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Electronic Zero-Point Oscillations in the Strong-Interaction Limit of Density Functional Theory

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Abstract: The exchange-correlation energy in Kohn–Sham density functional theory can be expressed exactly in terms of the change in the expectation of the electron–electron repulsion operator when, in the many-electron Hamiltonian, this same operator is multiplied by a real parameter λ varying between 0 (Kohn–Sham system) and 1 (physical system). In this process, usually called adiabatic connection, the one-electron density is kept fixed by a suitable local one-body potential. The strong-interaction limit of density functional theory, defined as the limit $\lambda \rightarrow \infty$, turns out to be like the opposite noninteracting Kohn–Sham limit ($\lambda \rightarrow 0$) mathematically simpler than the physical ($\lambda = 1$) case and can be used to build an approximate interpolation formula between $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$ for the exchange-correlation energy. Here we extend the systematic treatment of the $\lambda \rightarrow \infty$ limit [*Phys. Rev. A* **2007**, *75*, 042511] to the next leading term, describing zero-point oscillations of strictly correlated electrons, with numerical examples for small spherical atoms. We also propose an improved approximate functional for the zero-point term and a revised interpolation formula for the exchange-correlation energy satisfying more exact constraints.

1. Introduction

Kohn–Sham (KS) density functional theory (DFT)[1−3] is a very successful method for electronic structure calculations thanks to its unique combination of low computational cost and remarkable accuracy. In the Kohn–Sham formalism, the ground-state energy of a many-electron system in a given external potential $\hat{V}_{ext} = \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i)$ is rewritten as a functional of the one-electron density $\rho(\mathbf{r})$

$$E[\rho] = F[\rho] + \int d^3 r \rho(\mathbf{r}) v_{ext}(\mathbf{r}) \tag{1}$$

where

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$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \tag{2}$$

with the operators (in Hartree atomic units $e = m = \hbar = a_0 = 1$ used throughout)

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 \tag{3}$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i,j=1}^{N} \frac{1 - \delta_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{4}$$

In eq (2) the minimum search is carried over all antisymmetric wave functions yielding a given density ρ.[4] The universal functional $F[\rho]$ of eq (2) is further divided into

$$F[\rho] = T_s[\rho] + U[\rho] + E_{xc}[\rho] \tag{5}$$

where the noninteracting kinetic energy functional $T_s[\rho]$ is obtained by replacing $\hat{V}_{ee}$ with zero in eq (2)

$$T_s[\rho] = \min_{\psi \to \rho} \langle \psi | \hat{T} | \psi \rangle \qquad (6)$$

and the Hartree functional $U[\rho]$ is the classical electrostatic repulsion energy

$$U[\rho] = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad (7)$$

The only quantity that needs to be approximated is the functional for the exchange-correlation energy, $E_{xc}[\rho]$, defined as the quantity needed to make eq (5) exact. The great success of KS DFT in solid state physics stems from the fact that even the simplest approximation for $E_{xc}[\rho]$, the local-density approximation (LDA), already gives remarkable results for basic properties of simple solids. A fundamental step forward to improve the solid-state physics results, and to spread the use of KS DFT into the quantum chemistry world, has been the advent of generalized gradient approximations (GGA), which are, to a large amount, due to the work of John P. Perdew and his co-workers.[5−7]

Despite its success in scientific areas now ranging from material science to biology, KS-DFT is far from being perfect, and a huge effort is put forth nowadays in trying to improve the approximations for $E_{xc}[\rho]$ (for recent reviews see, e.g., refs 8 and 9). The focus of a large part of the scientific community working in this area has shifted from seeking explicit functionals of the density (like the GGAs) to implicit density functionals that construct the exchange-correlation energy from the KS orbitals. For example, predicted atomization energies of molecules have been improved by meta-GGAs (MGGA)[10,11] which make use of the orbital kinetic energy density, by hybrid functionals (see, e.g., refs 12 and 13) which mix a fraction of exact exchange with GGA exchange and correlation, and by range-separated hybrids, in which only long- or short-range exact exchange is used (see, e.g., refs 14−18).

The next step[19] toward higher accuracy could be fully nonlocal functionals, which use 100% of exact exchange (for a recent review, see ref 20). Despite several attempts and the increasing understanding of the crucial problems,[21] the construction of a fully nonlocal correlation energy functional compatible with exact exchange is still an issue. A possible way to address this problem is to use the information contained in the strong-interaction limit of DFT.[22] To explain this strategy, we have first to recall an exact formula[23−25] for $E_{xc}[\rho]$

$$E_{xc}[\rho] = \int_0^1 d\lambda \, W_\lambda[\rho] \qquad (8)$$

The integrand $W_\lambda[\rho]$ is given by

$$W_\lambda[\rho] = \langle \Psi_\lambda[\rho] | \hat{V}_{ee} | \Psi_\lambda[\rho] \rangle - U[\rho] \qquad (9)$$

where $\Psi_\lambda[\rho]$, for a given value of $\lambda \geq 0$, is the wave function that minimizes $\langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle$ and yields the density ρ. If ρ is v-representable for all $\lambda \geq 0$, $\Psi_\lambda[\rho]$ is the ground-state of a fictitious N-electron system with the Hamiltonian

$$\hat{H}_\lambda[\rho] = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{ext}^\lambda[\rho] \qquad (10)$$

where the λ-dependent external potential

$$\hat{V}_{ext}^\lambda[\rho] = \sum_{i=1}^N v_{ext}^\lambda([\rho]; \mathbf{r}_i) \qquad (11)$$

ensures that $\hat{H}_\lambda[\rho]$ have the same given ($\lambda = 1$) ground-state density $\rho(\mathbf{r})$ for all λ. When $\lambda = 0$, the Hamiltonian of eq (10) becomes the KS Hamiltonian, and $v_{ext}^{\lambda=0}([\rho]; \mathbf{r}) = v_{KS}(\mathbf{r})$, the familiar KS potential, while for $\lambda = 1$ we recover the Hamiltonian of the physical system.

