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 parametrization 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.

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I. INTRODUCTION

In recent years, there has been a growing interest in approaches that combine density functional theory [1–3] (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. [4–12]). 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 wave-function 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),

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

are often used [5,6,8,10,11] 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 μ 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 [13],

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

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

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

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

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

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

$$\bar{F}_{\mathrm{LR}}^{\mu}[n] = F[n] - F_{\mathrm{SR}}^{\mu}[n]. \quad (4)$$

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 wave function Ψ^{μ} 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. [5,7–11].

The paper is organized as follows. In Sec. II we define the long-range and short-range correlation energy functionals that are the object of the present study. In Sec. III we analyze the short-range properties of the pair density of a general many-electron system with interaction $\mathrm{erf}(\mu r_{12})/r_{12}$ when μ gets larger and larger: we derive an expansion for $\mu \to \infty$ of the on-top (zero electron-electron distance) pair density, and, following (and partly correcting) the work of Ref. [10], an expansion for $\mu \to \infty$ of the correlation energy functionals. Section IV is devoted to the special case of the uniform electron gas: starting from the exact high-density limit, a

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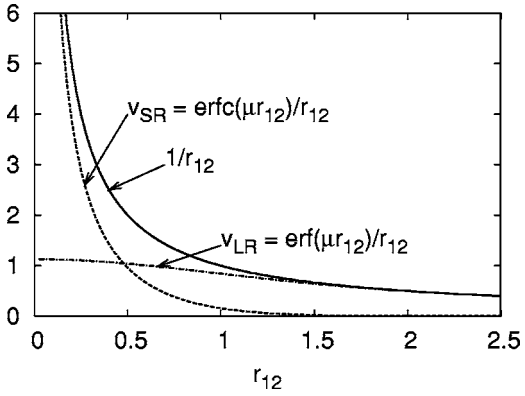

FIG. 1. The splitting of the Coulomb interaction $1/r_{12}$ into a short-range (SR) and a long-range (LR) part as defined in Eq. (1). Here $\mu=1$. When $\mu\to\infty$ we have $v_{SR}\to 0$ and $v_{LR}\to 1/r_{12}$, and when $\mu\to 0$ we have $v_{SR}\to 1/r_{12}$ and $v_{LR}\to 0$.

simple parametrization of the on-top pair density as a function of μ is proposed, and is favorably compared with the results obtained from the "extended Overhauser model" [15,16] for the same quantity. The last Sec. V 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 wave function is denoted Ψ^μ, which has the same density $n(\mathbf{r})$ of the physical system and electron-electron interaction $\mathrm{erf}(\mu r_{12})/r_{12}$. When $\mu\to 0$ this model system becomes the Kohn-Sham system, with no electron-electron interaction, while when $\mu\to\infty$ the model system approaches the physical one, with interaction $1/r_{12}$. By definition, the density is the same for all values of μ. In the approach of Refs. [7–10] the model system at a fixed μ is treated with a multideterminantal wave function. In general, if μ is not too large, few determinants describe Ψ^μ 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 μ, the larger is the needed configuration space and thus the computational cost. The remaining part of the energy is provided by the complementary functional $\bar{F}^\mu_{\mathrm{SR}}[n]=F[n]-F^\mu_{\mathrm{LR}}[n]$ 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. [17]),

$$\bar{E}^\mu_{\mathrm{H,SR}}[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\, n(\mathbf{r})n(\mathbf{r}')v^\mu_{\mathrm{SR}}(|\mathbf{r}-\mathbf{r}'|), \tag{5}$$

$$\bar{E}^\mu_{x,\mathrm{SR}}[n]=\langle\Phi|V^\mu_{\mathrm{SR}}|\Phi\rangle-\bar{E}^\mu_{\mathrm{H,SR}}[n], \tag{6}$$

$$\bar{E}^\mu_{c,\mathrm{SR}}[n]=\bar{F}^\mu_{\mathrm{SR}}[n]-\bar{E}^\mu_{\mathrm{H,SR}}[n]-\bar{E}^\mu_{x,\mathrm{SR}}[n], \tag{7}$$

where Φ is the Kohn-Sham determinant. Notice that the Hartree and the exchange functional are linear in the interaction, so that $\bar{E}^\mu_{\mathrm{H,SR}}[n]=E^\mu_{\mathrm{H,SR}}[n]$ and $\bar{E}^\mu_{x,\mathrm{SR}}[n]=E^\mu_{x,\mathrm{SR}}[n]$, where $E^\mu_{\mathrm{H,SR}}[n]$ and $E^\mu_{x,\mathrm{SR}}[n]$ are the short-range functionals of the decomposition of Eq. (4). The correlation energy, instead, depends on the wave function Ψ^μ and we thus have $\bar{E}^\mu_{c,\mathrm{SR}}[n]\neq E^\mu_{c,\mathrm{SR}}[n]$. The complementary correlation functional $\bar{E}^\mu_{c,\mathrm{SR}}[n]$ is the difference between the usual Coulombic correlation energy $E_c[n]$, and the long-range correlation energy functional $E^\mu_{c,\mathrm{LR}}[n]$,

