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Strong-interaction limit of density-functional theory

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Electrons can have a given smooth density distribution $\rho(r)$, even if their Coulomb interaction is scaled to infinity. This strong-interaction limit of density-functional theory provides essential information on the correlation energy of real electron systems. The simple concept of strictly correlated electrons (SCE) is analyzed here as a model for that limit. SCE is solved exactly for any one-dimensional (1D) N-electron density and, in particular, for any 3D spherical two-electron system, such as the helium atom. Both the SCE interaction energy and the SCE external potential, which are obtained here as density functionals, obey all the relations known for the corresponding quantities in the unknown true strong-interaction limit. At large but finite interaction, the electrons are still strongly correlated, performing zero-point oscillations about the SCE limit.
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I. INTRODUCTION

The Hamiltonian of an interacting electron system is $\hat{H}=\hat{T}+\hat{V}_{ee}+\hat{V}_{\rm ext}$, with the kinetic-energy operator $\hat{T}$, the two-particle Coulomb interaction $\hat{V}_{ee}=\Sigma_{i<j}|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|^{-1}$, and the operator $\hat{V}_{\rm ext}$ of some external potential $v_{\rm ext}(\mathbf{r})$, which is usually the attractive Coulomb potential of atomic nuclei. In density-functional theory (DFT) [1], the ground-state energy of this system is presented as a functional of the ground-state electron density $\rho(\mathbf{r})$,

$$E[\rho]=T_s[\rho]+\int d^3r\, v_{\rm ext}(\mathbf{r})\rho(\mathbf{r})+U[\rho]+E_{\rm xc}[\rho]. \quad (1)$$

$T_s[\rho]$ is the ground-state kinetic energy of noninteracting electrons with density ρ. The second term is the interaction with the external potential. The remaining two terms describe the electron-electron interaction. The classical Coulomb or Hartree term,

$$U[\rho]=\tfrac{1}{2}\int d^3r\int d^3r'\,\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

treats the electrons as a continuous charge distribution with density $\rho(\mathbf{r})$. All the complex aspects of the quantum-mechanical many-body problem which are ignored in this continuum description are included in the explicitly unknown ‘‘*exchange-correlation*’’ functional $E_{\rm xc}[\rho]$. It corrects for the self-interaction error in $U[\rho]$ and accounts for the reduction of interaction energy resulting from electronic correlations due to both Pauli exclusion and Coulomb repulsion. In addition, since $T_s[\rho]$ is not the true kinetic energy $T[\rho]$ of interacting electrons, $E_{\rm xc}[\rho]$ has also a kinetic-energy contribution $T_c[\rho]\equiv T[\rho]-T_s[\rho]$.

Explicit knowledge of this important functional would reduce the many-body problem to solving the Kohn-Sham single-particle equations [1] of DFT. An exact relation is the coupling-constant integral [2],

$$E_{\rm xc}[\rho]=\int_0^1 d\alpha\, W_\alpha[\rho]. \quad (2)$$

The integrand is $W_\alpha[\rho]=V_{ee}^\alpha[\rho]-U[\rho]$, with the expectation value

$$V_{ee}^\alpha[\rho]\equiv\langle\Psi^\alpha[\rho]|\hat{V}_{ee}|\Psi^\alpha[\rho]\rangle \quad (3)$$

of the operator $\hat{V}_{ee}$ in the ground state $\Psi^\alpha[\rho]$ of a hypothetic system which has the same density ρ as the real system but where the electronic repulsion force is scaled by a factor (‘‘coupling constant’’) $\alpha\geqslant 0$. Precisely, $\Psi^\alpha[\rho]$ is that wave function which minimizes the expectation value $\langle\hat{T}+\alpha\hat{V}_{ee}\rangle$ subject to the constraint that it yields a given density $\rho(\mathbf{r})$. This mathematically imposed constraint can be satisfied in many cases if a suitable α-dependent external potential $v_{\rm ext}^\alpha(\mathbf{r})$, represented by an operator $\hat{V}_{\rm ext}^\alpha$, is introduced [1]. Then, the wave function $\Psi^\alpha[\rho]$ is the ground state of the Hamiltonian

$$\hat{H}^\alpha=\hat{T}+\alpha\hat{V}_{ee}+\hat{V}_{\rm ext}^\alpha. \quad (4)$$

According to the Hohenberg-Kohn theorem [1], the potential $v_{\rm ext}^\alpha(\mathbf{r})$ is, if it exists, unambiguously determined by the density $\rho(\mathbf{r})$ (apart from an arbitrary constant).

Representation (2) is particularly useful, because many analytical properties of the integrand $W_\alpha[\rho]$ are known. In the weak-interaction limit, it has the expansion

$$W_\alpha[\rho]=W_0[\rho]+W_0'[\rho]\alpha \quad (\alpha\to 0), \quad (5)$$

where $W_0[\rho]\equiv E_x[\rho]$ is the DFT exchange energy, explicitly given by the Fock integral with the occupied Kohn-Sham single-particle orbitals. We write $E_{\rm xc}[\rho]=E_x[\rho]+E_c[\rho]$, where the ‘‘correlation energy’’ $E_c[\rho]$ arises, because the integrand $W_\alpha[\rho]$ in Eq. (2), starting at $\alpha=0$ with the value $W_0[\rho]=E_x[\rho]$, is not constant as α grows (cf. Fig. 4). The linear expansion (5) yields in Eq. (2) the approximation

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$E_c^{\mathrm{GL2}}[\rho]=\frac{1}{2}W_0'[\rho]$ for the correlation energy. By virtue of Görling-Levy perturbation theory [3], the coefficient $W_0'[\rho]$ is, similarly to $W_0[\rho]$, explicitly known in terms of the (occupied and unoccupied) Kohn-Sham orbitals [Eq. (4) for $E_c^{\mathrm{GL2}}[\rho]$ in Ref. [3](a)]. Unfortunately, the information in the quantities $W_0[\rho]$ and $W_0'[\rho]$ is in most real systems not sufficient for an accurate prediction of $E_c[\rho]$. Rare exceptions are high-density systems with weakly correlated electrons.

Direct access to the realistic situation with finite interaction ($\alpha=1$) is traditionally difficult. Recently [4], however, the integral (2) was for different systems accurately interpolated between the extreme limits $\alpha\to 0$ and $\alpha\to\infty$, respectively, using no direct information on the complex situation at $\alpha=1$. In the present work, we focus on this strong-interaction limit $\alpha\to\infty$, where [4]

$$W_\alpha[\rho]=W_\infty[\rho]+W_\infty'[\rho]\alpha^{-1/2}\quad(\alpha\to\infty). \tag{6}$$

We will obtain a model [4] for the coefficient $W_\infty[\rho]$ from a theory which is also simple, but in a different way than the familiar weak-interaction limit $\alpha\to 0$. As $\alpha\to\infty$, single-particle orbitals become completely meaningless, since the many-particle wave function is dominated by correlations between different electrons.

The strongly repulsive electrons in the state $\Psi^\alpha[\rho]$ with $\alpha\gg 1$ cannot escape from each other, since they must form the given density distribution $\rho(\mathbf{r})$. Minimizing the expectation value $\langle\hat{T}+\alpha\hat{V}_{ee}\rangle$, these electrons seek a distribution in the density $\rho(\mathbf{r})$ with maximum separation possible from each other. This implies strong correlation between their positions. The kinetic energy grows unlimitedly as these correlations are strengthened. In Sec. VI, we will find evidence indicating that $\langle\Psi^\alpha[\rho]|\hat{T}|\Psi^\alpha[\rho]\rangle\propto\alpha^{1/2}$ as $\alpha\to\infty$ (see also Appendix A). If this is true, minimizing $\langle\hat{T}+\alpha\hat{V}_{ee}\rangle$ in this limit is equivalent to minimizing $\langle\hat{V}_{ee}\rangle$ alone, since $\langle\hat{T}\rangle$ grows more slowly than $\langle\alpha\hat{V}_{ee}\rangle$. Correspondingly, we describe the limit $\alpha\to\infty$ by the concept of ‘‘strictly correlated electrons’’ (SCE) [4], which probably yields exactly the minimum interaction energy $\langle\hat{V}_{ee}\rangle$ possible in a given density ρ. The asymptotic $\alpha^{-1/2}$ term in Eq. (6) is expected to result from zero-point oscillations of strongly correlated electrons at large $\alpha\gg 1$ about the SCE limit (see Sec. VI).