We can use perturbation theory to obtain an expansion of $W_\lambda[\rho]$ in powers of λ starting from $\lambda = 0$

$$W_\lambda[\rho] = E_x[\rho] + 2\lambda E_c^{GL2}[\rho] + O(\lambda^2) \qquad (12)$$

where $E_x[\rho]$ is the exchange energy, and $E_c^{GL2}[\rho]$ is the second-order correlation energy in Görling-Levy[26] perturbation theory. However, like in the Møller−Plesset case,[27] this perturbation series expansion seems to have a finite radius of convergence which for many atoms and molecules is less than 1.[22] Moreover, evaluating terms of ever higher order becomes impracticably expensive. Nevertheless, the exact lowest-order terms $E_x[\rho]$ and $E_c^{GL2}[\rho]$ can be used for an alternative approach,[22] called interaction-strength interpolation (ISI), to approximate the integrand in eq (8). The basic idea of ISI is to combine the $\lambda \to 0$ limit of eq (12) with the information from the opposite strong-interaction limit, $\lambda \to \infty$, to construct an interpolation formula for $W_\lambda[\rho]$. This way, the information on the physical system at $\lambda = 1$ is extracted from an interpolation between $\lambda \to 0$ and $\lambda \to \infty$. ISI is based on previous ideas and attempts to construct approximate formulas for $W_\lambda[\rho]$ when $0 \leq \lambda \leq 1$.[12,13,28,29] Its novelty is the introduction of the strong-interaction limit, thus extending the construction of $W_\lambda[\rho]$ to the whole domain $\lambda \in [0,\infty]$.

In the strong-interaction limit, $\lambda \to \infty$, we will show in the next sections that $W_\lambda[\rho]$ has the asymptotic expansion

$$W_\lambda[\rho] = W_\infty[\rho] + \frac{W_\infty'[\rho]}{\sqrt{\lambda}} + O(\lambda^{-p}) \qquad (13)$$

where $p \geq 5/4$. The expansion (13) was justified from physical arguments in refs 30 and 31, and a simple approximation for the two functionals $W_\infty[\rho]$ and $W_\infty'[\rho]$, the point-charge plus continuum (PC) model,[32] has been used for the ISI, yielding atomization energies with errors within 4.3 kcal/mol.[22] In a recent paper,[33] the functional $W_\infty[\rho]$ of eq (13) has been constructed exactly. The main object of the present work is the extension of the systematic treatment of ref 33 to the next term, $W_\infty'[\rho]$.

The paper is organized as follows. In the next section 2, we briefly review the results of ref 33, recalling that the strong-interaction limit of DFT reduces to a $3N$-dimension classical equilibrium problem whose minimum is degenerate over a three-dimensional subspace. In sections 3 and 4 we define local curvilinear coordinates based on the local normal modes around the degenerate minimum. These local curvilinear coordinates will be used, in section 5, to expand the Hamiltonian of eq (10) for $\lambda \to \infty$, up to the order $\lambda^{1/4}$. The corresponding expansion of $\Psi_\lambda[\rho]$ is carried out in section 6, and the exact expression for $W_\infty'[\rho]$ is obtained in section

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7, where we also report numerical results for small spherical atoms, and we propose an improved PC functional for $W'_\infty[\rho]$. In section 8 we revise the interpolation formula for the ISI functional in order to satisfy the exact expansion of eq (13) up to $O(\lambda^{-1})$. The last section 9 is devoted to conclusions and perspectives. More details of the derivation of our expansion are given in Appendix A, and a fully analytic example is reported in Appendix B.

2. Strictly Correlated Electrons (SCE)

In the $\lambda \rightarrow \infty$ limit it has been shown[30,33] that, in order to keep the N electrons in the given density ρ, the external potential in eq (10) must compensate the infinitely strong interelectronic repulsion, thus becoming proportional to λ

$$\lim_{\lambda \rightarrow \infty} \frac{v_{ext}^{\lambda}([\rho], \mathbf{r})}{\lambda} = v_{SCE}([\rho], \mathbf{r}) \tag{14}$$

with a smooth finite function $v_{SCE}([\rho], \mathbf{r})$. (For brevity, the argument $[\rho]$ will be often dropped in the following).