$$E^\mu_{c,\mathrm{LR}}[n]=\langle\Psi^\mu|T+V^\mu_{\mathrm{LR}}|\Psi^\mu\rangle-\langle\Phi|T+V^\mu_{\mathrm{LR}}|\Phi\rangle, \tag{8}$$

$$\bar{E}^\mu_{c,\mathrm{SR}}[n]=E_c[n]-E^\mu_{c,\mathrm{LR}}[n]. \tag{9}$$

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

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

$$\frac{\partial}{\partial\mu}\bar{E}^\mu_{c,\mathrm{SR}}[n]=-\frac{2}{\sqrt{\pi}}\int_0^\infty 4\pi r_{12}^2 f^\mu_c(r_{12})e^{-\mu^2 r_{12}^2}dr_{12}, \tag{10}$$

where the spherically and system-averaged pair density (or intracule density) $f^\mu(r_{12})$ is obtained by integrating $|\Psi^\mu|^2$ over all variables but $r_{12}=|\mathbf{r}_2-\mathbf{r}_1|$: we first define the spherical average of the pair density (with $\mathbf{r}=\mathbf{r}_1$),

$$\tilde{P}^\mu_2(\mathbf{r},r_{12})=\frac{N(N-1)}{2}\sum_{\sigma_1\cdots\sigma_N}\int|\Psi^\mu(\mathbf{r},\mathbf{r}_{12},\mathbf{r}_3,\ldots,\mathbf{r}_N)|^2\times\frac{d\Omega_{\mathbf{r}_{12}}}{4\pi}d\mathbf{r}_3\ldots d\mathbf{r}_N, \tag{11}$$

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

$$f^\mu(r_{12})=\int\tilde{P}^\mu_2(\mathbf{r},r_{12})d\mathbf{r}. \tag{12}$$

The correlated part of $f^\mu(r_{12})$ appearing in Eq. (10) is $f^\mu_c=f^\mu-f_{\mathrm{KS}}$, where $f_{\mathrm{KS}}(r_{12})$ is obtained by replacing Ψ^μ with the Kohn-Sham determinant Φ in Eq. (11).

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

$$f^\mu_c(r_{12})=\sum_{n=0}^{M-1}c_n(\mu)r_{12}^n+O(r_{12}^M). \tag{13}$$

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

$$\frac{\partial}{\partial\mu}\bar{E}^\mu_{c,\mathrm{SR}}[n]=-4\sqrt{\pi}\sum_{n=0}^{M-1}\frac{c_n(\mu)}{\mu^{n+3}}\Gamma\left(\frac{n+3}{2}\right)+O\left(\frac{1}{\mu^{M+3}}\right). \tag{14}$$

This means that when $\mu\to\infty$, i.e., when we are approaching the full interaction $1/r_{12}$, the correlation energy functional $\bar{E}^\mu_{c,\mathrm{SR}}[n]$ has an expansion in powers of μ^{-1} whose coefficients are determined by the short-range behavior of f^μ_c. In order to determine as many coefficients as possible in the

expansion of Eq. (14) we thus have to know how the $c_n(\mu)$ behave in the limit of large μ. 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 the general problem of determining the short-range behavior of $f^\mu(r_{12})$ in the limit $\mu\to\infty$. We find the same result of Ref. [10] for the first term ($\propto\mu^{-3}$) of Eq. (14), but a different result for the second term ($\propto\mu^{-4}$), and we explain why. Moreover, we obtain the first-order (in μ^{-1}) term of the expansion for large μ of the on-top $f^\mu(0)$.

III. SHORT-RANGE BEHAVIOR OF A SYSTEM WITH INTERACTION $\mathrm{erf}(\mu r_{12})/r_{12}$ WHEN $\mu\to\infty$

We start from the Schrödinger equation for the wave function Ψ^μ,

$$H^\mu\Psi^\mu = E^\mu\Psi^\mu,$$

$$H^\mu = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2} + \sum_{i>j=1}^{N}\frac{\mathrm{erf}(\mu|\mathbf{r}_i-\mathbf{r}_j|)}{|\mathbf{r}_i-\mathbf{r}_j|} + \sum_{i=1}^{N} v_\mu(\mathbf{r}_i), \quad (15)$$

where the one-body potential $v_\mu(\mathbf{r})$ keeps the density equal to the one of the physical system for every μ.

