) with \( 0 < q < 1 \)). For such value of \( r_0 \) we have \( \mu r_0 \gg 1 \) so that from Eqs. (24) and (28) we obtain

\[
f^{\mu}(r_0) = f(0) \left( 1 + r_0 + \frac{2A_1}{\mu} \right) + ..., \tag{29}
\]

where the next leading terms are of order \( 1/\mu^2 \) and/or \( r_0^3 \). We then notice that \( A_1 \) cannot be equal to \(-1/\sqrt{\pi}\), since any value of \( A_1 < 0 \) would make \( f^{\mu}(r_0) \) smaller than the full interacting value \( f(r_0) \), while, because for small \( r_{12} \) the long-range interaction \( \text{erf}(\mu r_{12})/r_{12} \) is less repulsive than \( 1/r_{12} \), for \( r_0 \) small enough we expect that \( f^{\mu}(r_0) \geq f(r_0) \). So \( A_1 \geq 0 \), and thus the correction to the on-top value must be of order \( 1/\mu \). However, the argument of Ref. \cite{10} should be valid when \( r_{12} \gg 1/\mu \).

That is, we still expect from Eq. (28) that the perturbed \( \Psi^\mu \) differs from the Coulombic \( \Psi \) of an order higher than \( 1/\mu \) for \( r_{12} \gg 1/\mu \). This is achieved only if \( A_1 = 0 \), as shown by Eq. (29). The result corresponding to \( A_1 = 0 \) is illustrated in Fig. 2 where we compare the Coulomb cusp \( f(0)(1+r_{12}) \) to the short-range expansion of \( f^{\mu}(r_{12}) \) of Eq. (25), with \( A_1 = 0 \). Any value of \( A_1 \) larger than zero makes the difference between the Coulombic \( f(r_{12}) \) and \( f^{\mu}(r_{12}) \) of order \( 1/\mu \) also in the region \( r_{12} \gg 1/\mu \), while with \( A_1 = 0 \) (as in Fig. 2) this difference is of higher order, as expected from Eq. (28).

We thus conclude that

\[
f^{\mu}(0) = f(0) \left( 1 + \frac{2}{\sqrt{\pi} \mu} \right) + O\left( \frac{1}{\mu^2} \right). \tag{30}
\]

This equation is also confirmed in the next Sec. \text{X} for the case of the high-density electron gas that can be treated exactly.

The final expansion of the short-range functional \( E_{c,SR}[\mu] \) for large \( \mu \) is then

\[
E_{c,SR}[\mu] = f_c(0) \frac{\pi}{\mu^2} + f(0) \frac{4\sqrt{2\pi}}{3 \mu^3} + O\left( \frac{1}{\mu^4} \right), \tag{31}
\]

where \( f(0) \) and \( f_c(0) \) are the on-top value and its correlated part, \( f_c = f - f_{KS} \), of the physical system. This expansion differs from the one of Ref. \cite{10} by a factor \( \sqrt{2} \) in the second term (see Appendix A for comments on this discrepancy). The two expansions for the case of the He atom are compared in Fig. 3 with the "exact" results \cite{4, 10} for \( E_{c,SR}[\mu] = E_c - E_{c,1R}[\mu] \). The "exact" on-top value \( f(0) \) is taken from Ref. \cite{22}. We see that the new expansion more accurately reproduce the "exact" data for large \( \mu \), and that the \( \mu \)-value for which it breaks down (i.e., where the expansion has its minimum) coincides with the minimum value of \( \mu \) for which it still gives accurate short-range correlation energies.
In general the on-top value of the physical system, $f(0)$, is not accessible. A plausible approximation proposed in Ref. 10 consists in replacing $f(0)$ in Eq. 31 with its local-density approximation (LDA) value,

$$f_{\text{LDA}}(0) = \frac{1}{2} \int n(r)^2 g(r_{12} = 0; n(r)) \, dr,$$  

(32)

where $g(r_{12}; n)$ is the pair distribution function of the standard electron gas model (with Coulomb interaction $1/r_{12}$) of uniform density $n$. The new Eq. 30 allows to estimate the physical on-top value starting from the one of the model system $\Psi^\mu$. Potential applications of this idea are discussed in Sec. V together with simple examples. Notice also that Eq. 30 is also valid locally, i.e., we have

$$\tilde{P}^\mu_2(r, r_{12} = 0) = \tilde{P}_2(r, r_{12} = 0) \left( 1 + \frac{2}{\sqrt{\pi} \mu} + O \left( \frac{1}{\mu^2} \right) \right),$$  

(33)

where $\tilde{P}_2(r, r_{12})$ was defined in Eq. 11, and $\tilde{P}_2(r, r_{12} = 0)$ is the pair density of the physical system ($\mu = \infty$).

