

Strictly correlated electrons in density functional theory: A general formulation with applications to spherical densities

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We reformulate the strong-interaction limit of electronic density functional theory in terms of a classical problem with a degenerate minimum. This allows us to clarify many aspects of this limit, and to write a general solution, which is explicitly calculated for spherical densities. We then compare our results with previous approximate solutions and discuss the implications for density functional theory.

I. INTRODUCTION

Density functional theory [1–3] (DFT) is by now the most popular method for electronic structure calculations in condensed matter physics and quantum chemistry, because of its unique combination of low computational cost and reasonable accuracy for many molecules and solids.

In applying DFT to a given electron system, the only quantity that must be approximated in practice is the functional $E_{xc}[\rho]$ for the exchange-correlation energy. An exact expression for this functional is the coupling-constant integral,

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

The integrand is defined as

$$W_\alpha[\rho] = \langle \Psi_\alpha[\rho] | \hat{V}_{ee} | \Psi_\alpha[\rho] \rangle - U[\rho]. \quad (2)$$

Here, $U[\rho] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ is the functional of the Hartree energy and the operator $\hat{V}_{ee}$ describes the Coulomb repulsion between the N electrons,

$$\hat{V}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (3)$$

(Atomic units are used throughout this work.) Eventually, out of all antisymmetric N -electron wave functions Ψ that are associated with the same given electron density $\rho = \rho(\mathbf{r})$, $\Psi_\alpha[\rho]$ denotes the one that yields the minimum expectation of the operator $\hat{T} + \alpha \hat{V}_{ee}$. Here, $\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$ is the kinetic-energy operator. Notice that the parameter α works as an adjustable interaction strength or coupling “constant”.

At $\alpha = 0$, $W_\alpha[\rho]$ starts out with the value

$$E_x[\rho] = \langle \Psi_0[\rho] | \hat{V}_{ee} | \Psi_0[\rho] \rangle - U[\rho] \quad (4)$$

which is the density functional for the exchange energy. Generally, $W_\alpha[\rho]$ is a monotonically decreasing function of α , since the electrons in the state $\Psi_\alpha[\rho]$ increasingly

tend to avoid each other in space as the repulsion strength α grows. Thus, the expectation of $\hat{V}_{ee}$, which is a measure for the average inverse distances between the electrons, must decrease. However, it cannot decrease indefinitely, since the electrons are forced to stay within the fixed density $\rho(\mathbf{r})$.

Schematically, the traditional quantum chemistry approach to electron correlation often consists in trying to *extrapolate* the information on the physical system ($\alpha = 1$) from the non-interacting limit ($\alpha = 0$) by using, e.g., perturbation theory or more sophisticated methods. This work, instead, follows the early idea of Wigner [4], further developed in the DFT framework in Refs. 5 and 6, in which the information at $\alpha = 1$ is obtained by *interpolating* between the two limits of weak interaction, $\alpha \rightarrow 0$, and infinitely strong interaction, $\alpha \rightarrow \infty$. In this context, we carry out a detailed study of the limit

$$W_\infty[\rho] = \lim_{\alpha \rightarrow \infty} W_\alpha[\rho]. \quad (5)$$

Although the limit of Eq. (5) was investigated in previous work [5, 7–9], the solution presented here was found only in the special case of two electrons in a spherical density, using physical arguments. For the general case with N electrons, the point-charge-plus-continuum (PC) model was proposed [5, 8],

$$W_\infty^{\text{PC}}[\rho] = \int d\mathbf{r} \left[A \rho(\mathbf{r})^{4/3} + B \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{4/3}} \right]. \quad (6)$$

where $A = -\frac{9}{10}(\frac{4\pi}{3})^{1/3}$ and $B = \frac{3}{350}(\frac{3}{4\pi})^{1/3}$. This approximation, together with a similar one for the next leading term, $W'_\infty[\rho]$, describing zero-point motion oscillations, was used to construct an interpolation for $W_\alpha[\rho]$ between $\alpha = 0$ and $\alpha = \infty$, called interaction strength interpolation (ISI) model [6]. ISI predicts accurate atomization energies (with a mean absolute error of 3.4 kcal/mole) [6, 10], showing that the general idea of interpolating between the weak- and the strong-interaction limits in DFT can work.

It should be emphasized that ISI uses as ingredients exclusively the two functionals $E_x[\rho]$ and $E_c^{\text{GL2}}[\rho]$ (of

the second-order correlation energy in Görling-Levy perturbation theory [11]) from the relatively simple non-interacting limit $\alpha \rightarrow 0$ (with single-particle orbitals), plus the two functionals $W_\infty[\rho]$ and $W'_\infty[\rho]$ from the opposite $\alpha \rightarrow \infty$ limit of infinitely strong repulsion, which are, so far, not known exactly (as said, except for $W_\infty[\rho]$ in the special case of two electrons in a spherical density [7]).

In this work we reformulate the $\alpha \rightarrow \infty$ limit of DFT in terms of a classical problem with a degenerate minimum. This allows us to construct the general solution for $W_\infty[\rho]$, and to clarify many aspects of this limit. As $\alpha > 0$ grows beyond its real-world value $\alpha = 1$, the concept of single-particle orbitals becomes completely meaningless. When $\alpha \rightarrow \infty$, however, an entirely new type of simplicity with so-called “co-motion” functions arises, as we shall see in Secs. II-IV. The “co-motion” functions, which entirely determine $W_\infty[\rho]$, can be directly constructed from the one-electron density $\rho(\mathbf{r})$.

The paper is organized as follows. In Sec. II we first give a general overview of the problem, anticipating the solution on intuitive physical grounds, and leaving the mathematical details in Secs. III and IV. We then use our formalism to explicitly evaluate the limit of Eq. (5) in the case of spherical densities, with applications to atoms (Sec. V). In Sec. VI we compare our solution with the approximation of Eq. (6), and we discuss the implications for the ISI functional. The last Sec. VII is devoted to conclusions and perspectives. In the Appendix we also consider the simple case of harmonic forces, in order to analyze how the nature of the electron-electron interaction affects the solution.

II. SMOOTH DENSITIES FROM A CLASSICAL PROBLEM

For a given N -electron density $\rho = \rho(\mathbf{r})$ we generally wish to find the limit (5) or, equivalently,

$$W_\infty[\rho] + U[\rho] = \lim_{\alpha \rightarrow \infty} \langle \Psi_\alpha[\rho] | \hat{V}_{ee} | \Psi_\alpha[\rho] \rangle. \quad (7)$$

If the density ρ is both N - and v -representable for every α , there exists an α -dependent external potential $\hat{V}_{\text{ext}}^\alpha[\rho] = \sum_{i=1}^N v_{\text{ext}}^\alpha([\rho], \mathbf{r}_i)$ such that $\Psi_\alpha[\rho]$ is the ground state of the Hamiltonian

$$\hat{H}^\alpha[\rho] = \hat{T} + \alpha \hat{V}_{ee} + \hat{V}_{\text{ext}}^\alpha[\rho]. \quad (8)$$

As $\alpha \rightarrow \infty$, the binding external potential $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$ in the Hamiltonian (8) must compensate the strong repulsion $O(\alpha)$ between the electrons. Therefore, we expect

$$\lim_{\alpha \rightarrow \infty} \frac{v_{\text{ext}}^\alpha([\rho], \mathbf{r})}{\alpha} = v([\rho], \mathbf{r}), \quad (9)$$

with $v([\rho], \mathbf{r})$ a smooth function of $\mathbf{r}$. Thus, for large $\alpha \gg 1$, the kinetic energy in the state $\Psi_\alpha[\rho]$ is mainly due to zero-point oscillations of strongly repulsive electrons, bound by a strong attractive force that has the

order of $O(\alpha)$. Therefore, $\langle \Psi_\alpha[\rho] | \hat{T} | \Psi_\alpha[\rho] \rangle$ has the order of $O(\sqrt{\alpha})$ and we may write in Eq. (7)

$$\begin{aligned} W_\infty[\rho] + U[\rho] &= \lim_{\alpha \rightarrow \infty} \left\langle \Psi_\alpha[\rho] \left| \frac{1}{\alpha} \hat{T} + \hat{V}_{ee} \right| \Psi_\alpha[\rho] \right\rangle \\ &= \lim_{\alpha \rightarrow \infty} \min_{\Psi \rightarrow \rho} \left\langle \Psi \left| \frac{1}{\alpha} \hat{T} + \hat{V}_{ee} \right| \Psi \right\rangle. \end{aligned} \quad (10)$$

In the second step we have applied the definition of the wave function $\Psi_\alpha[\rho]$; the constraint “ $\Psi \rightarrow \rho$ ” addresses all those wave functions Ψ that are associated with the same given density ρ . Provided that the limit $\alpha \rightarrow \infty$ can be applied directly to the operators in Eq. (10) (there is no rigorous proof for this reasonable conjecture – see also the Appendix), it is simplified to

$$W_\infty[\rho] + U[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle. \quad (11)$$

In this case, the expectation of $\hat{V}_{ee}$ alone is to be minimized, regardless of the kinetic-energy operator $\hat{T}$. This apparently purely classical problem corresponds to the quantum-mechanical limit of infinitely large masses.