When $\mu\to\infty$ the interaction $\mathrm{erf}(\mu r_{12})/r_{12}$ gets larger and larger for small r_{12} ($r_{12}\ll 1/\mu$). If we thus fix a finite but very large value of μ, we can use the same arguments that lead to the derivation of the electron-electron cusp condition for the Coulomb interaction [18–21], i.e., we can isolate two coalescing electrons (say, 1 and 2) in the Hamiltonian of Eq. (15), and switch to variables $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$ and $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$. In the limit $r_{12}=|\mathbf{r}_{12}|\to 0$ there must be a term in $H^\mu\Psi^\mu$ that compensates the divergence (or, more precisely, the very large value) of $\mathrm{erf}(\mu r_{12})/r_{12}$. As for the Coulombic systems, 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 [18–20] approaching each other with relative angular momentum $\ell=0$. Higher ℓ, in fact, will contribute to $|\Psi^\mu|^2$ to orders $r_{12}^{2\ell}$ 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 ℓ are allowed [19] (triplet symmetry); this case is considered in Appendix B. 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 [18–20], we thus focus on the relative wave function $\psi^\mu(r_{12})$ for two electrons in the $\ell=0$ state. By defining $x=r_{12}$ and $u^\mu(x)=x\psi^\mu(x)$, the relevant Schrödinger-like equation reads

$$\left[-\frac{d^2}{dx^2}+\frac{\mathrm{erf}(\mu x)}{x}\right]u^\mu(x) = \mathcal{E}^\mu(\mathbf{x},\mathbf{R},\mathbf{r}_3,\ldots,\mathbf{r}_N)u^\mu(x), \quad (16)$$

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) [18–20]. We change variable $y=\mu x$, and divide both members of Eq. (16) by μ^2 to obtain

$$\left[-\frac{d^2}{dy^2}+\frac{1}{\mu}\frac{\mathrm{erf}(y)}{y}\right]u^\mu(y) = \frac{1}{\mu^2}\mathcal{E}^\mu(\mathbf{y},\mathbf{R},\mathbf{r}_3,\ldots,\mathbf{r}_N)u^\mu(y). \quad (17)$$

We then expand $u^\mu(y)$ for large μ,

$$u^\mu(y) = u^{(\infty)}(y) + \frac{1}{\mu}u^{(-1)}(y) + O\left(\frac{1}{\mu^2}\right), \quad (18)$$

insert this expansion into Eq. (17), and impose that the left-hand side be of order μ^{-2} as the right-hand side. With the boundary condition that $\psi^\mu(x)$ is finite at $x=0$, we obtain

$$u^{(\infty)}(y) = ay, \quad (19)$$

$$\frac{d^2u^{(-1)}(y)}{dy^2} = a\,\mathrm{erf}(y), \quad (20)$$

and we find that the final solution for $\psi^\mu(x)$ from Eqs. (19) and (20) is

$$\psi^\mu(x) = a\left[1 + xp_1(\mu x) + \frac{1}{\sqrt{\pi}\mu} + \frac{A_1}{\mu} + \cdots\right], \quad (21)$$

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

$$p_1(y) = \frac{e^{-y^2}-2}{2\sqrt{\pi}y} + \left(\frac{1}{2}+\frac{1}{4y^2}\right)\mathrm{erf}(y), \quad (22)$$

and has the following asymptotic behaviors:

$$p_1(y\to 0) = \frac{y}{3\sqrt{\pi}} + O(y^3), \quad (23)$$

$$p_1(y\to\infty) = \frac{1}{2} - \frac{1}{\sqrt{\pi}y} + O\left(\frac{1}{y^2}\right). \quad (24)$$

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

$$f^\mu(r_{12}) = f(0)\left[1 + 2r_{12}p_1(\mu r_{12}) + \frac{2}{\sqrt{\pi}\mu} + \frac{2A_1}{\mu}\right], \quad (25)$$

where $f(0)$ is the on-top value corresponding to the full interacting system [$f(0)$ is proportional to a^2, where a determines $u^{(\infty)}(y)$ in Eq. (19)]. 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 μ go to ∞ we recover the Coulombic cusp, $f(r_0)=f(0)(1+r_0+\cdots)$. But for any finite large μ, Eq. (23) shows that we always obtain a quadratic behavior for small r_{12}, $f^\mu(r_{12})=f(0)(1+2r_{12}^2\mu/3\sqrt{\pi}+\cdots)$. This is how the cuspless wave function corresponding to the interaction $\mathrm{erf}(\mu r_{12})/r_{12}$ 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 [18–21], is reported in Appendix A.