In Appendix B we also consider the case of a fully polarized system, for which we find that the short-range correlation energy has the large-$\mu$ expansion

$$E_{\text{c, SR}}[n = n_t] = f''(0) \frac{3\pi}{8\mu^2} + f''(0) \frac{3\sqrt{2\pi}}{10\mu^3} + O \left( \frac{1}{\mu^4} \right),$$  

(34)

where $f''(0)$ and $f''(0)$ are the second derivative at $r_{12} = 0$ and its correlated part of the physical, fully interacting, system 24. We also found that, again only in the case of a fully polarized system, the second derivative of $f''(r_{12})$ at $r_{12} = 0$ approaches the one of the Coulombic system as

$$(f''(0))' = f''(0) \left( 1 + \frac{2}{3\sqrt{\pi} \mu} + O \left( \frac{1}{\mu^2} \right) \right).$$  

(35)

IV. ON-TOP PAIR DENSITY OF A UNIFORM SYSTEM WITH INTERACTION $\epsilon f(\mu r_{12})/r_{12}$

Before coming to applications, we consider the special case of the uniform electron gas, for which something more than Eq. 30 can be done. We consider a uniform system with long-range-only interaction,

$$H^\mu = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 V_{\text{LR}}^\mu + V_{\text{eb}}^\mu + V_{bb}^\mu,$$  

(36)

where $V_{\text{LR}}^\mu$ is the modified electron-electron interaction

$$V_{\text{LR}}^\mu = \frac{1}{2} \sum_{i \neq j=1}^N \frac{\text{erf}(\mu|r_i - r_j|)}{|r_i - r_j|},$$  

(37)

$V_{eb}^\mu$ is, accordingly, the interaction between the electrons and a rigid, positive, uniform background of density $n = (4\pi r_s^2/3)^{-1}$

$$V_{eb}^\mu = -n \int d\mathbf{x} \frac{\text{erf}(\mu|\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|},$$  

(38)

and $V_{bb}^\mu$ is the corresponding background-background interaction

$$V_{bb}^\mu = \frac{n^2}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\text{erf}(\mu|\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|}.$$  

(39)

When $\mu \rightarrow \infty$ $H^\mu$ tends to the standard jellium hamiltonian, while when $\mu \rightarrow 0$ we recover the noninteracting electron gas.

We focus on the $\mu$-dependence of the on-top value of the pair-distribution function 17, 23 $g(r_{12} = 0, r_s, \mu)$, which has its own interest to construct the LDA approximation for the long-range and short-range functionals, and for spin-density functional theory in the framework of the alternative on-top interpretation 23. The relation between the function $g$ and the function $f$ of Eq. 12 is $g = 2f/nN$.

A. High-density limit

As in the Coulomb gas, by switching to scaled units $s_i = r_i/r_s$, we see that when $r_s \rightarrow 0$ the potential of Eqs. 37 - 39 becomes a perturbation to the noninteracting gas. Defining the correlation contribution to the on-top value, $g_c(0, r_s, \mu) = g(0, r_s, \mu) - \frac{1}{2}$, and following Kimball 26, the first-order correction (with respect to the interaction potential) to the on-top pair density is

$$g_c(0, r_s \rightarrow 0, \mu) = 6 \int_0^\infty \Delta S_D(t, \mu) t^2 \, dt + \ldots,$$  

(40)

where $\Delta S_D(t, \mu)$ is the direct second-order contribution to the static structure factor 26,

$$\Delta S_D(q, \mu) = \frac{4}{N} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} \nu_{ee}(q) \frac{n_F(k) n_F(k')}{k^4 + k'^4 - (k + q)^2 - (k' - q)^2}.$$

(41)
where the function \( h(z) \) that determines the high-density limit of the on-top pair density of the “erf” gas [see Eq. (42)]. The numerical evaluation of Eq. (48) (points) is compared to the fitting function of Eq. (45) (solid line).