The leading term in eq (10) when $\lambda \rightarrow \infty$ is then a purely multiplicative potential-energy operator

$$\hat{H}_{\lambda \rightarrow \infty}[\rho] = \lambda(\hat{V}_{ee} + \hat{V}_{SCE}) + O(\sqrt{\lambda}) \tag{15}$$

The square $|\Psi_{\lambda \rightarrow \infty}[\rho]|^2$ of the corresponding wave function is a distribution that is zero everywhere except for electronic configurations for which $\hat{V}_{ee} + \hat{V}_{SCE}$ has its global minimum. In order to guarantee a given *smooth* density $\rho(\mathbf{r})$ in such a "classical" state, this global minimum must be degenerate over a three-dimensional subspace of $\mathbb{R}^{3N}$[33] (otherwise, the density would be a sum of delta peaks centered in the equilibrium positions of the N electrons). We call this classical state with a smooth density "strictly correlated electrons" (SCE). The square of the SCE wave function $|\Psi_{SCE}[\rho]|^2 = |\lim_{\lambda \rightarrow \infty} \Psi_\lambda[\rho]|^2$ reads

$$|\Psi_{SCE}(\mathbf{r}_1, ..., \mathbf{r}_N)|^2 = \frac{1}{N!} \sum_P \int ds \frac{\rho(\mathbf{s})}{N} \delta(\mathbf{r}_1 - f_{P(1)}(\mathbf{s})) \delta(\mathbf{r}_2 - f_{P(2)}(\mathbf{s})) ... \delta(\mathbf{r}_N - \mathbf{f}_{P(N)}(\mathbf{s})) \tag{16}$$

where $\mathbf{f}_1, .., \mathbf{f}_N$ are "comotion functions", with $\mathbf{f}_1(\mathbf{r}) = \mathbf{r}$, and P denotes a permutation of $\{1, ... N\}$. This means that the N points $\mathbf{r}_1, ..., \mathbf{r}_N$ in 3D space found upon simultaneous measurement of the N electronic positions in the SCE state always obey the $N - 1$ relations

$$\mathbf{r}_i = \mathbf{f}_i(\mathbf{r}_1) \quad (i = 2, ..., N) \tag{17}$$

If the $N - 1$ comotion functions $\mathbf{f}_i(\mathbf{s})$ satisfy the differential equation

$$\rho(\mathbf{f}_i(\mathbf{r})) d^3 f_i(\mathbf{r}) = \rho(\mathbf{r}) d^3 r \tag{18}$$

together with special transformation properties[33] (see also ref 34), the SCE wave function of eq (16) yields the given density $\rho(\mathbf{r})$. One has then to find the initial conditions for the integration of eq (18) that minimize the expectation of $\hat{V}_{ee}$. The leading coefficient $W_\infty[\rho]$ in eq (13) has a simple

analytic expression in terms of the $\mathbf{f}_i(\mathbf{s})$ [see eq (80)] and has been evaluated for spherical atoms with up to $N = 10$ electrons.[33]

In order to treat the next leading term, $W'_\infty[\rho]$ of eq (13), we have to consider the next terms in the $\lambda \rightarrow \infty$ expansion of the Hamiltonian of eq (10), i.e., the kinetic energy $\hat{T}$ and the next orders of $\hat{V}_{ext}^\lambda$. Physically, we expect that $W'_\infty[\rho]$ is determined by zero-point oscillations around the degenerate SCE minimum. In the following, we give a formal justification to this physical argument.

3. The SCE Potential-Energy Minimum

Writing $\underline{r} \equiv (\mathbf{r}_1, ..., \mathbf{r}_N) \in \mathbb{R}^{3N} \equiv \Omega$, we consider the asymptotic potential-energy function $(\Omega \rightarrow \mathbb{R})$

$$E_{pot}(\underline{r}) := \lim_{\lambda \rightarrow \infty} \frac{\hat{H}_\lambda[\rho]}{\lambda}$$

$$= \frac{1}{2} \sum_{i,j=1}^N \frac{1 - \delta_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{SCE}(\mathbf{r}_i)$$

$$= \hat{V}_{ee} + \hat{V}_{SCE} \tag{19}$$

As said, the SCE external potential $v_{SCE}(\mathbf{r})$ has the very special property that the function $E_{pot}(\underline{r})$ has a degenerate minimum E_{SCE} on the 3D subset

$$\Omega_0 = \{\underline{f}(\mathbf{s}) | \mathbf{s} \in \mathbb{R}^3\} \subset \Omega \tag{20}$$

where $\underline{f}(\mathbf{s}) = (\mathbf{s}, \mathbf{f}_2(\mathbf{s}), ..., \mathbf{f}_N(\mathbf{s}))$, with the $\mathbb{R}^3 \rightarrow \mathbb{R}^3$ comotion functions $\mathbf{f}_i(\mathbf{s})$. In other words, for all $\underline{r} \in \Omega_0$, the function $E_{pot}(\underline{r})$ assumes the same constant value

$$E_{SCE} = W_\infty[\rho] + U[\rho] + \sum_{i=1}^N v_{SCE}(\mathbf{f}_i(\mathbf{s})) \tag{21}$$

which, in particular, is its global minimum within Ω. For illustration, see the analytical example of eq (108) in Appendix B.