Section II provides a definition of SCE. From Sec. III on, we focus on spherically symmetric two-electron systems, a 3D case for which this concept is solved exacly. Section IV presents the corresponding interaction-energy functional $V_{ee}^{\mathrm{SCE}}[\rho]$, along with a candidate $W_{\mathrm{SCE}}[\rho]$ for the unknown coefficient $W_\infty[\rho]$ in Eq. (6). $V_{ee}^{\mathrm{SCE}}[\rho]$ and the SCE external potential $w(r)$, constructed in Sec. V, exactly obey conditions on the unknown true $\alpha\to\infty$ limits of $V_{ee}^\alpha[\rho]$ and $(1/\alpha)v_{\mathrm{ext}}^\alpha(r)$, as we show in Appendix B. At large but finite $\alpha\gg 1$, we find in Sec. VI that strongly correlated electrons perform zero-point oscillations about the SCE limit. In Sec. VII, the expansions (5) and (6) are examined numerically for the helium atom. Results and conclusions are summarized in Sec. VIII.

II. STRICTLY CORRELATED ELECTRONS (SCE)

A system of N electrons with a given smooth density distribution $\rho(\mathbf{r})$ is called ‘‘strictly correlated’’ [4] if, after measurement, the N discrete electronic positions always represent the continuous density $\rho(\mathbf{r})$ as well as possible. To explain this in more detail, we focus at first on one-dimensional (1D) systems. From Sec. III on, we shall switch to 3D.

In any 1D quantum state, the positions of the N electrons on the x axis can be measured simultaneously, resulting in a set $\{x_1,\ldots,x_N\}$ of N discrete numbers $x_1<x_2<\ldots<x_N$. For the SCE state with a given smooth density distribution $\rho(x)$, we claim that the density between any two adjacent positions x_n and x_{n+1} always exactly integrates to unity,

$$\int_{x_n}^{x_{n+1}}dx\,\rho(x)=1,\quad n=1,\ldots,N-1. \tag{7}$$

Any accidental clustering of the electrons is strictly suppressed. In this way, the set of the x_n represents the continuous distribution $\rho(x)$ as well as this can be achieved by N discrete positions.

As a result, the position of any one electron determines the positions of all the others. This is almost perfectly opposite to the familiar situation with noninteracting electrons which are moving independently in single-particle orbitals φ_n. To highlight this formally, we can introduce N correlation functions f_n so that the positions $x_2,\ldots,x_N$ in any strictly correlated set $\{x_1,\ldots,x_N\}$ are always related to x_1 by

$$x_{n+1}=f_n(x_1),\quad n=0,\ldots,N-1. \tag{8}$$

Note that $f_0(x)\equiv x$. Due to Eq. (7), these correlation functions are determined by the condition $\int_x^{f_n(x)}dx'\rho(x')=n$. Taking here the derivative with respect to x, we obtain a nonlinear first-order differential equation for $f_n(x)$,

$$f_n'(x)=\frac{\rho(x)}{\rho(f_n(x))}. \tag{9}$$

This is the analog of Eq. (14) below for the correlation function $f(r)$ in 3D spherical two-electron systems. The starting condition for numerical integration of Eq. (9) is $f_n(0)=y$, where y is obtained from $\int_0^y dx\,\rho(x)=n$. Therefore, these correlation functions are determined unambiguously by the density $\rho(x)$. From the same condition which led us to Eq. (9), we conclude $f_n(f_m(x))=f_{n+m}(x)$, where $f_{n+N}(x)\equiv f_n(x)$. Therefore, only $f_1(x)$ needs to be calculated. Since $f_0(x)\equiv x$, the inverse function of $f_n(x)$ is $f_{N-n}(x)$. In the case $N=2$, $f_1(x)$ is its own inverse. Figure 1 shows a plot of these functions, obtained numerically for the five-electron 1D density $\rho(x)=\frac{5}{2}\pi^{-1/2}\exp(-[x/2]^2)$.

An ansatz for the probability distribution of the sets $\{x_1,\ldots,x_N\}$ of electronic positions possible in the SCE state is

$$P_{\mathrm{SCE}}(x_1,\ldots,x_N)=\frac{\rho(x_1)}{N}\prod_{n=2}^{N}\delta(x_n-f_{n-1}(x_1)). \tag{10}$$

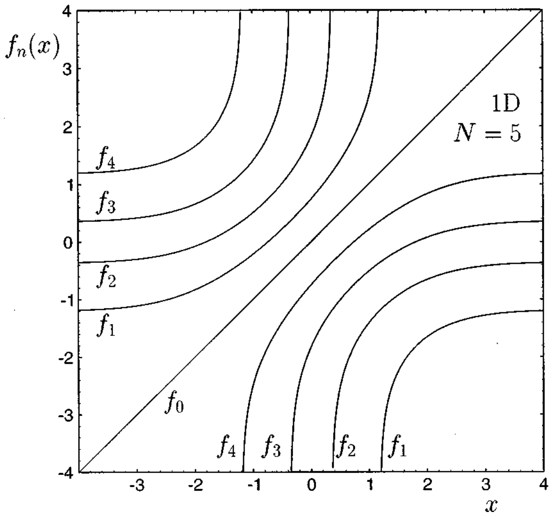

FIG. 1. The correlation functions $f_n(x)$, obtained from solving the differential equation (9) for the five-electron 1D density $\rho(x) = 5\lambda\pi^{-1/2}\exp(-[\lambda x]^2)$, with $\lambda = 0.5$ [x and $f(x)$ are in the same but otherwise arbitrary length units here]. While $f_0(x) \equiv x$, each one of the remaining functions $f_n(x)$ has two branches and a pole at x_{n0}, where $x_{10} = 1.19$, $x_{20} = 0.36$, $x_{30} = -0.36$, and $x_{40} = -1.19$. Note that $f_1^{-1} \equiv f_4$ and $f_2^{-1} \equiv f_3$. A vertical line, drawn at any position x, always has five intersection points with these curves, representing the positions of the five strictly correlated electrons as functions of the position x of the first one.

The integral of this expression, performed over all x_n except for x_k, is always $(1/N)\rho(x_k)$, the probability distribution for the position of one electron. This is evident in the case $k = 1$. For $k \neq 1$, it can be verified by using the differential equation (9) in combination with the general rule for δ functions, $\int dx\, f(x)\delta(g(x)) = f(x_0)/|g'(x_0)|$, where x_0 is the zero of $g(x)$. An explicit antisymmetric wave function Ψ_α which has in the limit $\alpha \to \infty$ the probability distribution (10) is given in Appendix A.

The counterpart of the SCE state is a state of noninteracting electrons which are moving independently in single-particle orbitals φ_n. The wave function is now a Slater determinant (SD) with the probability distribution

$$P_{\mathrm{SD}}(x_1,\dots,x_N) = \sum_{\sigma_1,\dots,\sigma_N} \left| \hat{A} \prod_{n=1}^{N} \varphi_n(x_n,\sigma_n) \right|^2 . \tag{11}$$

Here, $\hat{A}$ is the antisymmetrization operator for fermions and the σ_n are spin variables.