\( a_F \) is the usual Fermi occupation function \( \left[ \text{Eq. (42)} \right] \) and \( v_{ee}(q) \) is the Fourier transform of the electron-electron interaction. In Eq. (49) the scaled variable \( t = q/2k_F \) \( (k_F = (\alpha_r s)^{-1}, \alpha = (\alpha s)^{1/3}) \) has been used. The function \( \Delta S_D(t, \mu) \) is thus equal to the one computed by Kimball \( \left[ \text{Eq. (46)} \right] \) and reported in his Eq. (11), except for a multiplying factor \( e^{-\pi k_F^2/\mu^2} \) coming from the Fourier transform of \( \text{erf}(\mu r_0)/r_0 \). From Eqs. (40) and (41) we find

\[
g_c(0, r_s \to 0, \mu) = r_s h(\mu/k_F) + ..., \tag{42}
\]

where the function \( h(z) \) has the following asymptotic behaviors

\[
h(z \to 0) = -\frac{\ln(1 - 2z^2)}{5\pi} + O(z^3), \tag{43}
\]

\[
h(z \to \infty) = a_{\text{HD}} + \frac{\alpha}{\sqrt{\pi} z} + O(z^{-2}), \tag{44}
\]

and \( a_{\text{HD}} = -\alpha(\pi^2 + 6\ln 2 - 3)/5\pi \approx -0.36583 \) is the high-density limit of the standard jellium model. Notice that Eq. (44) confirms, for the high-density electron gas, Eq. (30).

For intermediate values of \( z \) we computed numerically the function \( h(z) \), and we found that it can be accurately fitted by the Padé form

\[
h(z) = \frac{a_1 z^2 + a_2 z^3}{1 + b_1 z + b_2 z^2 + b_3 z^3}, \tag{45}
\]

with \( a_1 = -\frac{\ln(1 - 2)}{5\pi}, b_1 = 1.4919, b_2 = 1.91528, a_2 = a_{\text{HD}} b_1, b_3 = (a_1 - b_2 \alpha/\sqrt{\pi})/a_{\text{HD}}. \) The numerical results and the fitting function of Eq. (45) are reported in Fig. 4.

B. Interpolation formula

The high-density limit of Eq. (12) and of Fig. 4 tells us how (at least for small \( r_s \)) \( g_c(0, r_s, \mu) \) approaches the two limits, the noninteracting gas \( (\mu \to 0) \) and the Coulomb gas \( (\mu \to \infty) \).

A simple interpolation formula for all densities can be built by assuming that the \( \mu \) dependence of \( g_c(0, r_s, \mu) \) is roughly the same at each \( r_s \). We thus start from the parameterization of the on-top pair density of the jellium model given in Ref. 16

\[
g(0, r_s, \mu = \infty) = \frac{1}{2} \left( 1 - B r_s + C r_s^2 + D r_s^3 + E r_s^4 \right) e^{-d r_s}, \tag{46}
\]

where \( C = 0.08193, D = -0.01277, E = 0.001859, d = 0.7524 \) and \( B = -2 a_{\text{HD}} - d \), and we simply rescale homogeneously all the coefficients with the function \( h(z = \mu/k_F)/a_{\text{HD}}, \)

\[
g_c(0, r_s, \mu) = \frac{e^{-d r_s h(z)/a_{\text{HD}}}}{2} \left[ 1 - B \frac{h(z)}{a_{\text{HD}}} r_s + C \frac{h(z)^2}{a_{\text{HD}}^2} r_s^2 \right.
\]

\[
\left. + D \frac{h(z)^3}{a_{\text{HD}}^3} r_s^3 + E \frac{h(z)^4}{a_{\text{HD}}^4} r_s^4 \right] - \frac{1}{2}. \tag{47}
\]

This simple guess smoothly interpolates between the \( \mu \to 0 \) and \( \mu \to \infty \) limits, and is exact when \( r_s \to 0 \).

C. Results from the Overhauser model

To check the validity of the interpolation formula of Eq. (47) we evaluated the on-top \( g_c(0, r_s, \mu) \) within the “extended Overhauser model” \( \left[ \text{Eq. (46)} \right] \), which gave good results for the standard jellium model \( \left[ \text{Eq. (45)} \right] \) and for two-electron atoms \( \left[ \text{Eq. (46)} \right] \). Notice that the on-top value is not known exactly. The differences between the jellium on-top pair densities from different approximate methods (including the “extended Overhauser model”) are discussed in Refs. 28, 29, 30.