If Eq. (9) holds, that is if the density $\rho(\mathbf{r})$ is both N - and v -representable also in the very $\alpha \rightarrow \infty$ limit, the minimizing Ψ in Eq. (11) is the ground state of the pure multiplicative operator $\hat{V}_{ee} + \hat{V}$. The local one-body potential V is the Lagrange multiplier for the constraint “ $\Psi \rightarrow \rho$ ”, and can be found via the Legendre-transform formulation of Eq. (11) [12],

$$W_\infty[\rho] + U[\rho] = \max_v \left\{ \min_{\Psi} \langle \Psi | \hat{V}_{ee} + \hat{V} | \Psi \rangle - \int \rho v \right\}. \quad (12)$$

To start to address the problem of N -representability in the $\alpha \rightarrow \infty$ limit, we write the minimizing wavefunction Ψ in Eq. (12) as the product

$$\Psi = \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \chi(\sigma_1, \dots, \sigma_N), \quad (13)$$

where ψ is a spatial wavefunction and χ is a chosen eigenstate of the total spin $\hat{S}^2$ and its projection $\hat{S}_z$. In Sec. III we analyze the N -representability problem in more detail, showing that, in the special $\alpha \rightarrow \infty$ case, we can always construct an antisymmetric Ψ of the form (13), and that the choice of the spin eigenfunction χ does not affect the square of the spatial wavefunction $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ and thus, as shown by Eq. (15) below, the energy. For this reason, in what follows we only consider the spatial wavefunction $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$.

As said,

$$\hat{V}_{ee} + \hat{V} \equiv E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N) \quad (14)$$

is a pure multiplicative operator, so that, after integrating out the spin variables, the unconstrained minimization in the brackets of Eq. (12) reads

$$\min_{\psi} \int d\mathbf{r}_1 \dots d\mathbf{r}_N |\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N). \quad (15)$$

We see that the minimum in Eq. (15) is reached when the square of the spatial wavefunction $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ is a distribution that is zero everywhere except for values $(\mathbf{r}_1, \dots, \mathbf{r}_N) \in M$, where

$$M \equiv \left\{ (\mathbf{r}_1, \dots, \mathbf{r}_N) : E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N) = \min \right\} \quad (16)$$

is the set of all configurations $(\mathbf{r}_1, \dots, \mathbf{r}_N)$ for which the $3N$ -dimensional function E_{pot} of Eq. (14) assumes its absolute (global) minimum. Notice that the set M is purely determined by the choice of $v(\mathbf{r})$, $M = M[v]$. We shall see in the next Sec. III that to such a minimizing distribution $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ we can indeed associate an antisymmetric wavefunction of the form (13).

For a given reasonable (attractive) potential $v(\mathbf{r})$, we may expect that M will comprise only one single configuration (plus its permutations) or a small finite number of configurations: the set M corresponds, in fact, to the solution of the classical electrostatic equilibrium problem for N identical point charges in the external potential $v(\mathbf{r})$. The density associated with the corresponding spatial wave function ψ will then be a finite sum of delta functions,

$$\rho(\mathbf{r}) \propto \sum_{k=1}^K \delta(\mathbf{r} - \mathbf{r}_k), \quad (17)$$

where the $\mathbf{r}_k$ are the $K \geq N$ different position vectors forming the configurations in M . When $v(\mathbf{r})$ has some symmetry (e.g., spherical), M can also be a low-dimensional continuum (e.g., the surface of a sphere).

For a quantum-mechanical system (atom, molecule, solid), the electronic density is typically *smooth*, so that Eq. (17) seems in contradiction with the final requirement “ $\Psi \rightarrow \rho$ ” [or the maximization (12)]. In other words, it seems like there is a v -representability problem for smooth densities in the very $\alpha \rightarrow \infty$ limit. The solution to this apparent problem is that the potential $v(\mathbf{r})$ must be such that $M[v]$ is a continuum with at least three dimensions. That is, the absolute minimum of the $3N$ -dimensional function E_{pot} must be degenerate over (at least) a 3-dimensional subspace of $\mathbb{R}^{3N}$, which we write as

$$M = \left\{ (\mathbf{r}, \mathbf{f}_2(\mathbf{r}), \dots, \mathbf{f}_N(\mathbf{r})) : \mathbf{r} \in P \right\}, \quad (18)$$

where $P \subseteq \mathbb{R}^3$ is the region of space where $\rho(\mathbf{r}) \neq 0$. As we shall see in Sec. IV, the ansatz (18) can be consistent with the requirement that E_{pot} is minimum over M only when the functions $\mathbf{f}_n(\mathbf{r})$ satisfy special properties.

From the physical point of view, the corresponding spatial wavefunction ψ (which is zero everywhere except on M), describes a state in which the position of one of the electrons can be freely chosen in P , $\mathbf{r}_1 = \mathbf{r}$, but it then fixes the positions of all the other electrons through the functions $\mathbf{f}_n(\mathbf{r})$, $\mathbf{r}_2 = \mathbf{f}_2(\mathbf{r})$, ..., $\mathbf{r}_N = \mathbf{f}_N(\mathbf{r})$. This is what we call [5, 7] “strictly correlated electrons” (SCE).

The requirement “ $\Psi \rightarrow \rho$ ” can of course be fulfilled also if the degeneracy of the absolute minimum of E_{pot} is higher, e.g., if M is a 6D subspace described by $\{(\mathbf{r}, \mathbf{r}', \mathbf{f}_3(\mathbf{r}, \mathbf{r}'), \dots, \mathbf{f}_N(\mathbf{r}, \mathbf{r}')) : \{\mathbf{r}, \mathbf{r}'\} \in P\}$, which corresponds to the physical state in which the position of two electrons fixes the positions of all the others. However, we have to keep in mind that we can affect M only by varying the one-body potential $v(\mathbf{r})$. Physically, this means that $v(\mathbf{r})$ must compensate the repulsive forces of the other $N - 1$ electrons acting on the electron in $\mathbf{r}$. If the position of the other $N - 1$ electrons only depends on $\mathbf{r}$ [as in Eq. (18)], then it may be possible to find such a $v(\mathbf{r})$. If, instead, we require the degeneracy of M to be higher, finding such a $v(\mathbf{r})$ seems a daunting task.

We shall go through these physical considerations more in detail in Sec. IV, where we analyze the solution (18) and write down an explicit equation for $v(\mathbf{r})$. Before doing so, we first show that we can consistently construct an antisymmetric wavefunction Ψ of the form (13) such that $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ is a distribution that is zero everywhere except on the minimizing set M .

III. ANTISYMMETRY OF THE WAVEFUNCTION

We want to construct an antisymmetric wavefunction of the form (13) such that its spatial part $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ is a distribution that is zero everywhere except in the set M where E_{pot} has its global minimum. Given a configuration $(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of M , we first notice that all its electronic positions $\mathbf{r}_i$ must be different from each other: without the kinetic energy operator $\hat{T}$, two or more electrons on-top of each other would make E_{pot} infinite because of the singular nature of Coulomb repulsion at short distances. Moreover, for any configuration $\in M$, also all its $N!$ permutations are $\in M$, since E_{pot} is invariant under permutation of its variables $\mathbf{r}_i$. Then, given the value of the wavefunction for one configuration $(\mathbf{r}_1, \dots, \mathbf{r}_N) \in M$, with spins $(\sigma_1, \dots, \sigma_N)$, its value for the permutations π of this configuration must be simply defined as

$$\begin{aligned} \psi(\mathbf{r}_{\pi(1)}, \dots, \mathbf{r}_{\pi(N)}) \chi(\sigma_{\pi(1)}, \dots, \sigma_{\pi(N)}) = \\ (-1)^\pi \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \chi(\sigma_1, \dots, \sigma_N) \end{aligned} \quad (19)$$

where $(-1)^\pi$ denotes the sign of the permutation π . Because the $\mathbf{r}_i$ in a given configuration are all different from each other, and ψ is zero everywhere except on M , the N electrons are always localized in different regions of space that have exactly zero overlap. This means that when we consider the square of the spatial wavefunction $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ all the cross terms are exactly zero, and thus $|\psi|^2$ is completely independent of the choice of the spin eigenstate χ .