Both these situations are mathematically much simpler than the realistic situation with finite interaction. On a computer, expressions (10) or (11) can be stored as small sets of simple functions, $\rho(x)$, $f_1(x)$, or, respectively, the $\varphi_n(x,\sigma)$. If, e.g., 1000 mesh points are used for x, only a few thousand numbers need to be stored. In contrast, the probability distribution $P(x_1,\dots,x_N) = \Sigma_{\sigma_1,\dots,\sigma_N} |\Psi(1,\dots,N)|^2$ in the wave function Ψ of a real system with finite interaction cannot be expressed in terms of a few functions of one variable. Now, $(1/N!)1000^N$ numbers must be stored to achieve the same level of accuracy.

The generalization of the SCE concept to 3D systems is straightforward for spherically symmetric two-electron densities, as we shall see in the next section. In the general case of any 3D N-electron density, we can say that the electronic positions $\mathbf{r}_n$ in any simultaneously measured set $\{\mathbf{r}_1,\dots,\mathbf{r}_N\}$ are in the strictly correlated limit as uniformly distributed over the density $\rho(\mathbf{r})$ as possible. No accidental clustering of electrons can occur. This situation is accurately described by the simple point-charge-plus-continuum (PC) approximation for SCE, which is presented in detail in Ref. [5].

III. THE CORRELATION FUNCTION $f(r)$ FOR SPHERICAL TWO-ELECTRON SYSTEMS

Strict correlation in a spherical two-electron system implies that, if electron 1 is at a distance r_1 from the center, then electron 2 is on the opposite side of the center at a distance r_2 which is some monotonically decreasing exact function of r_1,

$$r_2 = f(r_1). \tag{12}$$

Since the electrons are identical particles, we conclude $r_1 = f(r_2) = f(f(r_1))$ or $f(r) \equiv f^{-1}(r)$, which is confirmed by Eq. (13) below. $f(r)$ is its own inverse, similar to the case of 1D two-electron systems in the preceding section.

It is easily demonstrated that the correlation function $f(r)$ is entirely determined by the given spherical density $\rho(r)$. Since $f(r)$ is monotonically decreasing, the probability to find electron 1 *inside* a sphere with radius r must be the same as the probability that electron 2 is *outside* the sphere with radius $f(r)$,

$$4\pi \int_0^r du\, u^2 \rho(u) = 4\pi \int_{f(r)}^{\infty} du\, u^2 \rho(u). \tag{13}$$

If, for a particular density ρ, these integrals can be evaluated explicitly, we obtain a simple equation for $f(r)$. For the general case, we take the derivative of Eq. (13) with respect to r to obtain a nonlinear first-order differential equation for $f(r)$,

$$f'(r) = \frac{r^2 \rho(r)}{f(r)^2 \rho(f(r))}. \tag{14}$$

The starting condition for the integration of Eq. (14) is $f(r_0) = r_0$, where, due to Eq. (13), r_0 is obtained from $4\pi\int_0^{r_0} dr\, r^2 \rho(r) = N/2 = 1$. Consequently, f is determined by ρ.

Figure 2 shows the correlation functions $f(r)$, obtained numerically for three different densities $\rho(r)$. Since $f(r) \equiv f^{-1}(r)$, the graphical representation of $f(r)$ is always symmetric with respect to the diagonal (dashed) line. As an analytical example, we consider the two-electron density

$$\rho(r) = \frac{15}{\pi R^5}(R-r)^2 \Theta(R-r), \quad R > 0. \tag{15}$$

In this case, $r_0 = R/2$ and Eq. (14) has the solution $f(r) = (R-r)\Theta(R-r)$, which fulfills $f(R/2) = R/2$. Therefore, the distance $r + f(r)$ between these two electrons is always R and their interaction energy is exactly $\langle \hat{V}_{ee} \rangle = 1/R$.

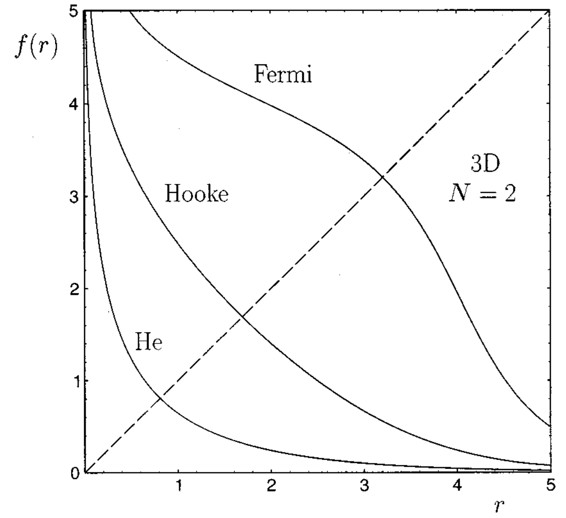

FIG. 2. The correlation functions $f(r)$, obtained from solving the differential equation (14) for three different spherical two-electron densities. For the helium atom (''He''; $r_0=0.81$), the density from Ref. [7] was used. Hooke's-law atom (''Hooke''; $r_0=1.69$) is an interacting two-electron system in the oscillator-type external potential $v_{\mathrm{ext}}(r)=r^2/8$, whose ground state is known analytically [6]. ''Fermi'' ($r_0=3.20$) refers to the Fermi-function density $\rho(r)\sim[1+e^{(r-R)/a}]^{-1}$ with $R=4$ and $a=0.2$. The plots are symmetric with respect to the diagonal (dashed) line which they intersect with at $r=r_0$. [For He, r and $f(r)$ are in units of 1 bohr $=0.529$ Å.]

Once we know the correlation function $f(r)$ for a particular two-electron density $\rho(r)$, we can easily construct it for the entire class of scaled densities,

$$\rho_\lambda(r)=\lambda^3\rho(\lambda r)\quad(\lambda>0),\tag{16}$$

where the λ-dependent starting radius is $r_0[\rho_\lambda]=(1/\lambda)r_0[\rho]$. The correlation function for any λ is $f_\lambda(r)=(1/\lambda)f(\lambda r)$, because this is a solution to the differential equation (14) with $\rho=\rho_\lambda$ and fulfills $f_\lambda(r_0[\rho_\lambda])=r_0[\rho_\lambda]$.

IV. THE INTERACTION-ENERGY FUNCTIONAL $V_{ee}^{\mathrm{SCE}}[\rho]$

In these strictly correlated spherical systems, the distance $|\mathbf{r}_1-\mathbf{r}_2|$ between the two electrons is always $r+f(r)$, where $r=|\mathbf{r}_1|$. Therefore, averaging over the position $\mathbf{r}_1$ of the first electron with its probability distribution $\frac{1}{2}\rho(\mathbf{r}_1)$, we find for the expectation value of the Coulomb interaction $\hat{V}_{ee}$,

$$V_{ee}^{\mathrm{SCE}}[\rho]=2\pi\int_0^\infty dr\,\frac{r^2\rho(r)}{r+f(r)}.\tag{17}$$

Since the function $f(r)$ is determined by the density $\rho(r)$, Eq. (17) is the exact density functional for the interaction energy of strictly correlated, spherical two-electron systems. It is a candidate for the $\alpha\to\infty$ limit $V_{ee}^{\infty}[\rho]$ of the functional (3) and has exactly the properties of $V_{ee}^{\infty}[\rho]$ in Appendix B.

For the density ρ_{He} of the helium atom [7], the functional (17) takes the value $V_{ee}^{\mathrm{SCE}}[\rho_{\mathrm{He}}]=0.549$ (hartrees). As a result of the strong correlation, this is considerably lower than the true interaction energy $V_{ee}^{\alpha=1}[\rho_{\mathrm{He}}]=0.946$ [8] of the helium atom. In the opposite limit $\alpha=0$, where the two electrons are moving without any correlation in one single-particle orbital, $\langle\hat{V}_{ee}\rangle$ takes the even larger value $V_{ee}^{\alpha=0}[\rho_{\mathrm{He}}]=1.025$ [8]. $V_{ee}^{\mathrm{SCE}}[\rho]$ is probably the *minimum* interaction energy possible for any two-electron wave function with given spherical density ρ.