The scattering equations of the “extended Overhauser model” are widely explained in Refs. 16, 51. Here we sim-
ply solved the same equations with the electron-electron interaction $\text{erf}(\mu r_{12})/r_{12}$ screened by a sphere of radius $r_s$ of uniform positive charge density $n$ and attracting the electrons with the same modified interaction,

$$V_{\text{eff}}(r_{12}, r_s, \mu) = \frac{\text{erf}(\mu r_{12})}{r_{12}} - \int_{|r'| \leq r_s} n \frac{\text{erf}(\mu |r' - r_{12}|)}{|r' - r_{12}|} \, dr'.$$

(48)

This potential is reported in the Appendix of Ref. [27], where it has been used for two-electron atoms with rather accurate results for the corresponding short-range correlation energy. $V_{\text{eff}}(r_{12}, r_s, \mu)$ is a screened potential that tends to the “Overhauser potential” [11] when $\mu \to \infty$, and which goes to zero when $\mu \to 0$. As in the original Overhauser model, the idea behind Eq. (48) is that the radius of the screening “hole” is exactly equal to $r_s$.

The results for the on-top $g_c(0, r_s, \mu)$ from the Overhauser model are reported in Fig. 5 as a function of $r_s$ for different values of $\mu$. We see that the simple interpolation formula of Eq. (47) accurately captures the $\mu$ and $r_s$ dependence of $g_c(0, r_s, \mu)$.

V. APPLICATIONS, PERSPECTIVES, AND CONCLUSIONS

The main results of this work are (i) the corrected expansion of the short-range correlation energy functional, Eq. (31), (ii) the expansion of the on-top pair density of Eqs. (29) and (33), and (iii) the parameterization of the $\mu$-dependence of the on-top pair density of the uniform electron gas, Eq. (44). All these results (i-iii) can be useful for the construction of approximate short-range correlation energy functionals:

(i) In Ref. [10] the large-$\mu$ expansion of the correlation energy functional has been already used to construct approximations: the idea is [10] to interpolate between a given density functional approximation (DFA) of standard KS theory [32] at $\mu = 0$, and the $\mu \to \infty$ expansion of $E_{\text{c,SR}}[\mu]$. In the spirit of the usual DFT approximations, this interpolation is done locally, i.e.,

$$E'_{\text{c,SR}}[\mu] = \int dr \, n(r, \mu) \, \tau'_{\text{c,SR}}(r),$$

(49)

where $\tau'_{\text{c,SR}}(r)$ is built, e.g., as [10]

$$\tau'_{\text{c,SR}} \approx \frac{E'_{\text{c,SR}}}{1 + d_1 \mu + d_2 \mu^2}.$$  

(50)

The parameters $d_1$ and $d_2$ are fixed by the condition that Eq. (49) recovers the correct $\mu \to \infty$ expansion of $E_{\text{c,SR}}[\mu]$, and $E'_{\text{c,SR}}$ can be, e.g., the PBE correlation functional [33] of standard Kohn-Sham theory or any other available approximation. This correlation functional can be combined with a similar interpolation for exchange [10], or with the exchange functional of Heyd, Scuseria, and Ernzerhof [8]. This way of constructing approximations should be improved by using the corrected expansion of Eq. (31), as suggested by Fig. 4. In Fig. 6 we also show similar data for the Be atom: again, the corrected expansion is closer to the “exact” data [9, 10] at large $\mu$ than the previous expansion used in Ref. [10].

(ii) To impose the correct large-$\mu$ expansion in approximations like the one of Eq. (31) we need an estimate of the physical ($\mu = \infty$) on-top pair density $\tilde{P}_2(r, r_{12} = 0)$. In Ref. [10] the LDA approximation [the integrand of the right-hand side of Eq. (32)] was used. The new Eq. (33) allows to use the on-top pair density of the partially correlated wavefunction $\tilde{\Psi}_c^\mu$ to estimate $\tilde{P}_2(r, r_{12} = 0)$. In fact, once we have made a calculation at a given (moderately large) $\mu$ (say, $\mu = \mu_0$) we can estimate $\tilde{P}_2(r, r_{12} = 0)$ as

$$\tilde{P}_2(r, r_{12} = 0) \approx \tilde{P}^{\mu_0}_2(r, r_{12} = 0) \left(1 + \frac{2}{\sqrt{\pi \mu_0}}\right)^{-1}.$$  

(51)

There are cases in which this estimate could be much better than the one obtained by using the LDA approximation for the physical on-top pair density. In fact, the use of the partially correlated $\tilde{P}^{\mu_0}_2(r, r_{12} = 0)$ would correct the self-interaction error of LDA, becoming exactly equal to zero for any one-electron density. Consider the example of the stretched H$_2$ molecule, for which the estimate from Eq. (51) would be essentially exact (equal to zero for any $\mu > 0$), while LDA gives a spurious nonzero on-top value, unless we consider the spin broken-symmetry solution.