Similarly, for repulsive bosons (with any spin), Ψ can be *symmetrized*. Both the symmetric and the antisymmetric choice give the same spatial $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$, and

thus the same expectation for $\hat{V}_{ee}$: when Coulomb repulsion between the particles becomes dominant with respect to the kinetic energy, particle-particle overlap is suppressed, so that the particles no longer know whether they are fermions or bosons.

The same construction (19) applies to the SCE state in which M has the form (18), since all the considerations made so far are obviously still valid for any configuration in M characterized by a given $\mathbf{r} \in P$.

IV. CO-MOTION FUNCTIONS

We have seen that the potential $v(\mathbf{r})$ of Eq. (9) for the $\alpha \rightarrow \infty$ limit of DFT must be such that the minimum of the $3N$ -dimensional function E_{pot} of Eq. (14) is degenerate over the 3-dimensional subspace M of Eq. (18). We shall now analyze how to construct such a $v(\mathbf{r})$, and thus which properties the functions $\mathbf{f}_n(\mathbf{r})$ must satisfy, and how they can be determined from the density $\rho(\mathbf{r})$. Since the solution (18) corresponds to a state in which the position of one electron dictates the positions of all the others, we call the functions $\mathbf{f}_n(\mathbf{r})$ *co-motion* functions.

A. Properties of the co-motion functions

If we assume that the $v(\mathbf{r})$ we are looking for is a smooth potential with a continuous gradient $\nabla v(\mathbf{r})$, then $E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N)$ is a continuous and smooth function of its variables $\mathbf{r}_n$, except for configurations with two or more electrons on top of each other, which, as explained in Sec. III, cannot belong to the minimizing set M . In this case, a minimizing configuration $(\mathbf{r}_1, \dots, \mathbf{r}_N) \in M$ must satisfy the stationarity conditions for the function $E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N)$, i.e.,

$$\begin{cases} \nabla v(\mathbf{r}_1) = \sum_{i \neq 1}^N \frac{\mathbf{r}_1 - \mathbf{r}_i}{|\mathbf{r}_1 - \mathbf{r}_i|^3} \\ \nabla v(\mathbf{r}_2) = \sum_{i \neq 2}^N \frac{\mathbf{r}_2 - \mathbf{r}_i}{|\mathbf{r}_2 - \mathbf{r}_i|^3} \\ \vdots \end{cases} \quad (20)$$

If we insert the solution (18) into Eqs. (20) we obtain

$$\begin{cases} \nabla v(\mathbf{r}) = \sum_{i \neq 1}^N \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3} \\ \nabla v(\mathbf{x})|_{\mathbf{x}=\mathbf{f}_2(\mathbf{r})} = \sum_{i \neq 2}^N \frac{\mathbf{f}_2(\mathbf{r}) - \mathbf{f}_i(\mathbf{r})}{|\mathbf{f}_2(\mathbf{r}) - \mathbf{f}_i(\mathbf{r})|^3} \\ \vdots \end{cases} \quad (21)$$

where we have defined $\mathbf{f}_1(\mathbf{r}) \equiv \mathbf{r}$. Now, suppose that we have found $N-1$ functions $\mathbf{f}_i(\mathbf{r})$ and a potential $v(\mathbf{r})$ such that the first of the Eqs. (21) is satisfied for all $\mathbf{r} \in \mathbb{R}^3$. If we now evaluate this first equation for $\mathbf{r} = \mathbf{f}_n(\mathbf{s})$ and then put $\mathbf{s} = \mathbf{r}$, we see that its left-hand-side coincides with the left-hand-side of the n^{th} equation. It is then easy to verify that, if we want also the right-hand-sides to be the same, the functions $\mathbf{f}_i(\mathbf{r})$ must satisfy the transformation

properties

$$\{\mathbf{f}_2(\mathbf{f}_n(\mathbf{r})), \dots, \mathbf{f}_N(\mathbf{f}_n(\mathbf{r}))\} = \{\mathbf{f}_1(\mathbf{r}), \dots, \mathbf{f}_N(\mathbf{r})\} \setminus \{\mathbf{f}_n(\mathbf{r})\}, \quad (22)$$

i.e., the set of $N-1$ functions $\mathbf{f}_i(\mathbf{x})$ with $i = 2, \dots, N$, when evaluated in $\mathbf{x} = \mathbf{f}_n(\mathbf{r})$ must yield any permutation of the set of $N-1$ $\mathbf{f}_i(\mathbf{r})$ with $i = 1, \dots, N$ and $i \neq n$ (thus including $\mathbf{f}_1(\mathbf{r}) = \mathbf{r}$). This means that applying one co-motion function $\mathbf{f}_k$ to one position $\mathbf{r}_n$ of a given SCE configuration $C \in M$ must always yield a position of the same C again. If the functions $\mathbf{f}_i$ satisfy this property, then the fulfillment of the first of the Eqs. (21) automatically implies the fulfillment of the other $N-1$ equations, and thus the stationarity of the solution (18) for any $\mathbf{r}$. One has then to verify that such a stationary solution is the global minimum of the $3N$ -dimensional function $E_{\text{pot}}([v], \mathbf{r}_1, \dots, \mathbf{r}_N)$.

B. The SCE external potential

Once we have found some functions $\mathbf{f}_i(\mathbf{r})$ that satisfy the properties (22), Eqs. (21) provide N equivalent equations for the potential $v(\mathbf{r})$,

$$\nabla v(\mathbf{r}) = \sum_{i \neq 1}^N \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}. \quad (23)$$

Equation (23) has the clear physical meaning anticipated in Sec. II: the potential $v(\mathbf{r})$ must compensate the net force acting on the electron in $\mathbf{r}$, resulting from the repulsion of the other $N-1$ electrons at positions $\mathbf{f}_i(\mathbf{r})$.

We start now to see that the $\alpha \rightarrow \infty$ limit of DFT is entirely characterized by the co-motion functions $\mathbf{f}_i(\mathbf{r})$, which also give, as a byproduct via Eq. (23), the external potential $v(\mathbf{r})$. In the next Subsec. IV C we shall see how to determine these functions from the density $\rho(\mathbf{r})$.

C. Co-motion functions for a given density

The SCE problem for a given density $\rho(\mathbf{r})$ reduces then to the construction of the appropriate co-motion functions $\mathbf{f}_n(\mathbf{r})$. To do this, we simply use the quantum mechanical meaning of the electronic density. Since in the SCE state the position of the first electron determines the positions of all the others, the probability of finding the first electron in the volume element $d\mathbf{r}$ around the position $\mathbf{r}$ must be the same of finding the n^{th} electron in the volume element $d\mathbf{f}_n(\mathbf{r})$ around the position $\mathbf{f}_n(\mathbf{r})$. This means that all the co-motion functions $\mathbf{f}_n(\mathbf{r})$ must satisfy the differential equation

$$\rho(\mathbf{f}_n(\mathbf{r}))d\mathbf{f}_n(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}, \quad n = 2, \dots, N. \quad (24)$$

In order to construct the co-motion functions we thus have to find the initial conditions for the integration of (24) that (i) satisfy the properties (22), (ii) yield a

smooth potential $v(\mathbf{r})$ via Eq. (23), and (iii) give the minimum expectation of $\hat{V}_{ee}$. In Sec. V we solve this problem explicitly for spherically symmetric N -electron densities.

Equations (24) can also be proven by explicitly constructing the square of the spatial wavefunction $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ that is zero everywhere except on M of Eq. (18), and by imposing that the expectation value of the operator $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ on $|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ is $\rho(\mathbf{r})$. In this way, we also see that the value of $|\psi(\mathbf{r}, \mathbf{f}_2(\mathbf{r}), \dots, \mathbf{f}_N(\mathbf{r}))|^2$ in a given SCE configuration $\in M$ must be set equal to $\frac{1}{N}\rho(\mathbf{r})$.