In the very limit $\lambda \rightarrow \infty$, when $\hat{H}_\lambda[\rho] \rightarrow \lambda E_{pot}(\underline{r}) + O(\sqrt{\lambda})$, the square of the wave function $|\Psi_\lambda[\rho]|^2$ becomes the distribution $|\Psi_{SCE}[\rho]|^2$ of eq (16), which is strictly zero everywhere in Ω except for the 3D subset Ω_0 where $E_{pot}(\underline{r})$ is minimum[33]

$$\Psi_{SCE}([\rho], \underline{r}) \equiv 0 \quad \forall \underline{r} \in \Omega \backslash \Omega_0 \tag{22}$$

For large, but finite $\lambda \gg 1$, the electrons are expected to perform small zero-point oscillations about the SCE configurations $\underline{r} \in \Omega_0$, within a narrow $3N$-D "envelope" Ω_ε (with a small width $\varepsilon > 0$) of the 3D subset $\Omega_0 \subset \Omega$

$$\Omega_\varepsilon = \{\underline{r} \in \Omega | d(\underline{r}, \Omega_0) < \varepsilon\} \tag{23}$$

Here, for a given $\underline{r} \in \Omega$, the quantity

$$d(\underline{r}, \Omega_0) := \min_{\mathbf{s} \in \mathbb{R}^3} |\underline{r} - \underline{f}(\mathbf{s})| \tag{24}$$

is the minimum $3N$-D distance between $\underline{r}$ and any $\underline{f}(\mathbf{s}) \in \Omega_0$. Notice that $\Omega_0 \subset \Omega_\varepsilon \subset \Omega$ and $\Omega_0 = \lim_{\varepsilon \rightarrow 0} \Omega_\varepsilon$.

For $\underline{r} \in \Omega_\varepsilon$, $E_{pot}(\underline{r})$ may be expanded about $\underline{f}(\mathbf{s}) \in \Omega_0$

$$E_{\text{pot}}(\underline{r}) = E_{\text{SCE}} + \frac{1}{2}\sum_{\mu,\nu=1}^{3N} M_{\mu\nu}(\mathbf{s})(r_\mu - f_\mu(\mathbf{s}))(r_\nu - f_\nu(\mathbf{s})) + ... \tag{25}$$

Since $E_{\text{pot}}(\underline{r})$ is minimum at $\underline{r} = \underline{f}(\mathbf{s})$, there are no first-order terms. [The dots represent the terms of third and higher orders.] For any given $\mathbf{s} \in \mathbb{R}^3$, the Hessian matrix $M_{\mu\nu}(\mathbf{s})$ in the second-order term has $3N$ non-negative eigenvalues $\omega_\mu(\mathbf{s})^2$ which can be labeled such that

$$\omega_\mu(\mathbf{s})^2 = 0 \ (\mu = 1, 2, 3)$$
$$\omega_\mu(\mathbf{s})^2 > 0 \ (\mu = 4, ..., 3N) \tag{26}$$

The corresponding $3N$-D normalized eigenvectors $\underline{e}^\mu(\mathbf{s})$, with components $e_\sigma^\mu(\mathbf{s})$ ($\sigma = 1,..., 3N$), are pairwise orthogonal

$$\underline{e}^\mu(\mathbf{s}) \cdot \underline{e}^\nu(\mathbf{s}) \equiv \sum_{\sigma=1}^{3N} e_\sigma^\mu(\mathbf{s})e_\sigma^\nu(\mathbf{s}) = \delta_{\mu\nu} \tag{27}$$

The first three eigenvectors, with zero eigenvalues, lie in the space "tangential" to Ω_0, and the remaining $3N - 3$ eigenvectors are "orthogonal" to Ω_0

$$\underline{e}^\mu(\mathbf{s}) \cdot \frac{\partial \underline{f}(\mathbf{s})}{\partial s_\alpha} = 0 \quad (\mu = 4, ..., 3N, \quad \alpha = 1, 2, 3) \tag{28}$$

where $\alpha = 1, 2, 3$ denotes the three Cartesian components (x, y, z) of $\mathbf{s}$.

4. Local Normal Modes

For sufficiently small $\varepsilon > 0$, we use these eigenvectors to introduce a set of $3N$ curvilinear coordinates in Ω_ε. A given point $\underline{r} = (r_{11}, r_{12}, r_{13},..., r_{N1}, r_{N2}, r_{N3}) \in \Omega_\varepsilon$ is written in terms of these local curvilinear coordinates as follows. The first three curvilinear coordinates are the Cartesian coordinates s_1, s_2, s_3 of the minimizing vector $\mathbf{s}$ in eq (24), fixed by the condition that the $3N$-D vector $\underline{r} - \underline{f}(\mathbf{s})$ in Ω is orthogonal to Ω_0 in the point $\underline{f}(\mathbf{s})$

$$(\underline{r} - \underline{f}(\mathbf{s})) \cdot \frac{\partial \underline{f}(\mathbf{s})}{\partial s_\alpha} = 0 \quad (\alpha = 1, 2, 3) \tag{29}$$

The remaining $3N - 3$ coordinates are the projections $q_4,..., q_{3N}$ of $\underline{r} - \underline{f}(\mathbf{s})$ onto the local eigenvectors $\underline{e}^4(\mathbf{s}),..., \underline{e}^{3N}(\mathbf{s})$

$$\underline{r} - \underline{f}(\mathbf{s}) = \sum_{\mu=4}^{3N} q_\mu \underline{e}^\mu(\mathbf{s}) \tag{30}$$