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

$$\frac{\partial}{\partial\mu}\bar{E}^{\mu}_{c,\mathrm{SR}}[n] = -2\pi\frac{f_c(0)}{\mu^3} - 4(\sqrt{2\pi}+A_1\pi)\frac{f(0)}{\mu^4} + O\left(\frac{1}{\mu^5}\right). \tag{26}$$

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 μ. In fact, from Eq. (25) 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. [10] the $\mu\to\infty$ limit of the long-range interaction was formally rewritten as the Coulomb interaction $1/r_{12}$ plus a perturbation [10]

$$\frac{\mathrm{erf}(\mu r_{12})}{r_{12}} = \frac{1}{r_{12}} - \frac{\pi}{\mu^2}\delta(\mathbf{r}_{12}) + O\left(\frac{1}{\mu^3}\right), \tag{28}$$

where $\delta(\mathbf{r})$ is the Dirac delta function. The fact that the perturbation is of order μ^{-2} leads to the conclusion [10] that the perturbation on Ψ^{μ} is also of order μ^{-2} with respect to the Coulombic case, which would correspond to $A_1=-1/\sqrt{\pi}$ in Eq. (27). 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 μ 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 (25) we obtain

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

where the next leading terms are of order $1/\mu^2$ and/or r_0^2. 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 $\mathrm{erf}(\mu r_{12})/r_{12}$ 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. [10] should be valid when $r_{12}\gg 1/\mu$. That is, we still expect from Eq. (28) that the perturbed Ψ^{μ} differs from the Coulombic Ψ 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

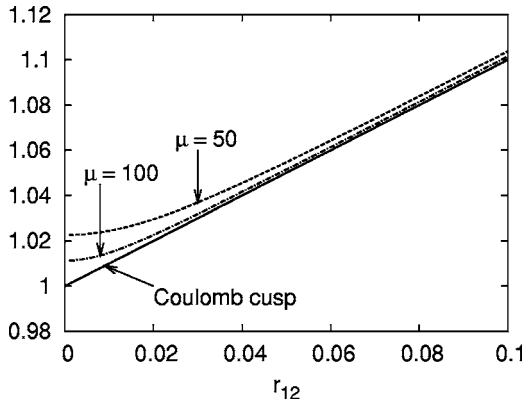

FIG. 2. The Coulombic cusp $f(0)(1+r_{12})$ (with $f(0)=1$) is compared to the expansion of $f^{\mu}(r_{12})$ in the $\mu\to\infty$ limit, $f^{\mu}(r_{12})=f(0)\times[1+2r_{12}p_1(\mu r_{12})+2/(\sqrt{\pi}\mu)+2A_1/\mu]$, with $A_1=0$. Any value $A_1>0$ makes $f^{\mu}(r_{12})$ differ from the Coulombic $f(r_{12})$ of orders $1/\mu$ also in the region $r_{12}\gg 1/\mu$.

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

This equation is also confirmed in the next section (IV), for the case of the high-density electron gas that can be treated exactly.

The final expansion of the short-range functional $\bar{E}^{\mu}_{c,\mathrm{SR}}[n]$ for large μ is then

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

where $f(0)$ and $f_c(0)$ are the on-top value and its correlated part, $f_c=f-f_{\mathrm{KS}}$, of the physical system. This expansion differs from the one of Ref. [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 [9,10] for $\bar{E}^{\mu}_{c,\mathrm{SR}}[n]=E_c-E^{\mu}_{c,\mathrm{LR}}[n]$. The "exact" on-top value $f(0)$ is taken from Ref. [22]. We see that the new expansion more accurately

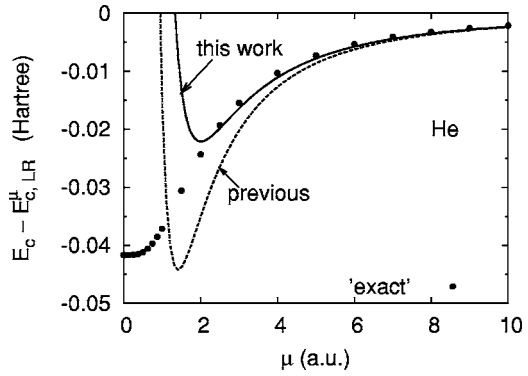

FIG. 3. The "exact" values of $\bar{E}^{\mu}_{c,\mathrm{SR}}[n]=E_c-E^{\mu}_{c,\mathrm{LR}}[n]$ for the He atom [9,10] are compared with the large-μ expansion of Eq. (31), and with the previous result for the same expansion given in Eq. (30) of Ref. [10]. In both expansions the "exact" on-top value is taken from Ref. [22].