D. The value of $W_\infty[\rho]$

After all, maximising with respect to the potential v in Eq. (12) seems to be equivalent to constructing the co-motion functions $\mathbf{f}_n(\mathbf{r})$. In terms of these functions, the expectation of the operator $\hat{V}_{ee}$ in the SCE state [see also Eqs. (2) and (5)] reads

$$W_\infty[\rho] + U[\rho] = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \int d\mathbf{r} \frac{\frac{1}{N}\rho(\mathbf{r})}{|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|}, \quad (25)$$

where, again, we have used the convention $\mathbf{f}_1(\mathbf{r}) = \mathbf{r}$. Equation (25) comes from the fact that, as said in the previous Subsec. IV C, for a given $\mathbf{r}$, the configuration $(\mathbf{r}, \mathbf{f}_2(\mathbf{r}), \dots, \mathbf{f}_N(\mathbf{r}))$ in M has a weight equal to $\frac{1}{N}\rho(\mathbf{r})$, and that the only possible electron-electron distances are $|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|$, with $i \neq j$, and $i, j = 1, \dots, N$.

V. THE SCE SOLUTION FOR N ELECTRONS IN A SPHERICAL DENSITY

As an example, we consider here N electrons in a spherical density, and we explicitly calculate the functions $\mathbf{f}_n(\mathbf{r})$ and the value $W_\infty[\rho]$ for a few atoms.

Given the symmetry of the problem, we choose a spherical-coordinate reference system $\mathbf{r}_i = (r_i, \theta_i, \phi_i)$ in which the position of the first electron defines the z -axis ($\theta_1 = 0, \phi_1 = 0$) and the second electron is on the xz plane ($\phi_2 = 0$). The $2N - 3$ relative angles $\{\theta_2, \theta_3, \phi_3, \dots, \theta_N, \phi_N\}$ are globally denoted by Ω . The total classical energy we want to minimize then reads

$$E_{\text{pot}}([v], r_1, \dots, r_N, \Omega) = \sum_{i=1}^N v(r_i) + V_{ee}(r_1, \dots, r_N, \Omega). \quad (26)$$

Since the external potential does not depend on the relative angles Ω , we can decouple the stationarity equations (20) into an angular part, which only involves V_{ee} , and a radial part that also involves $v(r)$. By solving the angular part for any given $r_1, \dots, r_N$ we can define a function $\Omega(r_1, \dots, r_N)$ for the minimizing angles, valid for any spherically-symmetric v . These angles are the solution of the electrostatic equilibrium problem for N neutral sticks

of lengths $r_1, \dots, r_N$ having the same point-charge q glued at one end, and the other end fixed in the origin, in such a way that they are free to rotate in the 3D space.

We now insert the function $\Omega(r_1, \dots, r_N)$ in the stationarity equations for the radial variables r_i ,

$$\begin{cases} v'(r_1) = -\frac{\partial}{\partial r_1} V_{ee}(r_1, r_2, \dots, r_N, \Omega) \Big|_{\Omega(r_1, \dots, r_N)} \\ v'(r_2) = -\frac{\partial}{\partial r_2} V_{ee}(r_1, r_2, \dots, r_N, \Omega) \Big|_{\Omega(r_1, \dots, r_N)} \\ \vdots \end{cases} \quad (27)$$

As explained in the previous Sec. IV, in order to have a smooth (e.g., atomic) radial density $\rho(r)$ we need to choose a $v(r)$ that makes these equations fulfilled by a set of radial distances $(r, f_2(r), \dots, f_N(r))$ in which r can take any value in the domain in which $\rho(r) \neq 0$. These radial co-motion functions $f_n(r)$ must have the same transformation properties of Eq. (22), as it can be verified by inspection of Eqs. (27).

To construct the radial co-motion functions $f_n(r)$ for a given density $\rho(r)$ we proceed as follows. Our starting point is Eq. (24) that becomes, in the case of spherical symmetry,

$$4\pi f_n(r)^2 \rho(f_n(r)) |f'_n(r)| dr = 4\pi r^2 \rho(r) dr. \quad (28)$$

We then define the function $N_e(r)$ that gives the expected number of electrons between 0 and r ,

$$N_e(r) = \int_0^r 4\pi x^2 \rho(x) dx. \quad (29)$$

$N_e(r)$ is a monotonously increasing function of r , and its inverse $N_e^{-1}(y)$ is well defined for $y \in [0, N]$. By integrating both sides of Eq. (28) we see that each function $f_n(r)$ is of the form

$$f_n(r) = \begin{cases} N_e^{-1}(N_e(f_n(0)) \pm N_e(r)) & 0 \leq r \leq a_1 \\ N_e^{-1}(N_e(f_n(a_1)) \mp N_e(a_1) \pm N_e(r)) & a_1 \leq r \leq a_2 \\ \vdots \end{cases} \quad (30)$$

where the upper (lower) sign corresponds to the case $f'_n \geq 0$ ($f'_n < 0$), and $[0, a_1]$, $[a_1, a_2]$, $\dots$, $[a_{k-1}, a_k]$ are the intervals in which (i) $f'_n(r)$ does not change sign and (ii) $N_e(f_n(a_i)) \mp N_e(a_i) \pm N_e(r) \in [0, N]$, so that N_e^{-1} is well defined.

The SCE problem for spherical densities thus consists in finding the signs, the intervals $[a_{i-1}, a_i]$, and the initial conditions $f_n(0), \dots, f_n(a_k)$ in Eqs. (30) that (i) make the $f_n(r)$ satisfy the transformation properties (22), (ii) yield, via Eq. (23), a $v(r)$ with a continuous first derivative, and (iii) give the minimum expectation value of $\hat{V}_{ee}$ when inserted in Eq. (25).

We shall now see how to proceed in the case of atomic densities. We first treat the case of the He atom, and we then generalize the solution to $N > 2$.

A. $N = 2$ (He atom)

Two electrons in a smooth spherical density in the $\alpha \rightarrow \infty$ limit have been already considered in Ref. 7, where the SCE state was proposed on the basis of physical considerations. Here, we restate the problem in terms of the formalism just derived, and we show that the solution proposed in Ref. 7 was indeed the correct one.

When $N = 2$ we have only one relative angle, θ_2 . By solving the stationarity equations for the angular part we immediately obtain $\theta_2 = 0$ or π . It is easy to verify that $\theta_2 = 0$ is a maximum and $\theta_2 = \pi$ is a minimum for any value r_1 and r_2 . By inserting the minimizing angle $\theta_2 = \pi$ in the stationarity equations for the radial variables, we obtain

$$\begin{cases} v'(r_1) = (r_1 + r_2)^{-2} \\ v'(r_2) = (r_1 + r_2)^{-2} \end{cases} \quad (31)$$

These equations admit a solution of the kind $(r, f(r))$ if and only if $f(r)$ satisfies the property $f(f(r)) = r$, in agreement with Eq. (22). This means that, among all the possible $f(r)$ of the form (30), we can only choose the ones for which $f^{-1} = f$. One can verify that the only possible choices are then

$$f(r) = N_e^{-1}(N_e(r)) = r \quad (32)$$

$$f(r) = \begin{cases} N_e^{-1}(N_e(f(0)) - N_e(r)) & r < f(0) \\ N_e^{-1}(2 + N_e(f(0)) - N_e(r)) & r > f(0) \end{cases} \quad (33)$$

$$f(r) = \begin{cases} N_e^{-1}(1 + N_e(r)) & r < N_e^{-1}(1) \\ N_e^{-1}(N_e(r) - 1) & r > N_e^{-1}(1) \end{cases} \quad (34)$$

We call the choice (32) the “breathing” solution: the two electrons are always at the same distance from the center, opposite to each other. It is a stationary solution valid for any density, since $f(r) = r$ satisfies the differential equation (28) independently of the choice of $\rho(r)$. The corresponding external potential is $v(r) = -\frac{1}{4r}$. The Hessian matrix shows that this stationary solution must be ruled out, since it is a maximum for $E_{\text{pot}}([v], r_1, r_2, \theta_2)$.

The choice (33) corresponds to a discontinuous $v'(r)$, except in the case $N_e(f(0)) = 2$, i.e., $f(0) = \infty$. We rule out a discontinuous $v'(r)$ because otherwise our whole construction is inconsistent: if $v'(r)$ is not continuous it is not necessary for a minimizing configuration of E_{pot} to satisfy the stationarity equations (20). As a double check, we also verified, in the case of the He atom, that the choice $N_e(f(0)) = 2$ in (33) is indeed the one that yields the lowest expectation of $\hat{V}_{\text{ee}}$, also when compared to the form (34) that, again, corresponds to a discontinuous $v'(r)$. The SCE solution for $N = 2$ electrons in a smooth spherical density is thus the one proposed in Ref. 7, i.e.,

$$f(r) = N_e^{-1}(2 - N_e(r)). \quad (35)$$

It is easy to verify that this stationary solution, with its corresponding potential,

$$v(r) = \int^r \frac{dx}{(1 + f(x))^2}, \quad (36)$$

is the true minimum of $E_{\text{pot}}([v], r_1, r_2, \theta_2)$.