Subtracting the Hartree energy $U[\rho]$, we obtain a candidate,

$$W_{\mathrm{SCE}}[\rho]=V_{ee}^{\mathrm{SCE}}[\rho]-U[\rho],\tag{18}$$

for the coefficient $W_\infty[\rho]$ in Eq. (6). It is used in Ref. [4] to predict accurate correlation energies of real systems at $\alpha=1$ by considering only the simple limits $\alpha\to0$ and $\alpha\to\infty$. Substituting the density (16), we find the scaling behavior $W_{\mathrm{SCE}}[\rho_\lambda]=\lambda W_{\mathrm{SCE}}[\rho]$.

V. THE EXTERNAL POTENTIAL FOR STRICTLY CORRELATED ELECTRONS

To bind the strongly repulsive electrons at large $\alpha\gg1$, the attractive external potential of the Hamiltonian (4) must become proportional to α,

$$v_{\mathrm{ext}}^{\alpha}(\mathbf{r})\to\alpha w_\infty(\mathbf{r})\quad(\alpha\to\infty).\tag{19}$$

Since the kinetic energy is expected to grow only at the order of $O(\alpha^{1/2})$, potential-energy effects should become dominant in this limit. Then, the electrons are moving with a constant potential energy and the local potential $w_\infty(\mathbf{r})$ must *exactly* compensate for the two-particle repulsion $\hat{V}_{ee}$. This can indeed be achieved with a simple function $w_\infty(\mathbf{r})$ if the electrons are in the SCE state.

If in a strictly correlated spherical two-electron system electron 1 is at a distance r from the center, the repulsive force exerted by electron 2 from the distance $r+f(r)$ has the magnitude $[r+f(r)]^{-2}$. An external potential $w(r)$ which shall *exactly* compensate for this force must necessarily fulfill the differential equation

$$w'(r)=[r+f(r)]^{-2}.\tag{20}$$

This condition is even sufficient, because it guarantees at the same time that the net force on electron 2, at distance $f(r)$ from the center, is also zero,

$$w'(f(r))=[f(r)+f(f(r))]^{-2}=[f(r)+r]^{-2}.\tag{21}$$

Here, we used $f(f(r))\equiv r$. The solution $w(r)$ of Eq. (20) is a candidate for the unknown function $w_\infty(r)$ in Eq. (19). It has exactly the properties of $w_\infty(r)$ in Appendix B.

As these strictly correlated electrons are moving in the density $\rho(r)$, their total potential energy V_{pot} is indeed constant,

$$\frac{d}{dr}\left\{\frac{1}{r+f(r)}+w(r)+w(f(r))\right\}=0.\tag{22}$$

This is a simple consequence of Eqs. (20) and (21). Applying the boundary condition $w(r\to\infty)=0$, the constant in curled brackets can be evaluated, e.g., at $r=0$, resulting in $V_{\mathrm{pot}}=w(0)$. Correspondingly, since $V_{\mathrm{pot}}=V_{ee}^{\mathrm{SCE}}[\rho]+V_{\mathrm{ext}}^{\mathrm{SCE}}[\rho]$,

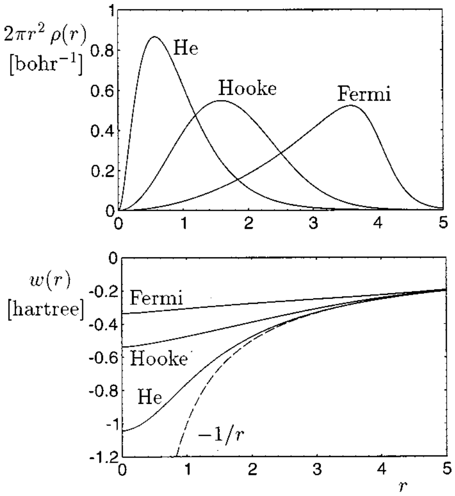

FIG. 3. The lower part of this figure displays the external potential $w(r)$ for strictly correlated electrons, obtained from solving the differential equation (20) for the three different two-electron densities whose correlation functions are shown in Fig. 2. At large r, $w(r)$ approaches in any spherical two-electron system the hydrogen external potential $-1/r$ (dashed curve). The upper part of the figure displays the radial probability distributions $4\pi r^2 \frac{1}{2}\rho(r)$ in these densities. For He, the potential is in units of 1 hartree $= 27.2$ eV and distance is in units of 1 bohr$= 0.526$ Å.

$$V_{ee}^{\rm SCE}[\rho] + \int d^3r\, \rho(r) w(r) = w(0). \tag{23}$$

Alternatively, evaluating the constant in Eq. (22) at $r = r_0$ yields $V_{\rm pot} = (1/2r_0) + 2w(r_0)$. Combining this with $V_{\rm pot} = w(0)$, we obtain

$$w(r_0) = -\frac{1}{2r_0} - [w(r_0) - w(0)]. \tag{24}$$

This is the starting condition for numerical integration of the differential equation (20). (The difference $[w(r_0) - w(0)] \equiv \int_0^{r_0} dr [r + f(r)]^{-2}$ can be evaluated unambiguously.) The resulting functions $w(r)$ for three different densities are plotted in Fig. 3. For the density (15), with $f(r) = (R-r)\Theta(R-r)$, we find analytically $w(r) = (r-2R)/R^2$ $(r \leqslant R)$ and $w(r) = -r^{-1}$ $(r > R)$.

In Sec. VI, we will study systematically the effect of the new external potential $w(r)$ on the electronic wave function. Here, we can already draw some simple conclusions. If the potential $w(r)$ is identical to the unknown limit $w_\infty(r)$ in Eq. (19), the Schrödinger equation with the Hamiltonian (4), divided by α, approaches at large α the form

$$\frac{1}{\alpha}\hat{T}\Psi^\alpha + \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + w(r_1) + w(r_2) \right\} \Psi^\alpha = \frac{E^\alpha[\rho]}{\alpha} \Psi^\alpha. \tag{25}$$

If the electrons become strictly correlated as $\alpha \to \infty$, the potential-energy factor in curled brackets has the constant value (23) wherever the wave function is different from zero. If the kinetic-energy term approaches zero as $\alpha \to \infty$, this indicates that the SCE state become asymptotically a solution of Eq. (25) with the eigenvalue $\lim_{\alpha\to\infty}(1/\alpha)E^\alpha[\rho] = w(0)$.

If this two-electron system is ionized at large α, the remaining single electron is localized around $\mathbf{r} = \mathbf{0}$, at the minimum of the strongly attractive external potential $\alpha w(r)$. As $\alpha \to \infty$, the wave function of this electron becomes δ-peaked at $\mathbf{r} = \mathbf{0}$ with a zero-point energy of the order of $O(\alpha^{1/2})$ so that the ground-state energy $E_+^\alpha[\rho]$ of the ionized system also fulfills $\lim_{\alpha\to\infty}(1/\alpha)E_+^\alpha[\rho] = w(0)$. Therefore, the ionization energy $I^\alpha[\rho] \equiv E_+^\alpha[\rho] - E^\alpha[\rho]$ has the property

$$\lim_{\alpha\to\infty} \frac{I^\alpha[\rho]}{\alpha} = 0. \tag{26}$$

This result is consistent with the fact that, at fixed density ρ, the ionization energy $I^\alpha[\rho]$ does not depend on α [9].