The first three eigenvectors $\underline{e}^{1,2,3}(\mathbf{s})$ are not needed, since they are tangential to Ω_0 at the point $\underline{f}(\mathbf{s})$ and therefore orthogonal to $\underline{r} - \underline{f}(\mathbf{s})$. Inverting eq (30) yields

$$q_\mu = \underline{e}^\mu \cdot (\underline{r} - \underline{f}(\mathbf{s})) \ (\mu = 4, ..., 3N) \tag{31}$$

For these new curvilinear coordinates, we also write

$$(s_1, s_2, s_3, q_4, ..., q_{3N}) = (\mathbf{s}, \underline{q}) \tag{32}$$

Notice that $\underline{r}$ has $3N$ components, while $\underline{q}$ has only $3N - 3$ ones. In this notation, eq (30) reads

$$r_\nu = f_\nu(\mathbf{s}) + \sum_{\mu=4}^{3N} e_\nu^\mu(\mathbf{s})q_\mu \ (\nu = 1, ..., 3N) \tag{33}$$

This is the transformation formula between the Cartesian coordinates $\underline{r}$ and the "local normal modes" $(\mathbf{s}, \underline{q})$ in the $3N$-D configuration space Ω.

In terms of the q_μ, the second-order contribution in the Taylor expansion (25) becomes diagonal

$$\tilde{E}_{\text{pot}}(\mathbf{s}, \underline{q}) = E_{\text{SCE}} + \frac{1}{2}\sum_{\mu=4}^{3N} \omega_\mu(\mathbf{s})^2 q_\mu^2 +$$
$$\frac{1}{3!}\sum_{\mu,\nu,\sigma=4}^{3N} E_{\mu\nu\sigma}^{(3)}(\mathbf{s})q_\mu q_\nu q_\sigma + ... \tag{34}$$

Here, the third-order term is derived from the corresponding term in eq (25) (in the present notation)

$$\frac{1}{3!}\sum_{\xi,\eta,\zeta=1}^{3N} \frac{\partial^3 E_{\text{pot}}(\underline{r})}{\partial r_\xi \partial r_\eta \partial r_\zeta}\bigg|_{\underline{r}=\underline{f}(\mathbf{s})} (r_\xi - f_\xi(\mathbf{s}))(r_\eta - f_\eta(\mathbf{s}))(r_\zeta - f_\zeta(\mathbf{s})) \tag{35}$$

Using here eq (33) for $r_\nu - f_\nu(\mathbf{s})$, we find

$$E_{\mu\nu\sigma}^{(3)}(\mathbf{s}) = \sum_{\xi,\eta,\zeta=1}^{3N} \frac{\partial^3 E_{\text{pot}}(\underline{r})}{\partial r_\xi \partial r_\eta \partial r_\zeta}\bigg|_{\underline{r}=\underline{f}(\mathbf{s})} e_\xi^\mu(\mathbf{s})e_\eta^\nu(\mathbf{s})e_\zeta^\sigma(\mathbf{s}) \tag{36}$$

Substituting eq (33) for $\underline{r}$ in the wave function $\Psi_\lambda(\underline{r})$ that represents the state $\Psi_\lambda[\rho]$ yields the transformed wave function $\tilde{\Psi}_\lambda(\mathbf{s}, \underline{q})$. While the original wave function obeys

$$\int d^3 r_1... \int d^3 r_N |\Psi_\lambda(\underline{r})|^2 \equiv \int d\underline{r}|\Psi_\lambda(\underline{r})|^2 = 1 \tag{37}$$

the transformed one is normalized according to

$$\int d^3 s \int d\underline{q} J(\mathbf{s}, \underline{q})|\tilde{\Psi}_\lambda(\mathbf{s}, \underline{q})|^2 = 1 \tag{38}$$

where $J(\mathbf{s}, \underline{q})$ is the Jacobian associated with the coordinate transformation (33), see eq (101) in Appendix A.

For sufficiently large $\lambda \gg 1$, the wave function $\Psi_\lambda(\mathbf{s}, \underline{q})$ strongly suppresses all configurations $\underline{r} \in \Omega$ except for the ones inside the narrow envelope Ω_ε of the 3D subset Ω_0. This means that $\tilde{\Psi}_\lambda(\mathbf{s}, \underline{q})$ is essentially different from zero only for $(q_4^2 +... + q_{3N}^2)^{1/2} < \varepsilon$, where ε decreases with growing $\lambda \gg 1$ and goes to zero in the limit $\lambda \to \infty$.