Besides the mathematical arguments, the choice (35) is the most “physical” one: it makes the two electrons always be in two different spherical shells, each one containing, on average in the quantum mechanical problem, one electron [7]. This is exactly what we expect for two electrons that repel each other infinitely strong, but that have to fulfill the constraint of yielding a given smooth, atomic-like density $\rho(r)$.

B. $N = 3$ (Li atom)

When $N = 3$ we have 3 angles, $\theta_2, \theta_3, \phi_3$, but we immediately obtain $\phi_3 = 0$: the three electrons must be on the same plane, containing the nucleus, to achieve compensation of the forces (see Sec. IV B). We then find numerically, for any given r_1, r_2, r_3 , the minimizing angles θ_2 and θ_3 .

To construct the radial co-motion functions $f_2(r)$ and $f_3(r)$ we should, in principle, try out all the possible $f_n(r)$ of the form (30) that satisfy the properties (22), and select the ones that yield a continuous $v'(r)$ and the lowest expectation for $\hat{V}_{\text{ee}}$. Instead, we use the physical idea that was behind the solution for two electrons of Eq. (35): we expect that the correct f_2 and f_3 are the ones that make the three electrons always occupy three different spherical shells, each containing, on average in the quantum mechanical problem, one electron. Such radial co-motion functions read

$$f_2(r) = \begin{cases} N_e^{-1}(2 - N_e(r)) & r \leq a_2 \\ N_e^{-1}(N_e(r) - 2) & r > a_2 \end{cases} \quad (37)$$

$$f_3(r) = \begin{cases} N_e^{-1}(2 + N_e(r)) & r \leq a_1 \\ N_e^{-1}(4 - N_e(r)) & r > a_1 \end{cases} \quad (38)$$

where $a_1 = N_e^{-1}(1)$ and $a_2 = N_e^{-1}(2)$. They are displayed, for the Li atom using an accurate fully correlated density [13], in Fig. 1.

To better grasp the physics behind such solution, we show, in Fig. 2, the positions of the three electrons in the SCE state for the same accurate Li atom density [13]. The two big circles are the radii of the spheres containing, on average in the quantum mechanical problem, one electron (a_1) and two electrons (a_2). The position r of the first electron is varied along the vertical z axis a) from 0 to a_1 , b) from a_1 to a_2 , and c) from a_2 to ∞ . The other two electrons have distances from the center given, respectively, by $f_2(r)$ and $f_3(r)$, and angular positions given by the minimizing angles $\theta_2(r, f_2(r), f_3(r))$ and $\theta_3(r, f_2(r), f_3(r))$. In each panel, the starting position of the three electrons is represented by a full circle (●) and their final position by an empty circle (○). The dashed curves represent the “trajectories” of the three electrons, and the arrows their direction. Thus, for each position r on the z axis of the first electron, the positions of the other two electrons are completely fixed, apart from the permutation symmetry of electron 2 with

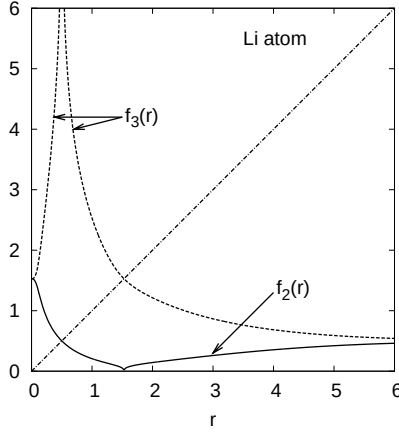


FIG. 1: The radial co-motion functions $f_2(r)$ and $f_3(r)$ for the Li atom density. Hartree atomic units are used.

electron 3. We clearly see from this figure, that in any SCE configuration the space is divided in three spherical shells, which never contain more than one electron. These three spherical shells are the same that, in the quantum mechanical problem, contain *on average* one electron: the SCE state makes them contain *always exactly* one electron, thus suppressing any accidental clustering (“correlation suppresses fluctuations” [14, 15]).

Because of the properties of the co-motion functions (which are a consequence of the fact that the electrons are indistinguishable), the three panels are equivalent. Our physical problem is in fact invariant for a rigid rotation of any of the configurations corresponding to a given r . This means that in panel b) we could, for each value of r , rigidly rotate the position of the three electrons in such a way that the electron in the inner shell moves on a straight line. In this way, we would reobtain a rigid rotation of panel a). The same can be done with panel c). Thus, to calculate the expectation of $\hat{V}_{ee}$ we only need to consider the case $0 \leq r \leq a_1$.

The solution of Eqs. (37)-(38) is thus very reasonable from the physical point of view. Moreover, it can be easily verified that it satisfies the properties required by stationarity of Eq. (22), and that it corresponds to a smooth external potential $v(r)$, which can be computed via

$$v'(r) = -\frac{\partial}{\partial r_1} V_{ee}(r_1, r_2, r_3, \theta_2, \theta_3) \Big|_{r, f_2(r), f_3(r), \theta_2(r), \theta_3(r)}, \quad (39)$$

where $\theta_i(r)$ is a shortened notation for $\theta_i(r, f_2(r), f_3(r))$. The potential obtained by integrating Eq. (39) (again using the accurate density for the Li atom of Ref. [13]) is reported in Fig. 3. Notice that $v(r)$ is finite, with a zero first derivative, at $r = 0$: the electron-nucleus cusp in the density $\rho(r)$ is compensated by the kinetic energy for any value of α (including the very limit $\alpha \rightarrow \infty$), as discussed in Ref. 16. For large r , we have $v(r \rightarrow \infty) = -\frac{N-1}{r}$, a necessary condition to include as a stationary

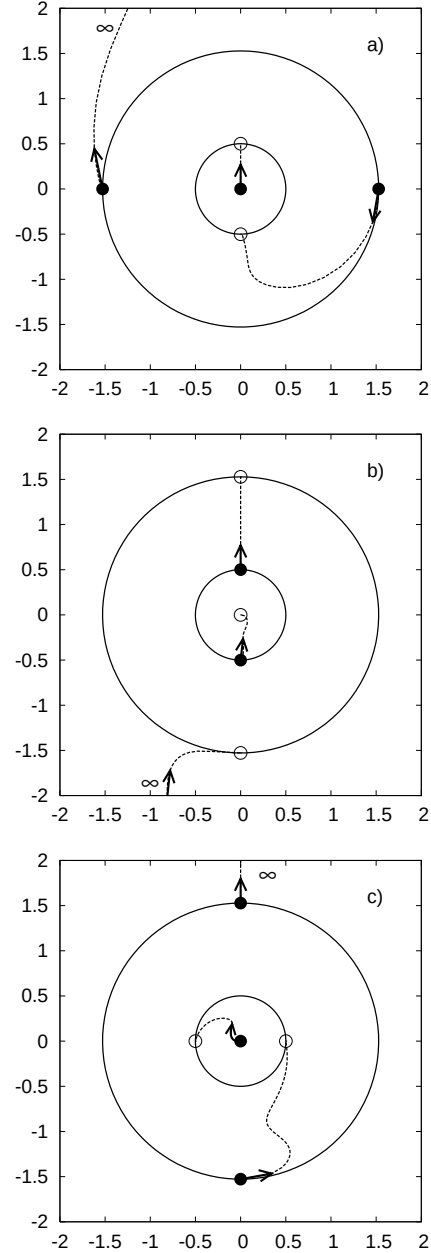


FIG. 2: The positions of the 3 electrons in the SCE state for the Li atom density. The two big circles are the projections of the spheres containing, on average in the quantum mechanical problem, 1 electron (radius a_1) and 2 electrons (radius a_2). The position r of the first electron is varied along the vertical z axis a) from 0 to a_1 , b) from a_1 to a_2 , and c) from a_2 to ∞ . The other two electrons have distances from the center given, respectively, by $f_2(r)$ and $f_3(r)$ of Eqs. (37)-(38), and angular positions given by the minimizing angles $\theta_2(r, f_2(r), f_3(r))$ and $\theta_3(r, f_2(r), f_3(r))$. In each panel, the starting position of the 3 electrons is represented by a full circle (●) and their final position by an empty circle (○). The dashed curves represent the “trajectories” of the 3 electrons, and the arrows their direction. The three panels are actually equivalent (see text). Distances are in atomic units.