To show that Eq. (31) gives indeed a quantitative reliable estimate of the physical on-top pair density we have considered the simple example of the He atom, and we have inserted Eq. (31) directly in the expansion of Eq. (31): the error on the estimated short-range correlation energy at $\mu_0 = 2.5$ is 3 mH; if we choose $\mu_0 = 2$ the error in $E_{\text{c,SR}}[\mu]$ is 5 mH, and for $\mu_0 = 1$ is 11 mH. Of course, when $\mu_0$ becomes too small, the large-$\mu$ expansion of Eqs. (31) and (51) is no longer valid.
(iii) The on-top pair density of the uniform electron gas with long-range-only interaction of Eq. (17) can be used, in combination with the correlation energy of the spin-polarized long-range electron gas [22], to implement the local approximation for the on-top pair density interpretation of spin density functional theory [25].

Another interesting application of Eq. (47) is connected to point (ii): the construction of functionals that explicitly depend on the on-top interaction error. The same kind of analysis can be also considered, e.g.,

$$f_c(0) = f_c(0) \frac{\int n(r)^2 \rho_c(0, r, \mu = \infty) \, dr}{\int n(r)^2 \rho_c(0, r, \mu_0) \, dr}.$$  \hspace{1cm} (52)

For example for the He atom Eq. (22) at $\mu_0 = 2$ gives $f_c(0) = -0.086$, while Eq. (31) gives $-0.090$. The corresponding “exact” value [22] is $-0.085$. Local versions of Eq. (32) can be also considered, e.g.,

$$f_c(0) \approx \frac{1}{n(r)^2} \rho_c(0, r_1, \mu = \infty) \, dr,$$  \hspace{1cm} (53)

where $\tilde{\rho}_2(\mu, r_{12})$ is obtained by subtracting the Kohn-Sham pair density from $\tilde{\rho}_2(\mu)$. Again, the advantage of including in the construction of short-range functionals the on-top $\tilde{\rho}_2(\mu, r_{12} = 0)$ is to locally remove the self-interaction error.

In conclusions, we have presented a comprehensive study of the short-range behavior of systems interacting with the potential $\text{erf}(\mu x)$, in connection with the properties of long- and short-range correlation energy density functionals. The same kind of analysis can be of course repeated for other splittings of the Coulomb energy density functionals. The same kind of analysis can

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APPENDIX A: ALTERNATIVE DERIVATION OF EQ. (25)

Start from Eq. (17) and consider the following series expansions around $x = 0$

$$u^x(x) = \sum_{n=0}^{\infty} a_n(x) x^{n+1},$$  \hspace{1cm} (A1)

$$\frac{\text{erf}(\mu x)}{x} = \sum_{n=0}^{\infty} b_n(x) \mu^{2n},$$  \hspace{1cm} (A2)

$$b_n = \frac{2}{\sqrt{\pi}} (-1)^n (2n+1)!.$$  \hspace{1cm} (A3)

This last series has an infinite radius of convergence for any finite $\mu$.

The complicated operator $\mathcal{E}^x$ can be also expanded in powers of $x$ around $x = 0$. Its expansion will only contain even powers of $x$ because the hamiltonian of Eq. (18) is even in $x = r_{12}$. As expected, the expansion of $\mathcal{E}^x$ does not play any role, so we do not consider its non-spherical components (moreover, in the end we are only interested in the spherically averaged pair density). The only important requirement is that $\mathcal{E}^x$ remains bounded when $\mu \to \infty$ and $x \to 0$, as it happens for the Coulomb interaction [18, 19]. We thus write

$$\mathcal{E}^x = \sum_{k=0}^{\infty} e_{2k}(\mu) x^{2k}.$$  \hspace{1cm} (A4)

By inserting Eqs. (A1), (A2) and (A3) into Eq. (16) we find that the $a_n(\mu)$ with odd $n$ are zero (as expected from the fact that $\text{erf}(\mu x)/x$ is an even function of $x$), while the even $n$ coefficients with $n \geq 2$ diverge as $\mu$ increases, and, to leading order when $\mu \to \infty$, they are all proportional to $a_0(\mu)$,

$$a_{2k+2}(\mu) = a_0(\mu) \left[ \frac{b_k \mu^{2k+1}}{(2k+2)(2k+3)} + \frac{\mu^{2k}}{2} \sum_{i=1}^{k} \frac{b_{k-i} b_{i-1}}{2i(2i+1)} \right] + O(\mu^{2k-1}).$$  \hspace{1cm} (A5)