More precisely, since the quadratic term in eq (34) is multiplied by λ in the Hamiltonian (10), the scale of the quantum fluctuation is $\varepsilon \sim \lambda^{-1/4} \equiv \alpha$ for $\lambda \to \infty$. Therefore, it will be useful to switch for a given value of $\lambda \gg 1$ from the present curvilinear coordinates $(\mathbf{s}, \underline{q})$ to scaled coordinates $(\mathbf{s}, \underline{u})$ where

$$\underline{u} = \lambda^{1/4}\underline{q} \leftrightarrow \underline{q} = \alpha\underline{u} \ (\alpha = \lambda^{-1/4}) \tag{39}$$

This second transformation yields the wave function

$$\Psi_\alpha(\mathbf{s}, \underline{u}) = \tilde{\Psi}_\lambda(\mathbf{s}, \alpha\underline{u}) \tag{40}$$

According to eq (38), we now have

$$\int d^3 s \int d\underline{u} K_\alpha(\mathbf{s}, \underline{u})|\Psi_\alpha(\mathbf{s}, \underline{u})|^2 = 1 \tag{41}$$

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with the scaled Jacobian

$$K_\alpha(\mathbf{s}, \underline{u}) = \alpha^{3N-3} J(\mathbf{s}, \alpha \underline{u}) \tag{42}$$

Later on, we shall make use of the expansion

$$J(\mathbf{s}, \underline{q}) = J(\mathbf{s}, \underline{0}) + \sum_{\mu=4}^{3N} J_\mu^{(1)}(\mathbf{s}) q_\mu + O(q_\nu^2) \tag{43}$$

whose derivation is reported in Appendix A.

5. Expansion of the Hamiltonian

To obtain an expansion for large $\lambda \gg 1$ (or, equivalently, for small $\alpha \equiv \lambda^{-1/4} \ll 1$), we must express the Hamiltonian $\hat{H}_\lambda[\rho]$ of eq (10) in terms of the scaled coordinates $(\mathbf{s}, \underline{u})$. To this end, we split $\hat{H}_\lambda[\rho]$ into three pieces

$$\hat{H}_\lambda[\rho] = \hat{T} + \lambda E_{\text{pot}}(\underline{r}) + (\hat{V}_{\text{ext}}^\lambda - \lambda \hat{V}_{\text{SCE}}) \tag{44}$$

and treat these separately now.

5.1. Kinetic Energy (First Term). For the kinetic-energy operator $\hat{T}$, the 3N-D Laplacian is obtained in Appendix A in terms of the curvilinear coordinates q_μ from the general transformation rule

$$\sum_{i=1}^{3} \nabla_i^2 \equiv \sum_{\mu=1}^{3N} \frac{\partial^2}{\partial r_\mu^2} = \sum_{\mu,\nu=1}^{3N} \frac{1}{\sqrt{G}} \frac{\partial}{\partial q_\mu} \left(\sqrt{G} G^{\mu\nu} \frac{\partial}{\partial q_\nu} \right) \tag{45}$$

(To simplify the notation, we write $s_\mu \equiv q_\mu$ for $\mu = 1, 2, 3$ in this subsection.) Here, the matrix $G^{\mu\nu}$ is the inverse of the metric tensor $G_{\mu\nu}$, defined by

$$G_{\mu\nu} = \sum_{\xi=1}^{3N} \frac{\partial r_\xi}{\partial q_\mu} \frac{\partial r_\xi}{\partial q_\nu} \equiv \frac{\partial \underline{r}}{\partial q_\mu} \cdot \frac{\partial \underline{r}}{\partial q_\nu} \tag{46}$$

and G is its determinant, $G = \det(G_{\mu\nu})$. Switching in a second step from the q_μ to the scaled coordinates u_μ yields the expansion (see Appendix A)

$$\hat{T} = \sqrt{\lambda}[\hat{T}^{(0)} + \alpha \hat{T}^{(1)} + \alpha^2 \hat{T}^{(2)} + O(\alpha^3)] \tag{47}$$

The operators $\hat{T}^{(n)}$ are independent of λ (or $\alpha \equiv \lambda^{-1/4}$)

$$\hat{T}^{(0)} = \frac{-1}{2} \sum_{\mu=4}^{3N} \frac{\partial^2}{\partial u_\mu^2} \tag{48}$$

$$\hat{T}^{(1)} = \frac{-1}{2} \sum_{\mu=4}^{3N} X_\mu(\mathbf{s}) \frac{\partial}{\partial u_\mu} \tag{49}$$

where $X_\mu(\mathbf{s})$ is reported in Appendix A. Notice that the α^2 term is constant, since $\alpha^2 \sqrt{\lambda} = 1$.

5.2. SCE Potential Energy (Second Term). For the second term in eq (44), we use the Taylor expansion (34), with $q_\mu = \alpha u_\mu$, to find

$$\lambda E_{\text{pot}}(\underline{r}) = \lambda \left[E_{\text{SCE}} + \frac{\alpha^2}{2} \sum_{\mu=4}^{3N} \omega_\mu(\mathbf{s})^2 u_\mu^2 + \right.$$
$$\frac{\alpha^3}{3!} \sum_{\mu,\nu,\sigma=4}^{3N} E_{\mu\nu\sigma}^{(3)}(\mathbf{s}) u_\mu u_\nu u_\sigma +$$
$$\left. \frac{\alpha^4}{4!} \sum_{\mu,\nu,\sigma,\tau=4}^{3N} E_{\mu\nu\sigma\tau}^{(4)}(\mathbf{s}) u_\mu u_\nu u_\sigma u_\tau + O(\alpha^5) \right] \tag{50}$$

5.3. The Remaining External Potential (Third Term). For the last term in eq (44), we make an ansatz that will later on turn out to be consistent

$$\hat{V}_{\text{ext}}^\lambda - \lambda \hat{V}_{\text{SCE}} = \sqrt{\lambda} \sum_{n=0}^{\infty} \alpha^n V^{(n)}(\underline{r}) \tag{51}$$