reproduces the "exact" data for large μ, and that the μ value for which it breaks down (i.e., where the expansion has its minimum) coincides with the minimum value of μ 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,

$$f_{\mathrm{LDA}}(0) = \frac{1}{2}\int n(\mathbf{r})^2 g(r_{12}=0;n(\mathbf{r}))d\mathbf{r}, \tag{32}$$

where $g(r_{12};n)$ is the pair-distribution function [16,23] of the standard electron gas model (with Coulomb interaction $1/r_{12}$) of uniform density n. The new Eq. (30) allows us to estimate the physical on-top value starting from the one of the model system Ψ^{μ}. 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

$$\widetilde{P}_2^{\mu}(\mathbf{r},r_{12}=0) = \widetilde{P}_2(\mathbf{r},r_{12}=0)\left(1+\frac{2}{\sqrt{\pi}\mu}\right)+O\left(\frac{1}{\mu^2}\right), \tag{33}$$

where $\widetilde{P}_2^{\mu}(\mathbf{r},r_{12})$ was defined in Eq. (11), and $\widetilde{P}_2(\mathbf{r},r_{12})$ 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-μ expansion

$$\bar{E}_{c,\mathrm{SR}}^{\mu}[n=n_{\uparrow}] = f_c''(0)\frac{3\pi}{8\mu^4}+f''(0)\frac{3\sqrt{2\pi}}{10\mu^5}+O\left(\frac{1}{\mu^6}\right), \tag{34}$$

where $f''(0)$ and $f_c''(0)$ 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 $f^{\mu}(r_{12})$ at $r_{12}=0$ approaches the one of the Coulombic system as

$$(f^{\mu})''(0) = f''(0)\left(1+\frac{2}{3\sqrt{\pi}\mu}\right)+O\left(\frac{1}{\mu^2}\right). \tag{35}$$

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

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,

$$H^{\mu} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_{\mathbf{r}_i}^2 + V_{\mathrm{LR}}^{\mu}+V_{eb}^{\mu}+V_{bb}^{\mu}, \tag{36}$$

where V_{LR}^{μ} is the modified electron-electron interaction

$$V_{\mathrm{LR}}^{\mu} = \frac{1}{2}\sum_{i\neq j=1}^{N}\frac{\mathrm{erf}(\mu|\mathbf{r}_i-\mathbf{r}_j|)}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{37}$$

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

$$V_{eb}^{\mu} = -n\sum_{i=1}^{N}\int d\mathbf{x}\frac{\mathrm{erf}(\mu|\mathbf{r}_i-\mathbf{x}|)}{|\mathbf{r}_i-\mathbf{x}|}, \tag{38}$$

and V_{bb}^{μ} is the corresponding background-background interaction

$$V_{bb}^{\mu} = \frac{n^2}{2}\int d\mathbf{x}\int d\mathbf{x}'\frac{\mathrm{erf}(\mu|\mathbf{x}-\mathbf{x}'|)}{|\mathbf{x}-\mathbf{x}'|}. \tag{39}$$

When $\mu\to\infty$ H^{μ} tends to the standard jellium Hamiltonian, while when $\mu\to 0$ we recover the noninteracting electron gas.

We focus on the μ dependence of the on-top value of the pair-distribution function [16,23] $g(r_{12}=0,r_s,\mu)$, 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 [25]. 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 $\mathbf{s}_i=\mathbf{r}_i/r_s$, we see that when $r_s\to 0$ 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

$$g_c(0,r_s\to 0,\mu) = 6\int_0^{\infty}\Delta S_D(t,\mu)t^2dt+\cdots, \tag{40}$$

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

$$\Delta S_D(q,\mu) = \frac{4}{N}\sum_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}v_{ee}(q) \times\frac{n_{\mathrm{F}}(\mathbf{k})n_{\mathrm{F}}(\mathbf{k}')[1-n_{\mathrm{F}}(\mathbf{k}+\mathbf{q})][1-n_{\mathrm{F}}(\mathbf{k}'-\mathbf{q})]}{k^2+k'^2-(\mathbf{k}+\mathbf{q})^2-(\mathbf{k}'-\mathbf{q})^2}, \tag{41}$$

n_{F} is the usual Fermi occupation function [26], and $v_{ee}(q)$ is the Fourier transform of the electron-electron interaction. In Eq. (40) the scaled variable $t=q/2k_F$ [$k_F=(\alpha r_s)^{-1}$, $\alpha=(4/9\pi)^{1/3}$] has been used. The function $\Delta S_D(t,\mu)$ is thus equal to the one computed by Kimball [26] and reported in his Eq. 11, except for a multiplying factor $e^{-t^2k_F^2/\mu^2}$ coming from the Fourier transform of $\mathrm{erf}(\mu r_{12})/r_{12}$. From Eqs. (40) and (41) we find

$$g_c(0,r_s\to 0,\mu) = r_s h(\mu/k_F)+\cdots, \tag{42}$$

where the function $h(z)$ has the following asymptotic behaviors:

$$h(z\to 0) = -\frac{6\alpha}{\pi}(1-\ln 2)z^2+O(z^3), \tag{43}$$

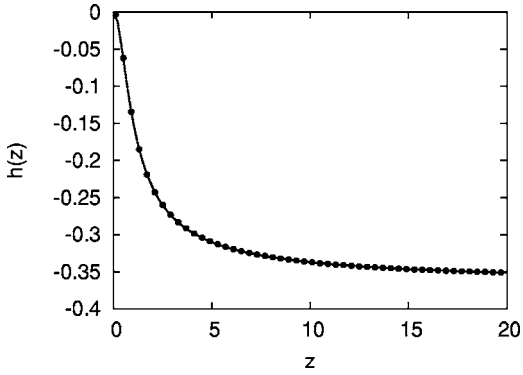

FIG. 4. The function $h(z)$ that determines the high-density limit of the on-top pair density of the "erf" gas [see Eq. (42)]. The numerical evaluation of Eq. (40) (points) is compared to the fitting function of Eq. (45) (solid line).

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

and $a_{\mathrm{HD}} = -\alpha(\pi^2 + 6\ln 2 - 3)/5\pi \approx -0.365\,83$ 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 numerically computed the function $h(z)$, and 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 $a_1 = -(6\alpha/\pi)(1 - \ln 2)$, $b_1 = 1.4919$, $b_3 = 1.915\,28$, $a_2 = a_{\mathrm{HD}} b_3$, $b_2 = (a_1 - b_3\alpha/\sqrt{\pi})/a_{\mathrm{HD}}$. The numerical results and the fitting function of Eq. (45) are reported in Fig. 4.

B. Interpolation formula

The high-density limit of Eq. (42) 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 μ dependence of $g_c(0, r_s, \mu)$ is roughly the same at each r_s. We thus start from the parametrization of the on-top pair density of the jellium model given in Ref. [16],

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

where $C = 0.081\,93$, $D = -0.012\,77$, $E = 0.001\,859$, $d = 0.7524$, and $B = -2a_{\mathrm{HD}} - d$, and we simply rescale homogeneously all the coefficients with the function $h(z = \mu/k_F)/a_{\mathrm{HD}}$,

$$g_c(0, r_s, \mu) = \frac{e^{-d r_s h(z)/a_{\mathrm{HD}}}}{2}\left(1 - B\frac{h(z)}{a_{\mathrm{HD}}} r_s + C\frac{h(z)^2}{a_{\mathrm{HD}}^2} r_s^2 + D\frac{h(z)^3}{a_{\mathrm{HD}}^3} r_s^3 + E\frac{h(z)^4}{a_{\mathrm{HD}}^4} r_s^4\right) - \frac{1}{2}. \tag{47}$$

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" [15,16], which gave good results for the standard jellium model [16] and for two-electron atoms [27]. 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. [28–30].

The scattering equations of the "extended Overhauser model" are widely explained in Refs. [16,31]. Here we simply solved the same equations with the electron-electron interaction $\mathrm{erf}(\mu r_{12})/r_{12}$ screened by a sphere of radius r_s of uniform positive charge density n and attracting the electrons with the same modified interaction,

$$V_{\mathrm{eff}}(r_{12}, r_s, \mu) = \frac{\mathrm{erf}(\mu r_{12})}{r_{12}} - \int_{|\mathbf{r}'| \leq r_s} n \frac{\mathrm{erf}(\mu|\mathbf{r}' - \mathbf{r}_{12}|)}{|\mathbf{r}' - \mathbf{r}_{12}|} d\mathbf{r}'. \tag{48}$$

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. $V_{\mathrm{eff}}(r_{12}, r_s, \mu)$ is a screened potential that tends to the "Overhauser potential" [15,16]; 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 μ. We see that the the simple interpolation formula of Eq. (47) accurately captures the μ 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. (30) and (33), and (iii) the parametrization of the μ dependence of the on-top pair density of the uniform electron gas, Eq. (47). All these results (i)–(iii) can be useful for the construction of approximate short-range correlation energy functionals:

(i) In Ref. [10] the large-μ 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 $\bar{E}^{\mu}_{c,\mathrm{SR}}[n]$. In the

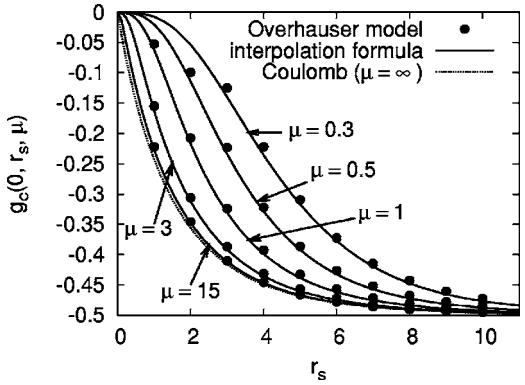

FIG. 5. The correlation on-top pair density of the electron gas with interaction $\mathrm{erf}(\mu r_{12})/r_{12}$ for different μ (in a.u.) as a function of the dimensionless density parameter r_s. The results from the Overhauser model are compared with the interpolation formula of Eq. (47). The dotted line corresponds to the standard jellium model with interaction $1/r_{12}$.