VI. ZERO-POINT OSCILLATIONS OF STRONGLY CORRELATED ELECTRONS

At large $\alpha \gg 1$, the electrons are expected to be strongly correlated, their relative positions performing zero-point oscillations about the strictly correlated limit $\alpha \to \infty$. To see this explicitly, we introduce the Hamiltonian

$$\begin{aligned} \hat{H}_0^\alpha &= \frac{\dot{\mathbf{r}}_1^2 + \dot{\mathbf{r}}_2^2}{2} + \alpha V(\mathbf{r}_1, \mathbf{r}_2), \\ V(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + w(r_1) + w(r_2) \quad (\alpha \gg 1). \end{aligned} \tag{27}$$

If the SCE potential $w(r)$ is identical to the unknown function $w_\infty(r)$ in Eq. (19), $\hat{H}_0^\alpha$ converges at large α asymptotically toward the Hamiltonian (4), which has, unlike $\hat{H}_0^\alpha$, for all different $\alpha \geqslant 0$ the same ground-state density ρ.

To study small deviations from the strictly correlated behavior, we consider a pair $\{\mathbf{r}_1, \mathbf{r}_2\}$ of electronic positions,

$$\mathbf{r}_1 = \mathbf{r}_{10} + \mathbf{u}_1, \quad \mathbf{r}_2 = \mathbf{r}_{20} + \mathbf{u}_2, \tag{28}$$

close to some strictly correlated pair $\{\mathbf{r}_{10}, \mathbf{r}_{20}\} = \{r\mathbf{e}, -f(r)\mathbf{e}\}$, where $\mathbf{e}$ is a unit vector. We express the small displacement vectors in Cartesian coordinates, $\mathbf{u}_i = \{x_i, y_i, z_i\}$, with the z_1 axis in direction $\mathbf{e}$ and the z_2 axis in direction $-\mathbf{e}$. Then, $|\mathbf{r}_1 - \mathbf{r}_2|^2 = [x_1 - x_2]^2 + [y_1 - y_2]^2 + [r + f(r) + z_1 + z_2]^2$, $r_1^2 = x_1^2 + y_1^2 + [r + z_1]^2$, and $r_2^2 = x_2^2 + y_2^2 + [f(r) + z_2]^2$. Using $w''(r) = -2[1 + f'(r)][r + f(r)]^{-3}$ from Eq. (20) and $f'(f(r)) = f'(r)^{-1}$ from $f(f(r)) \equiv r$, we can expand the potential-energy function in Eq. (27) about $\{\mathbf{r}_{10}, \mathbf{r}_{20}\}$,

$$\begin{aligned} V(\mathbf{r}_1, \mathbf{r}_2) &= w(0) \\ &\quad + \frac{1}{[r + f(r)]^3} \frac{r}{f(r)} \{[f^\circ(r) x_1 + x_2]^2 \\ &\quad + [f^\circ(r) y_1 + y_2]^2\} \\ &\quad - \frac{1}{[r + f(r)]^3} \frac{2}{f'(r)} [f'(r) z_1 - z_2]^2 \\ &\quad + O(\{x_i, y_i, z_i\}^3). \end{aligned} \tag{29}$$

In short-hand notation, $f^\circ(r)\equiv f(r)/r$. We have used the identity $[r+f(r)]^{-1}+w(r)+w(f(r))\equiv w(0)$, due to Eqs. (22) and (23).

Nothing new can be learned if $x_2=-f^\circ(r)x_1$, $y_2=-f^\circ(r)y_1$, and $z_2=f'(r)z_1$, since in this case, $\{\mathbf{r}_1,\mathbf{r}_2\}$ in Eq. (28) is still a strictly correlated pair like $\{\mathbf{r}_{10},\mathbf{r}_{20}\}$. To find an independent degree of freedom, we apply the orthonormal transformation,

$$X=\frac{-x_1+f^\circ(r)x_2}{\sqrt{1+f^\circ(r)^2}},\quad Y=\frac{-y_1+f^\circ(r)y_2}{\sqrt{1+f^\circ(r)^2}},$$

$$Z=\frac{z_1+f'(r)z_2}{\sqrt{1+f'(r)^2}}, \tag{30}$$

$$x=\frac{f^\circ(r)x_1+x_2}{\sqrt{1+f^\circ(r)^2}},\quad y=\frac{f^\circ(r)y_1+y_2}{\sqrt{1+f^\circ(r)^2}},\quad z=\frac{-f'(r)z_1+z_2}{\sqrt{1+f'(r)^2}}.$$

In terms of these new coordinates $\mathbf{S}=\{X,Y,Z\}$ and $\mathbf{s}=\{x,y,z\}$, strictly correlated motion is characterized by the condition $\mathbf{s}=\mathbf{0}$. Therefore, we expect that the coordinates $\mathbf{s}$ describe the wanted deviations from strictly correlated motion, if $\mathbf{S}=\mathbf{0}$.

For any given r, the Hamiltonian (27) can be expressed in terms of such coordinates,

$$\hat{H}_0^\alpha(r)=\tfrac{1}{2}(\dot{X}^2+\dot{Y}^2+\dot{Z}^2)+\alpha w(0)+\tfrac{1}{2}(\dot{x}^2+\dot{y}^2+\dot{z}^2)$$
$$+\alpha\left[\frac{k_1(r)}{2}(x^2+y^2)+\frac{k_3(r)}{2}z^2\right]+\alpha O(\{\mathbf{S},\mathbf{s}\}^3). \tag{31}$$

For small $|\mathbf{s}|,|\mathbf{S}|$, when the electronic positions (28) are close to the strictly correlated pair $\{\mathbf{r}_{10},\mathbf{r}_{20}\}$, this is a separated Hamiltonian. The coordinates $\mathbf{S}=\{X,Y,Z\}$ describe a free particle with constant potential energy $\alpha w(0)$. This effective free particle corresponds to strictly correlated motion of the two electrons. In contrast, the coordinates $\mathbf{s}=\{x,y,z\}$ describe an independent effective particle in an oscillator-type external potential. This degree of freedom corresponds to zero-point oscillations of strongly correlated electrons around the SCE limit. The spring constants are

$$k_1(r)=\frac{2}{[r+f(r)]^3}\left(\frac{r}{f(r)}+\frac{f(r)}{r}\right),$$
$$k_3(r)=\frac{-4}{[r+f(r)]^3}\left(\frac{1}{f'(r)}+f'(r)\right). \tag{32}$$

[Necessarily, $k_i(f(r))\equiv k_i(r)$.] This potential has its minimum at $s=\mathbf{0}$ [note that $k_i(r)>0$, since $f'(r)<0$], driving the electrons into the strictly correlated state as $\alpha\to\infty$. The ground-state energy of the Hamiltonian (31) is the constant potential energy of the free particle plus the zero-point energy of the harmonic oscillator,

$$E_0^\alpha(r)=\alpha w(0)+\alpha^{1/2}[\tfrac{2}{2}\omega_1(r)+\tfrac{1}{2}\omega_3(r)], \tag{33}$$

with r-dependent frequencies $\omega_i(r)=k_i(r)^{1/2}$ (we use atomic units where $\hbar=1$). Correspondingly, the ground-state energy of the Hamiltonian $\hat{H}_0^\alpha$ at large $\alpha\gg1$ is the average of $E_0^\alpha(r)$ in the probability distribution $\frac{1}{2}\rho(r)$,

$$E_0^\alpha[\rho]=\{V_{ee}^{\rm SCE}[\rho]+V_{\rm ext}^{\rm SCE}[\rho]\}\alpha+C[\rho]\alpha^{1/2}\quad(\alpha\to\infty), \tag{34}$$

where we have used Eq. (23) for $w(0)$. The coefficient in the zero-point energy is

$$C[\rho]=2\pi\int_0^\infty dr\,r^2\rho(r)[\tfrac{2}{2}\omega_1(r)+\tfrac{1}{2}\omega_3(r)]. \tag{35}$$

Note that $E_0^\alpha[\rho]$ is the ground-state energy of a Hamiltonian, $\hat{H}_0^\alpha$, which only in the limit $\alpha\to\infty$ has exactly the ground-state density ρ.