Using eq (30) for $\underline{r}$ and $q_\mu = \alpha u_\mu$, we may expand

$$V^{(n)}(\underline{r}) \equiv V^{(n)}(\underline{f}(\mathbf{s}) + \alpha \sum_{\mu=4}^{3N} \underline{e}^\mu(\mathbf{s}) u_\mu)$$

$$= V^{(n)}(\underline{f}(\mathbf{s})) + \alpha \sum_{\sigma=1}^{3N} V_\sigma^{(n)}(\underline{f}(\mathbf{s})) \sum_{\mu=4}^{3N} e_\sigma^\mu(\mathbf{s}) u_\mu +$$
$$+ \frac{\alpha^2}{2} \sum_{\sigma,\tau=1}^{3N} V_{\sigma\tau}^{(n)}(\underline{f}(\mathbf{s})) \sum_{\mu,\nu=4}^{3N} e_\sigma^\mu(\mathbf{s}) e_\tau^\nu(\mathbf{s}) u_\mu u_\nu +$$
$$+ O(\alpha^3) \tag{52}$$

Here, the coefficients $V_\sigma^{(n)}$, $V_{\sigma\tau}^{(n)}$, etc. denote the partial derivatives of $V^{(n)}(\underline{r})$ at $\underline{r} = \underline{f}(\mathbf{s})$

$$V_{\sigma\tau}^{(n)}(\underline{f}(\mathbf{s})) = \frac{\partial^2 V^{(n)}(\underline{r})}{\partial r_\sigma \partial r_\tau} \bigg|_{\underline{r} = \underline{f}(\mathbf{s})} \quad \text{etc.} \tag{53}$$

Now, eq (51) yields the expansion

$$\hat{V}_{\text{ext}}^\lambda - \lambda \hat{V}_{\text{SCE}} = \sqrt{\lambda}[\hat{V}^{(0)} + \alpha \hat{V}^{(1)} + \alpha^2 \hat{V}^{(2)} + O(\alpha^3)] \tag{54}$$

with α-independent (multiplicative) operators

$$\hat{V}^{(0)} = V^{(0)}(\underline{f}(\mathbf{s})) \tag{55}$$

$$\hat{V}^{(1)} = V^{(1)}(\underline{f}(\mathbf{s})) + \sum_{\sigma=1}^{3N} V_\sigma^{(0)}(\underline{f}(\mathbf{s})) \sum_{\mu=4}^{3N} e_\sigma^\mu(\mathbf{s}) u_\mu \tag{56}$$

$$V^{(2)} = V^{(2)}(\underline{f}(\mathbf{s})) + \sum_{\sigma=1}^{3N} V_\sigma^{(1)}(\underline{f}(\mathbf{s})) \sum_{\mu=4}^{3N} e_\sigma^\mu(\mathbf{s}) u_\mu +$$
$$+ \frac{1}{2} \sum_{\sigma,\tau=1}^{3N} V_{\sigma\tau}^{(0)}(\underline{f}(\mathbf{s})) \sum_{\mu,\nu=4}^{3N} e_\sigma^\mu(\mathbf{s}) e_\tau^\nu(\mathbf{s}) u_\mu u_\nu \tag{57}$$

5.4. Full Hamiltonian. Eventually, combining eqs (47), (50), and (54), we obtain the expansion (recall that $\alpha = \lambda^{-1/4}$)

$$\hat{H}_\lambda[\rho] = \lambda E_{\text{SCE}} + \sqrt{\lambda}[\hat{H}^{(0)} + \alpha \hat{H}^{(1)} + \alpha^2 \hat{H}^{(2)} + O(\alpha^3)] \tag{58}$$

with α-independent operators $\hat{H}^{(n)}$. The first two terms read

$$\hat{H}^{(0)} = -\frac{1}{2}\sum_{\mu=4}^{3N}\frac{\partial^2}{\partial u_\mu^2} + V^{(0)}(\underline{f}(\mathbf{s})) + \frac{1}{2}\sum_{\mu=4}^{3N}\omega_\mu(\mathbf{s})^2 u_\mu^2 \quad (59)$$

$$\hat{H}^{(1)} = -\frac{1}{2}\sum_{\mu=4}^{3N}X_\mu(\mathbf{s})\frac{\partial}{\partial u_\mu} + V^{(1)}(\underline{f}(\mathbf{s})) +$$

$$+ \sum_{\sigma=1}^{3N}V_\sigma^{(0)}(\underline{f}(\mathbf{s}))\sum_{\mu=4}^{3N}e_\sigma^\mu(\mathbf{s})u_\mu +$$

$$+ \frac{1}{3!}\sum_{\mu,\nu,\sigma=4}^{3N}E_{\mu\nu\sigma}^{(3)}(\mathbf{s})u_\mu u_\nu u_\sigma \quad (60)$$

6. Expansion of the Ground State

Due to eq (58), the lowest eigenvalue $E_\lambda[\rho]$ of $\hat{H}_\lambda[\rho]$ (i. e., its ground-state energy) has the expansion

$$E_\lambda[\rho] = \lambda E_{SCE} + \sqrt{\lambda}[E^{(0)} + \alpha E^{(1)} + \alpha^2 E^{(2)} + O(\alpha^3)] \quad (61)$$