This relation shows that $\psi^x(x)$ has the structure

$$\psi^x(x) = a_0(\mu)[1 + x p_1(\mu x) + x^2 p_2(\mu x) + ...]$$  \hspace{1cm} (A6)

where

$$p_1(y) = \sum_{k=0}^{\infty} \frac{b_{2k+1}}{(2k+2)(2k+3)}$$  \hspace{1cm} (A7)

Equation (A6) gives exactly the same function $p_1(y)$ of Eq. (22), and Eq. (A7) confirms that all the terms beyond
the ones considered in Eq. (25) contribute to Eq. (26) to orders $\mu^{-5}$ or higher.

We can now clearly see where the discrepancy with the result of Ref. 10 comes from: the small-$r_{12}$ expansion of $f^\mu(r_{12})$ only contains even powers of $r_{12}$ for any finite $\mu$. It is thus incorrect to insert the odd coefficient $c_1$ of the Coulombic system in Eq. (14), as it was done in Ref. 10. What happens, instead, is that all the even coefficients of the small-$r_{12}$ expansion of $f^\mu(r_{12})$ diverge for large $\mu$ and they all contribute to the term $\propto \mu^{-3}$ in Eq. (14). Furthermore, in Ref. 10 it was assumed that the leading order in the large-$\mu$ expansion of the on-top value $f^\mu(0)$ is $1/\mu^2$, while we have shown that to correct for $f^\mu(0)$ with respect to the Coulombic case is of order $1/\mu$.

APPENDIX B: THE CASE $\ell = 1$

We insert the expansion of $u^\mu(y)$ for large $\mu$ of Eq. (18) into the equivalent of Eq. (14) for the case $\ell = 1$,

$$\left[ -\frac{d^2}{dy^2} + \frac{2}{y^2} + \frac{1}{\mu y} \left( \frac{1}{y} \right) \right] u^\mu(y) = \frac{1}{\mu^2} \mathcal{E}^\mu u^\mu(y). \tag{B1}$$

The condition that the left-hand side be of order $1/\mu^2$ yields

$$u^{(\infty)}(y) = b y^2 \quad \text{and} \quad u^{(-1)}(y) = b y \text{erf}(y). \tag{B2}$$

By solving Eq. (B3) we find that the intracule $f^\mu(r_{12})$ has, for large $\mu$, the small-$r_{12}$ expansion

$$f^\mu(r_{12}) = \frac{f''(0)}{2} r_{12}^2 \left[ 1 + 2 r_{12} q_1(\mu r_{12}) + \frac{2}{3 \sqrt{\pi} \mu} + \frac{B_1}{\mu} \right], \tag{B4}$$

where the function $q_1(y)$ is equal to

$$q_1(y) = \frac{e^{-y^2}(2y^2 - 1)}{8 \sqrt{\pi} y^3} - \frac{1}{3 \sqrt{\pi} y} + \text{erf}(y)(4y^4 + 1) \frac{1}{16y^2}, \tag{B5}$$

and $B_1$ is a constant of integration that is not determined by the requirement that $f^\mu$ vanishes at $r_{12} = 0$. The function $q_1(y)$ has the asymptotic behaviors

$$q_1(y \to 0) = \frac{y}{5 \sqrt{\pi}} + O(y^3) \quad \text{and} \quad q_1(y \to \infty) = \frac{1}{4} - \frac{1}{3 \sqrt{\pi} y} + O\left(\frac{1}{y^3}\right). \tag{B7}$$

Again, we see that if we fix $r_{12} = r_0 \ll 1$, and then let $\mu \to \infty$ we find $f^\mu(r_0) \propto r_0^2[1 + r_0^2/2 + ...]$, which is the parallel-spin cusp condition for the Coulomb interaction [19]. But for any finite $\mu$ we have, for small $r_{12}$, $f^\mu(r_{12}) \propto r_{12}^2[1 + r_{12}^2/2\mu/3\sqrt{\pi} + ...]$. The proof that $B_1 = 0$, and thus of Eqs. (B4) and (B5) is then completely analogous to the one for the case $\ell = 0$.

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