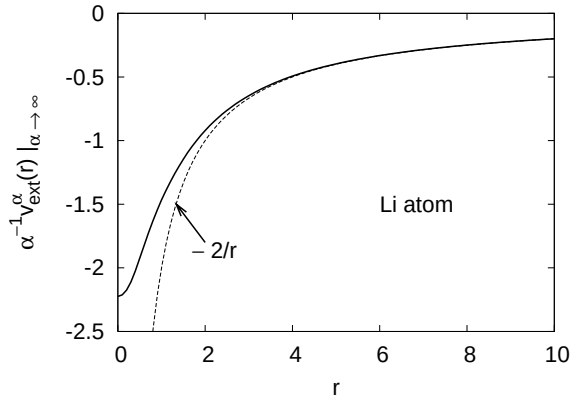


FIG. 3: The external potential $v(r)$ of Eq. (9) for the SCE state in the case of the Li atom. The asymptotic expansion for large r , $v(r \rightarrow \infty) = -\frac{N-1}{r}$, is also reported. All quantities are in Hartree atomic units.

configuration the one in which one of the N electrons is at infinity. The large- r asymptotic expansion $-2/r$ is also shown in the same Fig. 3.

With this potential $v(r)$ we have also verified that the stationary solution of Eqs. (37)-(38) is the absolute minimum of $E_{\text{pot}}([v], r_1, r_2, r_3, \theta_2, \theta_3, \phi_3)$. All these checks make us believe that Eqs. (37)-(38) are the correct SCE solution for the Li atom: it is difficult to imagine a different solution that yields a lower value for the expectation of $\hat{V}_{\text{ee}}$, since our solution is the one that makes the 3 electrons be always as far as possible from each other, without violating the constraint of yielding the smooth density $\rho(r)$.

We can thus finally obtain the value $W_{\infty}[\rho] = -2.6030$ Hartree for the Li atom, via

$$W_{\infty}[\rho] + U[\rho] = \int_0^{a_1} dr 4\pi r^2 \rho(r) V_{\text{ee}}(r, f_2(r), f_3(r), \theta_2(r), \theta_3(r)), \quad (40)$$

where we have used the fact that, because the three electrons are indistinguishable, integrating from 0 to ∞ is the same as integrating three times from 0 to a_1 .

As a final remark, we comment briefly on the fact that one never obtains the configuration in which the three electrons are at the same distance from the nucleus, at the vertices of an equilateral triangle. The reason is that the only $f_2(r)$ and $f_3(r)$ compatible with this configuration (even for only one single value of r , say r_0) that also satisfy the required properties (22) are the ones corresponding to the “breathing” solution, $f_2(r) = f_3(r) = r$, as it can be easily verified by integrating both sides of Eq. (28) with the initial condition $r = r_0$, $f_n(r_0) = r_0$. This gives the two possibilities $f_A(r) = r$ or $f_B(r) = N_e^{-1}(2N_e(r_0) - N_e(r))$: any choice for $f_2(r)$ and $f_3(r)$ which contains the function $f_B(r)$ does not satisfy the properties (22). This is a difference with the $N = 2$ case in which, instead, the solution is $f(r) = f_B(r)$ with $N_e(r_0) = 1$: two electrons in the SCE

state in a smooth density have one configuration in which they are both at the same distance from the nucleus, but for three electrons this does not happen. One can also easily check that, again, the “breathing” solution, with its potential $v(r) = -\frac{1}{\sqrt{3}r}$, is not a minimum for the corresponding $E_{\text{pot}}([v], r_1, r_2, r_3, \theta_2, \theta_3, \phi_3)$.

We can at this point clearly see the difference between the SCE state for a smooth atomic density (Fig. 2) and the more familiar Wigner-crystal-like state (for a case with three electrons see, e.g., Ref. 17), in which the three electrons are localized at the vertices of a triangle at a certain distance from the nucleus, say r_0 . In this latter case, the density becomes very peaked around r_0 , loosing any resemblance with an atomic density, and becoming more and more similar to Eq. (17).

C. $N = 4$ (Be atom)

We have now 5 relative angles to consider. As in the $N = 3$ case, we compute the minimizing angular function $\Omega(r_1, r_2, r_3, r_4)$ numerically.

We then construct the radial co-motion functions, $f_2(r)$, $f_3(r)$, $f_4(r)$, following the same ideas used for the case $N = 2$ and 3: we divide the space in four spherical shells, each containing, on average in the quantum mechanical problem, one electron. The radial co-motion functions that make the four electrons always be in four distinct shells are then

$$f_2(r) = \begin{cases} N_e^{-1}(2 - N_e(r)) & r \leq a_2 \\ N_e^{-1}(N_e(r) - 2) & r > a_2 \end{cases} \quad (41)$$

$$f_3(r) = \begin{cases} N_e^{-1}(2 + N_e(r)) & r \leq a_2 \\ N_e^{-1}(6 - N_e(r)) & r > a_2 \end{cases} \quad (42)$$

$$f_4(r) = N_e^{-1}(4 - N_e(r)), \quad (43)$$

where, again, $a_i = N_e^{-1}(i)$. These functions satisfy the transformation properties (22), and are reported in Fig. 4 for the case of an accurate correlated density [18] of the Be atom.

We can then obtain, using the analogue of Eq. (40) for $N = 4$, the value $W_{\infty}[\rho] = -4.0212$ Hartree for the Be atom.

To check our result, we also computed the corresponding external potential $v(r)$, which, as shown in Fig. 5, is continuous and smooth. We also verified that our stationary solution is the absolute minimum for the corresponding $E_{\text{pot}}([v], r_1, r_2, r_3, r_4, \Omega)$.

Interestingly, we found that, for the case of the Be atomic density, the four electrons always lie on the same plane, containing the nucleus. This effect seems to be due to the shell structure of the atomic density: by repeating the calculation using a simple exponential density, $\rho(r) = \beta^3 e^{-\beta r}/2\pi$, we found that the four electrons are often non-coplanar. Instead, by using other test densities with a shell structure, we found again the four electrons always on the same plane. The shell structure seems to force the four electrons to have distances from the nucleus

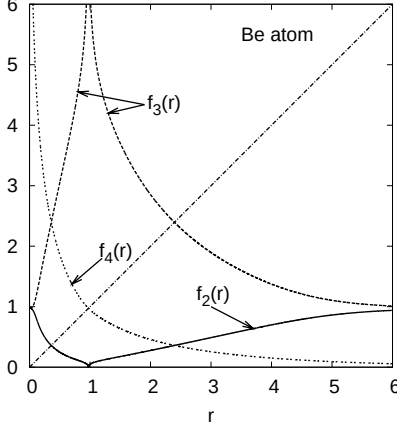


FIG. 4: The radial co-motion functions $f_2(r)$, $f_3(r)$ and $f_4(r)$ for the Be atom density. Hartree atomic units are used.

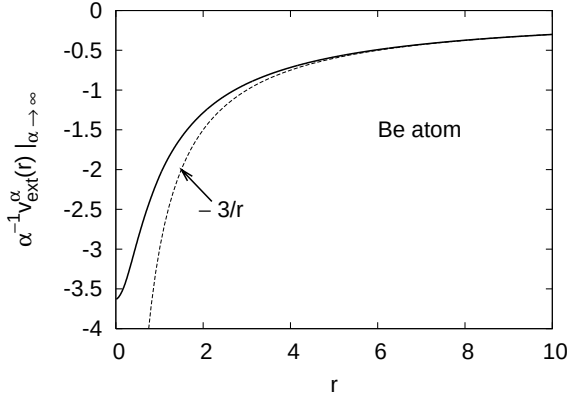


FIG. 5: The external potential $v(r)$ of Eq. (9) for the SCE state in the case of the Be atom. The asymptotic expansion for large r , $v(r \rightarrow \infty) = -\frac{N-1}{r}$, is also reported. All quantities are in Hartree atomic units.

that are distributed in a highly nonuniform way, so that forces compensation (see Sec. IV B) can be achieved only if they are on the same plane.