Due to the virial theorem for harmonic oscillators, exactly half of the zero-point energy $C[\rho]\alpha^{1/2}$ is kinetic. This indicates that the kinetic energy in the ground state of $\hat{H}_0^\alpha$ has the order of $O(\alpha^{1/2})$ as $\alpha\to\infty$, since the first term in Eq. (34) has only potential-energy contributions. The same must be expected for the original Hamiltonian $\hat{H}^\alpha$ of Eq. (4), since, presuming that the functions $w(r)$ and $w_\infty(r)$ are identical, the only difference between $\hat{H}^\alpha$ and $\hat{H}_0^\alpha$ are lower-order terms $O(\alpha^q)$ in the external potential, $v_{\rm ext}^\alpha(r)=\alpha w(r)+O(\alpha^q)$ $(q<1)$. These terms are required in $\hat{H}^\alpha$ to keep the density ρ fixed. They should, however, not affect the physical nature of the large-α kinetic energy as resulting from zero-point oscillations.

The above analysis reveals how the SCE state arises from a wave function with finite interaction, as $\alpha\to\infty$. In particular, we find a strong indication that the kinetic energy in the ground state of the Hamiltonian $\hat{H}^\alpha$ has the order of $O(\alpha^{1/2})$ in that limit. If $\hat{H}_0^\alpha$ was identical to $\hat{H}^\alpha$, which has for all different $\alpha\geq0$ exactly the same ground-state density $\rho(r)$, we could extract the coefficient $W'_\infty[\rho]$ of the asymptotic expansion (6) from expression (34). Precisely, $W'_\infty[\rho]\alpha^{1/2}$ would be the contribution of $V_{ee}^\alpha[\rho]$ to the $\alpha^{1/2}$ term of the functional (34). In Sec. VII, we will see that, for the helium atom, the coefficient $\frac{1}{2}C[\rho]$ of the zero-point potential energy in Eq. (34) is close to what is expected numerically for the value of $W'_\infty[\rho]$.

VII. NUMERICAL DISCUSSION

To examine the significance of the coefficients $W_\infty[\rho]$ and $W'_\infty[\rho]$ in expansion (6), we consider the analytical model, suggested in Ref. [4], for the coupling-constant integrand $W_\alpha[\rho]$,

$$W_\alpha^{\rm mod}[\rho]=W_\infty[\rho]+\frac{W_0[\rho]-W_\infty[\rho]}{\sqrt{1+2X[\rho]\alpha}}. \tag{36}$$

It has the correct small-α expansion (5) if we set [4] $X[\rho]=-W'_0[\rho]/(W_0-W_\infty)$. It also has the correct large-α expansion (6), predicting the value

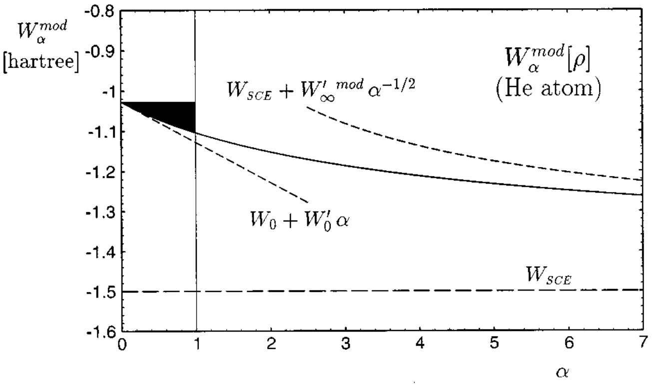

FIG. 4. The model (36) for the coupling-constant integrand $W_\alpha[\rho]$ of the helium atom (solid curve) in hartree units (1 hartree $=27.2$ eV). It is evaluated with the exact exchange energy of the helium atom, $W_0[\rho_{\rm He}]=-1.027$ [8], the accurate value $W_0'[\rho_{\rm He}]=-0.1006$ [10], and the present model $W_{\rm SCE}[\rho_{\rm He}]=-1.500$ for the coefficient $W_\infty[\rho]$ (horizontal dashed line), obtained from Eq. (18) for an accurate numerical density $\rho_{\rm He}(r)$ of the helium atom [7]. The expansions (5) and (6) of this integrand are indicated by dashed curves. The size of the shaded area in the figure is an accurate prediction of the correlation energy $E_c[\rho_{\rm He}]=-0.042$ in the helium ground state.

$$W_\infty'^{\,\rm mod}[\rho]=\frac{W_0[\rho]-W_\infty[\rho]}{\sqrt{2X[\rho]}} \tag{37}$$

for the coefficient $W_\infty'[\rho]$. A key property of the unknown exact integrand $W_\alpha[\rho]$, which is expected to be also a smooth function of α [12,13,4], is the scaling behavior [12]

$$W_\alpha[\rho]=\alpha W_1[\rho_{1/\alpha}], \tag{38}$$

where $\rho_\lambda(\mathbf{r})\equiv\lambda^3\rho(\lambda\mathbf{r})$ for any $\lambda>0$. Equation (38) dictates the scaling behavior of the coefficients in the expansions (5) and (6): $W_0[\rho_\lambda]=\lambda W_0[\rho]$, $W_0'[\rho_\lambda]=W_0'[\rho]$, $W_\infty[\rho_\lambda]=\lambda W_\infty[\rho]$, and $W_\infty'[\rho_\lambda]=\lambda^{3/2}W_\infty'[\rho]$. Therefore, the model integrand (36) also obeys condition (38) and the functional (37) has the correct scaling behavior of the coefficient $W_\infty'[\rho]$. (Note that the functional $W_{\rm SCE}[\rho]$, Eq. (18), which is a candidate for the unknown exact $W_\infty[\rho]$, has the correct scaling behavior, $W_{\rm SCE}[\rho_\lambda]=\lambda W_{\rm SCE}[\rho]$.)

Figure 4 displays the model integrand (36) for the density $\rho_{\rm He}$ of the helium atom (solid curve), using the probably exact functional $W_{\rm SCE}[\rho]$ for the unknown limit $W_\infty[\rho]$ (horizontal dashed line). Also shown are the expansions (5) and (6) of this integrand, where the unknown coefficient $W_\infty'[\rho]$ is replaced by the quantity (37). Clearly, this figure indicates that quantitative knowledge of the exact $W_\infty'[\rho]$, in addition to $W_\infty[\rho]$, would provide substantial information on the coupling-constant integrand $W_\alpha[\rho]$.

In Ref. [4], this analytical model integrand yields an accurate prediction for the ground-state correlation energy of helium, $E_c^{\rm mod}[\rho_{\rm He}]\equiv\int_0^1 d\alpha\, W_\alpha^{\rm mod}[\rho_{\rm He}]-W_0[\rho_{\rm He}]=-0.042$ (shaded area in Fig. 4), significantly improving the prediction $E_c^{\rm GL2}[\rho_{\rm He}]=-0.050$ from Eq. (5), where any information about $W_\infty[\rho]$ is ignored. (The exact correlation energy is $E_c[\rho_{\rm He}]=-0.042$ [8]). The functional (37) here takes the value $W_\infty'^{\,\rm mod}[\rho_{\rm He}]=0.729$, which is not far from the zero-point potential energy $\frac{1}{2}C[\rho_{\rm He}]=0.878$ as we mentioned at the end of Sec. VI. Note that the functional $C[\rho]$ has the same scaling behavior, $C[\rho_\lambda]=\lambda^{3/2}C[\rho]$, as the unknown exact coefficient $W_\infty'[\rho]$.