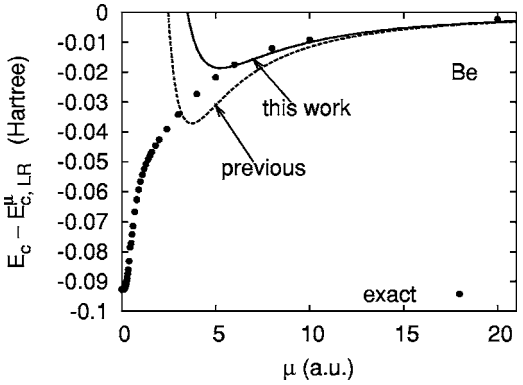

FIG. 6. The exact values of $\bar{E}^{\mu}_{c,\mathrm{SR}}[n]=E_c-E^{\mu}_{c,\mathrm{LR}}[n]$ for the Be atom [9,10] are compared with the large-μ expansion of Eq. (31), and with the previous result for the same expansion given in Eq. (30) of Ref. [10]. In both expansions the exact on-top value is taken from Ref. [22].

spirit of the usual DFT approximations, this interpolation is done locally, i.e.,

$$\bar{E}^{\mu}_{c,\mathrm{SR}}[n]=\int d\mathbf{r} n(\mathbf{r})\bar{\epsilon}^{\mu}_{c,\mathrm{SR}}(\mathbf{r}), \tag{49}$$

where $\bar{\epsilon}^{\mu}_{c,\mathrm{SR}}(\mathbf{r})$ is built, e.g., as [10]

$$\bar{\epsilon}^{\mu}_{c,\mathrm{SR}}\approx\frac{\epsilon_c^{\mathrm{DFA}}}{1+d_1\mu+d_2\mu^2}. \tag{50}$$

The parameters d_1 and d_2 are fixed by the condition that Eq. (49) recovers the correct $\mu\to\infty$ expansion of $\bar{E}^{\mu}_{c,\mathrm{SR}}[n]$, and $\epsilon_c^{\mathrm{DFA}}$ 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 [6]. This way of constructing approximations should be improved by using the corrected expansion of Eq. (31), as suggested by Fig. 3. 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 μ than the previous expansion used in Ref. [10].

(ii) To impose the correct large-μ expansion in approximations like the one of Eq. (50) we need an estimate of the physical ($\mu=\infty$) on-top pair density $\tilde{P}_2(\mathbf{r},r_{12}=0)$. In Ref. [10] the LDA approximation [the integrand of the right-hand side of Eq. (32)] was used. The new Eq. (33) allows us to use the on-top pair density of the partially correlated wave function Ψ^{μ} to estimate $\tilde{P}_2(\mathbf{r},r_{12}=0)$. In fact, once we have made a calculation at a given (moderately large) μ (say, $\mu=\mu_0$) we can estimate $\tilde{P}_2(\mathbf{r},r_{12}=0)$ as

$$\tilde{P}_2(\mathbf{r},r_{12}=0)\approx\tilde{P}_2^{\mu_0}(\mathbf{r},r_{12}=0)\left(1+\frac{2}{\sqrt{\pi}\mu_0}\right)^{-1}. \tag{51}$$

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 $\tilde{P}_2^{\mu}(\mathbf{r},r_{12}=0)$ 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. (51) 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. (51) 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 $\bar{E}^{\mu_0}_{c,\mathrm{SR}}[n]$ is 5 mH, and for $\mu_0=1$ is 11 mH. Of course, when μ_0 becomes too small, the large-μ 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. (47) can be used, in combination with the correlation energy of the spin-polarized long-range electron gas [34], 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 $f^{\mu}(0)$ [or locally on $\tilde{P}_2^{\mu}(\mathbf{r},r_{12}=0)$] of the partially correlated wave function could use the μ dependence of the on-top LDA value to go beyond Eq. (51),

$$f_c(0)\approx f_c^{\mu_0}(0)\frac{\int n(\mathbf{r})^2 g_c(0,r_s(\mathbf{r}),\mu=\infty)d\mathbf{r}}{\int n(\mathbf{r})^2 g_c(0,r_s(\mathbf{r}),\mu_0)d\mathbf{r}}. \tag{52}$$