D. The general N -electron solution

This way of constructing the solution can be generalized to any number of electrons N . The radial co-motion functions that make the N electrons always occupy N different shells containing, on average in the quantum mechanical problem, one electron, are as follows. Define an integer index k running for odd N from 1 to $(N-1)/2$, and for even N from 1 to $(N-2)/2$. Then

$$f_{2k}(r) = \begin{cases} N_e^{-1}(2k - N_e(r)) & r \leq a_{2k} \\ N_e^{-1}(N_e(r) - 2k) & r > a_{2k} \end{cases} \quad (44)$$

$$f_{2k+1}(r) = \begin{cases} N_e^{-1}(N_e(r) + 2k) & r \leq a_{N-2k} \\ N_e^{-1}(2N - 2k - N_e(r)) & r > a_{N-2k}, \end{cases} \quad (45)$$

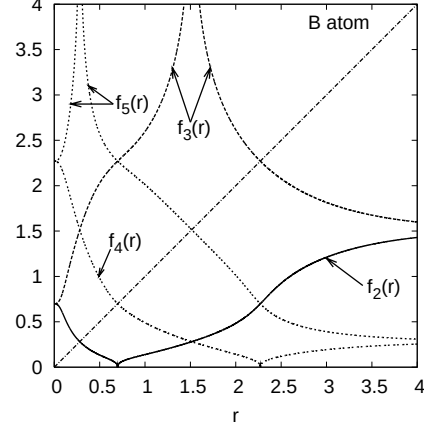


FIG. 6: The radial co-motion functions for the sphericalized B atom density. Hartree atomic units are used.

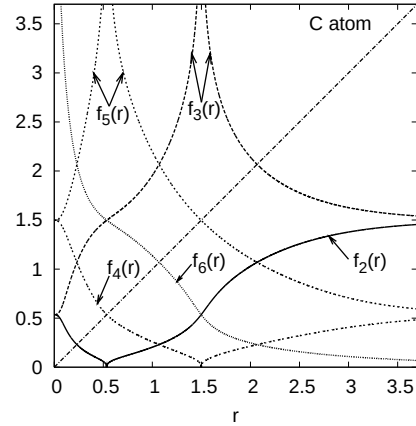


FIG. 7: The radial co-motion functions for the sphericalized C atom density. Hartree atomic units are used.

where $a_i = N_e^{-1}(i)$. For odd N , these equations give all the needed $N - 1$ radial co-motion functions, while for even N we have to add the last function,

$$f_N(r) = N_e^{-1}(N - N_e(r)). \quad (46)$$

Using these radial co-motion functions, which satisfy the properties (22) for any N , we calculated the SCE value $W_\infty[\rho]$ for accurate sphericalized densities of the B and C atoms [19], and for the Ne atom density [18, 20]. The resulting radial co-motion functions are displayed in Figs. 6-8. The results for $W_\infty[\rho]$ are reported in Table I, and the corresponding potentials $v(r)$ are shown in Fig. 9. In all cases we find the N electrons non-complanar.

VI. COMPARISON WITH THE PC MODEL

In the absence of spherical symmetry there seems to be no general strategy for finding the initial conditions to integrate Eqs. (24), although we are still investigating this

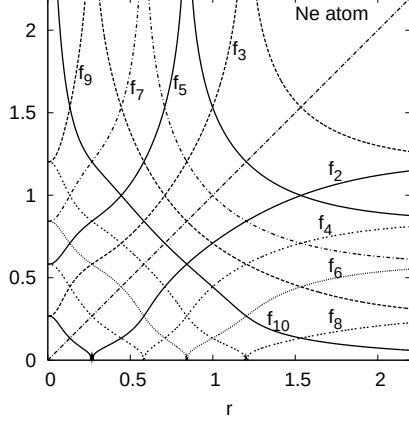


FIG. 8: The radial co-motion functions for the Ne atom density. Hartree atomic units are used.

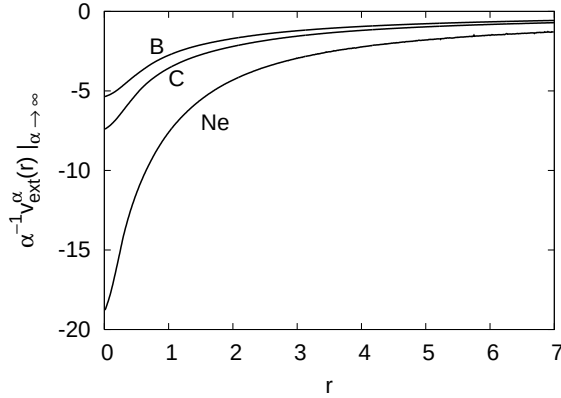


FIG. 9: The external potential $v(r)$ of Eq. (9) for the SCE state in the case of the Ne atom and of the sphericalized B and C atoms. All quantities are in Hartree atomic units.

problem. So far, such cases can only be treated approximately, using instead of the exact expression (25) the PC model (6) for the functional $W_\infty[\rho]$. The PC model has been tested successfully [8] against the meta-GGA functional of Ref. 21 that is expected to be accurate in the limit $\alpha \rightarrow \infty$. The present exact (SCE) results, in contrast, provide a rigorous test for the PC model.

Table I documents reasonable values from the PC model for all the atoms considered here. A severe test is the trivial case of the hydrogen atom H, with the one-electron density $\rho(r) = \frac{1}{\pi}e^{-2r}$, where $\langle \hat{V}_{ee} \rangle = 0$ for any value of α and thus $W_\infty[\rho] = -\frac{5}{16}$ Hartree. For the other atoms in Table I, the PC error is less than 63 mH $\approx$ 39 kcal/mole.

The quantity $W_\infty[\rho]$ refers to the limit of infinitely strong repulsion between electrons. Being the subject of the present paper, this extreme limit is not directly relevant for real electron systems such as atoms or molecules. Rather, it is studied here in order to be combined with additional information from the opposite

	$W_\infty^{\text{SCE}}[\rho]$ (H)	$W_\infty^{\text{PC}}[\rho]$ (H)	error (mH)
H	-0.3125	-0.3128	0.3
He	-1.500	-1.463	37
Li	-2.6030	-2.5559	47
Be	-4.0212	-3.9608	60
B	-5.7063	-5.6502	56
C	-7.7817	-7.7192	63
Ne	-20.035	-20.000	35

TABLE I: Comparison of the values $W_\infty[\rho]$ in Hartree atomic units obtained with the SCE construction, and with the PC model [8]. The absolute errors of the PC model are also reported.

weak-interaction limit $\alpha \rightarrow 0$. In this way, properties of real atoms and molecules, including those with weak correlations, can be predicted accurately [6] without dealing explicitly with the complicated wave function at the realistic interaction strength $\alpha = 1$. Both the extreme limits $\alpha \rightarrow 0$ and $\alpha \rightarrow \infty$ are mathematically much simpler than the realistic situation at $\alpha = 1$. Consequently, more relevant than the error of the quantity $W_\infty[\rho]$ itself is the error it causes in the ISI correlation energy [6] $E_c^{\text{ISI}}[\rho] = E_{\text{xc}}^{\text{ISI}}[\rho] - E_{\text{x}}[\rho]$. Since the ISI model of Ref. 6 uses, along with $W_\infty[\rho]$, also the coefficient $W'_\infty[\rho]$ which is not known exactly, we consider here the earlier ISI version SPL of Ref. 5,

$$W_\alpha^{\text{SPL}}[\rho] = W_\infty[\rho] + \frac{E_{\text{x}}[\rho] - W_\infty[\rho]}{\sqrt{1 + 2Q[\rho]\alpha}}, \quad (47)$$

with

$$Q[\rho] = \frac{2|E_c^{\text{GL2}}[\rho]|}{E_{\text{x}}[\rho] - W_\infty[\rho]}. \quad (48)$$

Analytical integration of $\int_0^1 d\alpha W_\alpha^{\text{SPL}}[\rho] - E_{\text{x}}[\rho]$ yields

$$E_c^{\text{SPL}}[\rho] = (E_{\text{x}}[\rho] - W_\infty[\rho]) \left[\frac{\sqrt{1 + 2Q[\rho]} - 1}{Q[\rho]} - 1 \right]. \quad (49)$$

The correlation energies $E_c^{\text{SPL}}[\rho]$, evaluated with the values $W_\infty[\rho]$ of Table I, are reported in the columns “(PC)” and “(SCE)” of Table II. While the SPL prediction comes quite close to the exact correlation energy of the He atom, the case of the Be and Ne atoms is less satisfying. Nevertheless, the improvement beyond the second-order correlation energy is remarkable, since the only additional information used here is the coefficient $W_\infty[\rho]$ (but not $W'_\infty[\rho]$).