VIII. SUMMARY AND CONCLUSIONS

As a model for the strong-interaction limit of DFT, we have analyzed here quantum-mechanical states with strictly correlated electrons (SCE) in a given density distribution $\rho(\mathbf{r})$. Remarkably, there exists for any spherical two-electron density $\rho(r)$ always a suitable local external potential $w(r)$, constructed in a way so that strictly correlated electrons are moving at a constant potential energy. This result strongly supports the SCE model, since in the strong-interaction limit the total energy to leading order is expected to have no kinetic contribution.

In spherical two-electron systems, the SCE state is characterized by a simple correlation function $f(r)$ which is unambiguously determined by the given spherical density profile $\rho(r)$. The SCE interaction energy is obtained as a density functional $V_{ee}^{\rm SCE}[\rho]$, explicitly in terms of the functions $\rho(r)$ and $f(r)$. It probably yields the minimum interaction energy possible in a given density distribution ρ. The functional $W_{\rm SCE}[\rho]\equiv V_{ee}^{\rm SCE}[\rho]-U[\rho]$ is a candidate for the unknown limit $W_\infty[\rho]$ of the coupling-constant integrand $W_\alpha[\rho]$.

By a transformation of coordinates, the strongly correlated motion of the two electrons in the external potential $\alpha w(r)$ at large but *finite* $\alpha\gg 1$ can be separated into pure strictly correlated motion at constant potential energy and an independent collective degree of freedom where the electronic coordinates perform zero-point oscillations about their SCE values. An oscillator-type effective external potential drives the electrons into the pure SCE state, as $\alpha\to\infty$. This result reveals how the strictly correlated state arises from a strongly correlated wave function in the limit $\alpha\to\infty$.

The SCE concept for the strong-interaction limit $\alpha\to\infty$ can be interpreted as the counterpart of the concept of single-particle orbitals for the opposite limit $\alpha\to 0$ of weak interaction. Unlike the complex wave function of a realistic system with finite interaction ($\alpha=1$), both these concepts are mathematically simple, but in different ways. Since several analytical properties of the coupling-constant integrand $W_\alpha[\rho]$ are known, the correlation energy of real systems can be obtained accurately from an interpolation between these simple limits. While the small-α corrections in $W_\alpha[\rho]$ to the exchange energy $W_0[\rho]$ ($\alpha\to 0$) are given in Görling-Levy perturbation theory, the large-α asymptotics of $W_\alpha[\rho]$ toward the SCE limit $W_{\rm SCE}[\rho]$ ($\alpha\to\infty$) can probably be extracted from the zero-point energy $O(\alpha^{1/2})$ of almost strictly correlated electrons.

APPENDIX A: EXAMPLE FOR A STRONGLY CORRELATED WAVE FUNCTION

The probability distribution $\Sigma_{\sigma_1,\ldots,\sigma_N}|\Psi_\alpha(1,\ldots,N)|^2$ (with the short-hand notation "n" for the coordinate-spin variables "x_n,σ_n") in the ground state Ψ_α of the Hamiltonian (4) is expected to approach the strictly correlated limit

(10) as $\alpha\to\infty$. To obtain an explicit expression for a strongly correlated antisymmetric wave function Ψ_α, we consider a uniform 1D system of two electrons, confined to an interval with length $L=2$ on the x axis, $0\leqslant x_1,x_2<2$. To achieve a uniform density $\rho(x)\equiv 1$, we impose periodic boundary conditions at the endpoints of this interval. Then, the electrons are treated as if they were moving on a closed ring with circumference L and the electronic interaction can be described in terms of two repulsive ''Coulomb-force springs,'' attached along the two curved segments of the ring between the electrons. Since these springs are compressed to the lengths $|x_1-x_2|$ and $2-|x_1-x_2|$, respectively, the corresponding interaction energy is

$$V_{ee}(x_1,x_2)=\frac{1}{2}\left(\frac{1}{|x_1-x_2|}+\frac{1}{2-|x_1-x_2|}\right)=1+\epsilon^2+O(\epsilon^4), \tag{A1}$$

where $\epsilon=|x_1-x_2|-1$. The SCE state of this uniform system is characterized by $\epsilon=0$ or $|x_2-x_1|=1$, keeping the two electrons always at opposite positions on the ring. Then, the energy (A1) has the constant value $V_{ee}^{\mathrm{SCE}}=1$, which is also its minimum value. Therefore, $\langle\hat{V}_{ee}\rangle>V_{ee}^{\mathrm{SCE}}$ for any state other than the strictly correlated one. Clearly, SCE yields in this example minimum repulsion energy.

The constant external potential of this uniform system may be chosen to be zero. Then, the Hamiltonian (4) becomes

$$\hat{H}_\alpha=-\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}\right)+\alpha V_{ee}(x_1,x_2). \tag{A2}$$

If the term $O(\epsilon^4)$ is neglected in the potential (A1), we can give an exact solution to the Schrödinger equation $\hat{H}_\alpha\Psi_\alpha=E_\alpha\Psi_\alpha$,

$$\Psi_\alpha(1,2)=\frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi^2}\right)^{1/8}\times\exp\left(-\frac{\sqrt{\alpha}}{2}(|x_1-x_2|-1)^2\right)\chi_{\mathrm{as}}(\sigma_1,\sigma_2), \tag{A3}$$

where χ_{as} is the antisymmetric two-electron spin singlet. The probability distribution $P_\alpha(x_1,x_2)=\Sigma_{\sigma_1,\sigma_2}|\Psi_\alpha(1,2)|^2$ of this strongly correlated wave function is plotted in Fig. 5 for $\alpha=1000$. The corresponding eigenvalue is

$$E_\alpha=\alpha+\sqrt{\alpha}. \tag{A4}$$

Expression (A3) is correctly normalized, $\Sigma_{\sigma_1,\sigma_2}\int_0^2 dx_1\int_0^2 dx_2|\Psi_\alpha(1,2)|^2=1$, if α is large enough so that the Gaussian in Eq. (A3) is sufficiently close to zero for $\epsilon=\pm 1$. At these values, where the full potential (A1), including the higher-order terms $O(\epsilon^4)$, becomes singular, the correct wave function must be exactly zero. For large α, the function (A3) is strongly peaked around $\epsilon=0$, so that $|\epsilon|\ll 1$ wherever the wave function is significantly different from zero. Therefore, the term $O(\epsilon^4)$ can be neglected at large α. As $\alpha\to\infty$, the probability distribution $\Sigma_{\sigma_1,\sigma_2}|\Psi_\alpha(1,2)|^2$ approaches the strictly correlated limit $P_{\mathrm{SCE}}(x_1,x_2)=\delta(\epsilon)\equiv\delta(|x_1-x_2|-1)$ from Eq. (10).

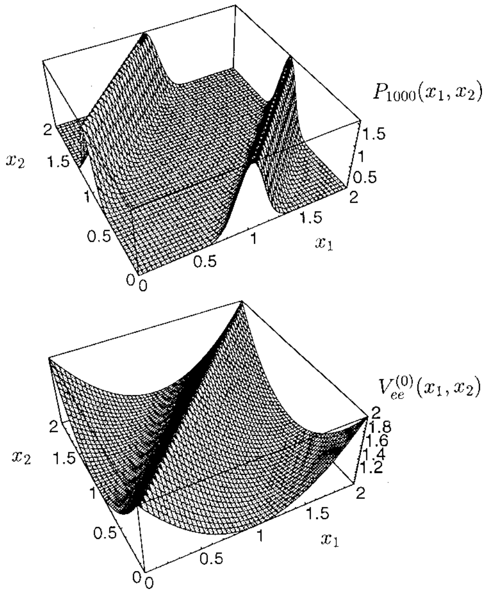

FIG. 5. The pair density $P_\alpha(x_1,x_2)=\Sigma_{\sigma_1,\sigma_2}|\Psi_\alpha(1,2)|^2$ in the strongly correlated wave function (A3) with $\alpha=1000$. The bottom part of the figure displays the corresponding interaction energy $V_{ee}^{(0)}(x_1,x_2)$, obtained from Eq. (A1) if the $O(\epsilon^4)$ term is dropped there. If $x_{1,2}$ are in units of 1 bohr$=0.526$ Å, then P_α has the unit of 1 bohr^{-2} and $V_{ee}^{(0)}$ has the unit of 1 hartree$=27.2$ eV.