For example for the He atom Eq. (52) at $\mu_0=2$ gives $f_c(0)=-0.086$, while Eq. (51) gives -0.090. The corresponding exact value [22] is -0.085. Local versions of Eq. (52) can be also considered, e.g.,

$$f_c(0) \approx \int n(\mathbf{r})^2 \widetilde{P}^{\mu_0}_{2,c}(\mathbf{r}, r_{12}=0) \frac{g_c(0, r_s(\mathbf{r}), \mu=\infty)}{g_c(0, r_s(\mathbf{r}), \mu_0)} d\mathbf{r}, \tag{53}$$

where $\widetilde{P}^{\mu_0}_{2,c}(\mathbf{r}, r_{12})$ is obtained by subtracting the Kohn-Sham pair density from $\widetilde{P}^{\mu_0}_2$. Again, the advantage of including in the construction of short-range functionals the on-top $\widetilde{P}^{\mu}_{2,c}(\mathbf{r}, r_{12}=0)$ 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 $\mathrm{erf}(\mu r_{12})/r_{12}$, 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 electron-electron interaction [7,35]. Future work will be mainly oriented to the exploration of the promising approach of short-range functionals that explictly depend on $\widetilde{P}^{\mu}_2(\mathbf{r}, r_{12}=0)$.

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APPENDIX A: ALTERNATIVE DERIVATION OF EQ. (25)

Start from Eq. (16), and consider the following series expansions around $x=0$:

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

$$\frac{\mathrm{erf}(\mu x)}{x} = \sum_{n=0}^{\infty} b_n \mu (\mu x)^{2n},$$

$$b_n = \frac{2}{\sqrt{\pi}} \frac{(-1)^n}{(2n+1)n!}. \tag{A2}$$

This last series has an infinite radius of convergence for any finite μ.

The complicated operator $\mathcal{E}^{\mu}$ 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. (15) is even in $\mathbf{x}=\mathbf{r}_{12}$. As expected, the expansion of $\mathcal{E}^{\mu}$ does not play any role, so we do not consider its nonspherical components (moreover, in the end we are only interested in the spherically averaged pair density). The only important requirement is that $\mathcal{E}^{\mu}$ remains bounded when $\mu \to \infty$ and $x \to 0$, as it happens for the Coulomb interaction [18,19]. We thus write

$$\mathcal{E}^{\mu} = \sum_{k=0}^{\infty} e_{2k}(\mu) x^{2k}. \tag{A3}$$

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

$$a_{2k+2}(\mu) = a_0(\mu) \left[\frac{b_k \mu^{2k+1}}{(2k+2)(2k+3)} + \frac{\mu^{2k}}{(2k+2)(2k+3)} \times \sum_{i=1}^{k} \frac{b_{k-i} b_{i-1}}{2i(2i+1)} \right] + O(\mu^{2k-1}). \tag{A4}$$

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

$$\psi^{\mu}(x) = a_0(\mu)[1 + x p_1(\mu x) + x^2 p_2(\mu x) + \cdots], \tag{A5}$$

where

$$p_1(y) = \sum_{k=0}^{\infty} \frac{b_k y^{2k+1}}{(2k+2)(2k+3)}, \tag{A6}$$

$$p_2(y) = \sum_{k=1}^{\infty} \left(\frac{y^{2k}}{(2k+2)(2k+3)} \sum_{i=1}^{k} \frac{b_{k-i} b_{i-1}}{2i(2i+1)} \right). \tag{A7}$$

Equation (A6) gives exactly the same function $p_1(y)$ of Eq. (22), and Eq. (A4) confirms that all the terms beyond the ones considered in Eq. (25) contribute to Eq. (26) to orders μ^{-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 μ. 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 μ and they all contribute to the term $\propto \mu^{-4}$ in Eq. (14). Furthermore, in Ref. [10] it was assumed that the leading order in the large-μ expansion of the on-top value $f^{\mu}(0)$ is $1/\mu^2$, while we have shown that the correction to $f^{\mu}(0)$ 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 μ of Eq. (18) into the equivalent of Eq. (17) for the case $\ell=1$,

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

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

$$u^{(\infty)}(y) = b y^2, \tag{B2}$$

$$\left[\frac{d^2}{dy^2} - \frac{2}{y^2} \right] u^{(-1)}(y) = b y \, \mathrm{erf}(y). \tag{B3}$$

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

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

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

$$q_1(y \to 0) = \frac{y}{5\sqrt{\pi}} + O(y^3), \quad \text{(B6)}$$

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

Again, we see that if we fix $r_{12}=r_0 \ll 1$, and then let $\mu \to \infty$ we find $f^\mu(r_0) \propto r_0^2[1+r_0/2+\cdots]$, which is the parallel-spin cusp condition for the Coulomb interaction [19]. But for any finite μ we have, for small r_{12}, $f^\mu(r_{12}) \propto r_{12}^2[1+r_{12}^2 2\mu/5\sqrt{\pi}+\cdots]$. The proof that $B_1=0$, and thus of Eqs. (34) and (35) is then completely analogous to the one for the case $\ell=0$.

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