For the He, Be, and Ne atoms, the error introduced by the PC model in $E_c^{\text{SPL}}[\rho]$ is always less than 1 mH, showing that in the case of neutral atoms the SPL-ISI correlation functional is not too sensitive to the exact value of $W_\infty[\rho]$. However, we have to keep in mind that neutral atoms are systems that resemble much more to the noninteracting KS system ($\alpha = 0$) than to the SCE state ($\alpha = \infty$). We expect that for more correlated systems (e.g., stretched bonds) the ISI correlation energy is

	$E_x[\rho]$	$E_c^{\text{GL2}}[\rho]$ (PC)	(SCE)	$E_c^{\text{exact}}[\rho]$
He	-1.0246	-0.0503	-0.0413	-0.0418
Be	-2.674	-0.125	-0.1054	-0.1061
Ne	-12.084	-0.469	-0.4205	-0.4207

TABLE II: The exchange energy $E_x[\rho]$, the second order Görling-Levy correlation energy $E_c^{\text{GL2}}[\rho]$ [22], and the estimate of the correlation energy $E_c[\rho]$ from the SPL ISI model [5] using the values $W_\infty^{\text{SCE}}[\rho]$ (SCE) and $W_\infty^{\text{PC}}[\rho]$ (PC), compared with “exact” values. All energies are in Hartree atomic units.

much more sensitive to the exact value of $W_\infty[\rho]$. The investigation of such cases will be the object of future work.

VII. CONCLUSIONS AND PERSPECTIVES

We have reformulated the strong-interaction limit of density functional theory in terms of a classical problem with a degenerate minimum, obtaining a consistent solution for this limit. Even if an antisymmetric wavefunction can be explicitly constructed, the strong-interaction limit of DFT is entirely characterized by much simpler quantities, the so called “co-motion” functions, which are related to the electronic density $\rho(\mathbf{r})$ via the differential equation (24). The results of this work can be useful to construct interpolations between the weak- and the strong-interaction limits of DFT, and to test other approximate functionals in the $\alpha \rightarrow \infty$ limit [23].

Future work will be mainly devoted to the calculation of this limit for non-spherical densities, and to study the generalization to the next leading term, $W'_\infty[\rho]$. The calculation of the intracule density (the probability distribution for the electron-electron distance) will be also carried out in connection with the correlation energy functional constructed in Ref. 24.

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APPENDIX A: HARMONIC INTERACTIONS

It is instructive to see how the SCE solution changes if we replace the Coulomb repulsion with an harmonic interaction. Since in this case we have the exact solution, we can also clarify how the SCE construction presented

in this paper gives the $\alpha \rightarrow \infty$ limit of DFT. We thus consider the exactly solvable 2-electron hamiltonian [25]

$$\hat{H}^\alpha = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{k_\alpha}{2}(r_1^2 + r_2^2) - \frac{\alpha}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2, \quad (\text{A1})$$

and we analyze the case in which $\alpha \rightarrow \infty$ and the density is kept fixed, equal to the one at $\alpha = 1$, by means of a suitable k_α .

The ground-state one-electron density of the hamiltonian $\hat{H}^\alpha$ is given by

$$\rho(r) = \frac{2\beta^{3/2}}{\pi^{3/2}} e^{-\beta r^2}, \quad \beta = \frac{2\sqrt{k_\alpha(k_\alpha - 2\alpha)}}{\sqrt{k_\alpha - 2\alpha} + \sqrt{k_\alpha}}, \quad (\text{A2})$$

so that k_α must keep β independent of α and thus satisfies the equation

$$\frac{\sqrt{k_\alpha(k_\alpha - 2\alpha)}}{\sqrt{k_\alpha - 2\alpha} + \sqrt{k_\alpha}} = \frac{\sqrt{k_1(k_1 - 2)}}{\sqrt{k_1 - 2} + \sqrt{k_1}}, \quad (\text{A3})$$

where $k_1 > 2$ in order to have a bound system. We easily find

$$k_{\alpha \rightarrow \infty} = 2\alpha + \frac{\beta^2}{4} + O(\alpha^{-1/2}). \quad (\text{A4})$$

The square of the spatial wavefunction is equal to

$$|\psi_\alpha(\mathbf{r}_1, \mathbf{r}_2)|^2 = \left[\frac{\sqrt{k_\alpha(k_\alpha - 2\alpha)}}{\pi^2} \right]^{3/2} \times e^{-\frac{1}{2}(\sqrt{k_\alpha} + \sqrt{k_\alpha - 2\alpha})(r_1^2 + r_2^2) - (\sqrt{k_\alpha} - \sqrt{k_\alpha - 2\alpha})\mathbf{r}_1 \cdot \mathbf{r}_2}. \quad (\text{A5})$$

Now, we want to compare the exact result with the SCE construction. We thus follow the same steps done for the case of the He atom in Subsec. V A. Again, we find that the minimizing angle is $\theta = \pi$ and that the radial co-motion function must satisfy the property $f(f(r)) = r$, so that the only possible choices are the ones of Eqs. (32)-(34). In this case, however, the “breathing” solution of Eq. (32), $f(r) = r$, is the one that yields the minimum expectation of “ $\hat{V}_{ee}$ ”, and that is the global minimum of the corresponding E_{pot} . The very different nature of harmonic forces with respect to Coulomb repulsion makes the solution completely different also from a qualitative point of view. The “breathing” solution, that was a maximum for Coulomb forces, becomes the true minimum in the case of harmonic forces. In this latter case, in fact, the interaction is not singular at zero electron-electron distance so that the two electrons can get on top of each other (and they do, at the “nucleus”). This means that in this case even in the $\alpha \rightarrow \infty$ limit the spin state can still play a role. The SCE one-body potential is obtained by

$$v'(r) = r + f(r) = 2r, \quad (\text{A6})$$

so that $v(r) = r^2$ agrees with the leading term ($O(\alpha)$) of Eq. (A4) (remember that in the SCE construction we directly consider all the quantities divided by α).

In order to compare the SCE solution with the exact wavefunction of Eq. (A5) in the $\alpha \rightarrow \infty$ limit, we have first to keep in mind that Eq. (A5) is the solution of the hamiltonian $\hat{H}^\alpha$, so that it includes also the kinetic energy operator $\hat{T}$. Equation (A4) shows that the external potential $\hat{V}_{\text{ext}}^\alpha$ that keeps the density fixed has the large- α expansion $\hat{V}_{\text{ext}}^\alpha = \alpha \hat{V}_\infty + \hat{V}_0 + O(\alpha^{-1/2})$. The SCE construction only gives $\hat{V}_\infty$, but the exact solution of Eq. (A5) always includes also the next term, $\hat{V}_0$, because it is of the same order of $\hat{T}$. The comparison with the SCE solution can be done in the following way. Replace in Eq. (A5) the large- α expansion of k_α up to orders α^0 , $k_\alpha \rightarrow 2\alpha + \frac{\beta^2}{4}$. We can rearrange the result, with $c = \frac{\beta^2}{4}$,

$$|\psi_\alpha(\mathbf{r}_1, \mathbf{r}_2)|^2 \rightarrow \left(\frac{\sqrt{2\alpha+c} - \sqrt{c}}{2\pi} \right)^{3/2} e^{-\frac{1}{2}(\sqrt{2\alpha+c} - \sqrt{c})|\mathbf{r}_1 + \mathbf{r}_2|^2} \\ \times \frac{1}{\pi^{3/2}} \left(\frac{2\sqrt{c(2\alpha+c)}}{\sqrt{2\alpha+c} - \sqrt{c}} \right)^{3/2} e^{-\sqrt{c}(r_1^2 + r_2^2)} \quad (\text{A7})$$

When $\alpha \rightarrow \infty$, the first gaussian in Eq. (A7) with its factor in front tends to the distribution $\delta(\mathbf{r}_1 + \mathbf{r}_2)$. The second gaussian gives $\frac{1}{2}\rho(\mathbf{r}_1)$. Thus, as $\alpha \rightarrow \infty$ we have

$$\lim_{\alpha \rightarrow \infty} |\psi_\alpha(\mathbf{r}_1, \mathbf{r}_2)|^2 = \frac{\rho(\mathbf{r}_1)}{2} \delta(\mathbf{r}_1 + \mathbf{r}_2), \quad (\text{A8})$$

which is exactly the SCE solution, since in the case of harmonic forces $\mathbf{f}(\mathbf{r}) = -\mathbf{r}$.

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