The contribution $\sqrt{\alpha}$ in Eq. (A4) is the zero-point energy of the strongly correlated electrons whose separation $|x_1-x_2|$ performs oscillations in the potential (A1) about its equilibrium or SCE value $|x_1-x_2|=1$ or $\epsilon=0$. Due to the virial theorem, half of this energy is kinetic, $\langle\hat{T}\rangle_\alpha=\frac{1}{2}\sqrt{\alpha}$ and $\langle\hat{V}_{ee}\rangle_\alpha=\alpha+\frac{1}{2}\sqrt{\alpha}$, so the potential energy becomes dominant at large α. Therefore, strong and even strict correlation is in the limit $\alpha\to\infty$ energetically favorable, although this makes the kinetic energy $\langle\hat{T}\rangle$ grow to infinity.

APPENDIX B: TESTS FOR THE FUNCTIONAL $V_{ee}^{\mathrm{SCE}}[\rho]$ AND THE POTENTIAL $w(r)$

The potential $w(r)$ and the functional $V_{ee}^{\mathrm{SCE}}[\rho]$, respectively, are candidates for the unknown exact function $w_\infty(r)$ in Eq. (19) and the unknown exact limit $V_{ee}^{\infty}[\rho]$ of the interaction functional (3). We demonstrate here that the ''candidates'' identically fulfill two relations, valid for the unknown exact quantities.

An exact relation for $V_{ee}^{\infty}[\rho]$ and $w_\infty(\mathbf{r})$ is [11]

$$V_{ee}^{\infty}[\rho]+\int d^3r\,\rho(\mathbf{r})w_\infty(\mathbf{r})=\min w_\infty(\mathbf{r}), \tag{B1}$$

where $w_\infty(\mathbf{r})\to 0$ as $r\to\infty$. Equation (B1) holds for any two-electron density $\rho(\mathbf{r})$. Due to Eq. (23), our functional $V_{ee}^{\mathrm{SCE}}[\rho]$ and the corresponding potential $w(r)$ fulfill this relation exactly for any spherical two-electron density $\rho(r)$. Note that $w(0)=\min w(r)$, since $w'(r)\equiv[r+f(r)]^{-2}\geqslant 0$.

Another test is provided by the virial relation for the exact correlation potential [12]. To formulate this relation, Eq.

(B3) below, we generalize the total-energy functional (1) to electron systems with interaction $\alpha\hat{V}_{ee}$ for any $\alpha\geqslant 0$,

$$E^{\alpha}[\rho]=T_s[\rho]+\int d^3r\, v_{\rm ext}^{\alpha}(\mathbf{r})\rho(\mathbf{r}) +\alpha U[\rho]+\alpha E_x[\rho]+E_c^{\alpha}[\rho]. \tag{B2}$$

Here, $\alpha E_x[\rho]+E_c^{\alpha}[\rho]$ is the generalization $E_{\rm xc}^{\alpha}[\rho]=\int_0^{\alpha}d\beta\, W_{\beta}[\rho]$ of the xc functional (2). For any $\alpha\geqslant 0$, the exact correlation potential $v_c^{\alpha}(\mathbf{r})\equiv\delta E_c^{\alpha}[\rho]/\delta\rho(\mathbf{r})$ fulfills the virial relation [12]

$$E_c^{\alpha}[\rho]+T_c^{\alpha}[\rho]=-\int d^3r\,\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}v_c^{\alpha}(\mathbf{r}), \tag{B3}$$

where $T_c^{\alpha}[\rho]=T^{\alpha}[\rho]-T_s[\rho]$, with the functional $T^{\alpha}[\rho]$ of the total kinetic energy.

Due to the general variational principle of DFT, $\delta E^{\alpha}[\rho]/\delta\rho(\mathbf{r})=0$ for the true ground-state density $\rho(\mathbf{r})$. Therefore, for two-electron systems where $E_x[\rho]=-\frac{1}{2}U[\rho]$, Eq. (B2) yields $v_c^{\alpha}(\mathbf{r})=-\delta T_s[\rho]/\delta\rho(\mathbf{r})-v_{\rm ext}^{\alpha}(\mathbf{r})-(\alpha/2)\phi(\mathbf{r})$, with the electrostatic potential $\phi(\mathbf{r})=\delta U[\rho]/\delta\rho(\mathbf{r})$. In particular, with the function $w_{\infty}(\mathbf{r})$ from Eq. (19),

$$\lim_{\alpha\to\infty}\frac{1}{\alpha}v_c^{\alpha}(\mathbf{r})=-w_{\infty}(\mathbf{r})-\tfrac{1}{2}\phi(\mathbf{r}). \tag{B4}$$

On the other hand, provided that $\lim_{\alpha\to\infty}(1/\alpha)T_c^{\alpha}[\rho]=0$ (cf. Sec. VI and Ref. [13]), we obtain $\lim_{\alpha\to\infty}(1/\alpha)(E_c^{\alpha}[\rho]+T_c^{\alpha}[\rho])=V_{ee}^{\infty}[\rho]-\frac{1}{2}U[\rho]$, since $E_c^{\alpha}[\rho]=\alpha V_{ee}^{\alpha}[\rho]-\alpha U[\rho]+T_c^{\alpha}[\rho]-\alpha E_x[\rho]$. Then, Eq. (B3) yields for spherical two-electron densities $\rho(r)$ in this limit the condition

$$V_{ee}^{\infty}[\rho]-\tfrac{1}{2}U[\rho]=4\pi\int_0^{\infty}dr\, r^3\rho(r)[w_{\infty}'(r)+\tfrac{1}{2}\phi'(r)].$$

To demonstrate that this relation is exactly fulfilled by our quantities $V_{ee}^{\rm SCE}[\rho]$ and $w(r)$ if used as candidates for $V_{ee}^{\infty}[\rho]$ and $w_{\infty}(r)$, respectively, we first note the virial relation $E_x[\rho]=-\int d^3r\,\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}v_x(\mathbf{r})$ for the exchange potential $v_x(\mathbf{r})\equiv\delta E_x[\rho]/\delta\rho(\mathbf{r})$ [12]. For two-electron systems, where $E_x[\rho]=-\frac{1}{2}U[\rho]$ and $v_x(\mathbf{r})=-\frac{1}{2}\phi(\mathbf{r})$, this virial relation becomes $-\frac{1}{2}U[\rho]=4\pi\int_0^{\infty}dr\, r^3\rho(r)\frac{1}{2}\phi'(r)$. Therefore, we are left with the proof that $V_{ee}^{\rm SCE}[\rho]=4\pi\int_0^{\infty}dr\, r^3\rho(r)w'(r)$, or, using $w'(r)=[r+f(r)]^{-2}$ and rearranging terms,

$$\int_0^{\infty}dr\,\frac{r^2\rho(r)}{[r+f(r)]^2}f(r)=\int_0^{\infty}dr\,\frac{r^3\rho(r)}{[r+f(r)]^2}.$$

Replacing here on the left-hand side $r^2\rho(r)$ by $-f'(r)f(r)^2\rho(f(r))$, according to Eq. (14), we may substitute $f'(r)dr=df$. Since $f(f(r))=r$, we may interchange the names of the variables r and f so we just obtain the integral on the right-hand side and the proof is complete.

ACKNOWLEDGMENTS

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