We define $E_\alpha'[\rho] = E^{(0)} + \alpha E^{(1)} + \alpha^2 E^{(2)} + O(\alpha^3)$ as the lowest eigenvalue of the operator

$$\hat{H}_\alpha'[\rho] = \hat{H}^{(0)} + \alpha\hat{H}^{(1)} + \alpha^2\hat{H}^{(2)} + O(\alpha^3) \quad (62)$$

Since E_{SCE} is a constant, $\hat{H}_\lambda[\rho]$ and $\hat{H}_\alpha'[\rho]$, with $\alpha = \lambda^{-1/4}$, have the same ground state

$$\overline{\Psi}_\alpha(\mathbf{s},\underline{u}) = \frac{\Psi^{(0)} + \alpha\Psi^{(1)} + \alpha^2\Psi^{(2)} + O(\alpha^3)}{\sqrt{\mathcal{N}_\alpha}} \quad (63)$$

For the α-dependent normalization constant

$$\mathcal{N}_\alpha = \int d^3s \int d\underline{u}\, K_\alpha(\mathbf{s},\underline{u})|\Psi^{(0)}(\mathbf{s},\underline{u}) + O(\alpha)|^2 \quad (64)$$

we obtain

$$\mathcal{N}_\alpha = \alpha^{3N-3}[1 + O(\alpha)] \quad (65)$$

when $\Psi^{(0)}$ is normalized according to

$$\int d^3s \int d\underline{u}\, J(\mathbf{s},\underline{0})|\Psi^{(0)}(\mathbf{s},\underline{u})|^2 = 1 \quad (66)$$

Collecting terms of equal orders $O(\alpha^n)$ in the eigenvalue equation $\hat{H}_\alpha'[\rho]\overline{\Psi}_\alpha = E_\alpha'[\rho]\overline{\Psi}_\alpha$ yields a hierarchy of equations. The leading one is $\hat{H}^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)}$, where $\hat{H}^{(0)}$ is given by eq (59). For a given fixed $\mathbf{s} \in \mathbb{R}^3$, the Hamiltonian $\hat{H}^{(0)}$ describes an uncoupled set of $3N - 3$ harmonic oscillators in 1D. To be more precise, these oscillators are coupled via the dynamical variable $\mathbf{s}$, but the dynamics of $\mathbf{s}$ is much slower, only appearing at orders $O(\lambda^0)$. Consequently, the leading term in the wave function factorizes into a product of Gaussians $\Phi_\omega(u) = (\omega/\pi)^{1/4}e^{-\omega u^2/2}$, with $\int_{-\infty}^\infty du|\Phi_\omega(u)|^2 = 1$

$$\Psi^{(0)}(\mathbf{s},\underline{u}) = C^{(0)}(\mathbf{s})\prod_{\mu=4}^{3N}\Phi_{\omega_\mu(\mathbf{s})}(u_\mu) \quad (67)$$

Since $V^{(0)}(\underline{f}(\mathbf{s}))$ is a pure multiplicative operator, the resulting eigenvalue of $\hat{H}^{(0)}$ is, for a given $\mathbf{s}$

$$E^{(0)}(\mathbf{s}) = V^{(0)}(\underline{f}(\mathbf{s})) + \sum_{\mu=4}^{3N}\frac{\omega_\mu(\mathbf{s})}{2} \quad (68)$$

Due to eq (61), this expression cannot depend on the variable $\mathbf{s}$, implying a condition on the $n = 0$ coefficient $V^{(0)}(\underline{r})$ in our ansatz (51)

$$V^{(0)}(\underline{f}(\mathbf{s})) = -\sum_{\mu=4}^{3N}\frac{\omega_\mu(\mathbf{s})}{2} + \text{const} \quad \forall\mathbf{s}\in\mathbb{R}^3 \quad (69)$$

The role of the external potential at the order $\sqrt{\lambda}$ in eq (10) is thus to keep the degeneracy of the SCE minimum (found at the order λ) through the order $\sqrt{\lambda}$. This is necessary in order to keep the given smooth density $\rho(\mathbf{r})$: if one of the SCE configurations (i.e., a given particular $\mathbf{s}_0$) had a lower energy than the others, the SCE wave function would collapse in that particular $\mathbf{s}_0$, and the density would become a sum of delta peaks centered in $\mathbf{f}_i(\mathbf{s}_0)$ (with $i = 1,..., N$).

The degeneracy with respect to $\mathbf{s}$ allows us to weight each configuration with the density $\rho(\mathbf{s})$ and to write

$$E^{(0)} = \int d^3s\frac{\rho(\mathbf{s})}{N}\left[V^{(0)}(\underline{f}(\mathbf{s})) + \sum_{\mu=4}^{3N}\frac{\omega_\mu(\mathbf{s})}{2}\right] \quad (70)$$

This expression for $E^{(0)}$ is consistent with the wave function of eq (67), as we we will now discuss. In order to determine the prefactor $C^{(0)}(\mathbf{s})$ of the wave function we observe that in the wave function $\tilde{\Psi}_\lambda(\mathbf{s}, \underline{q})$, the coordinate $\mathbf{s} \in \mathbb{R}^3$ has the probability distribution

$$\rho_\lambda(\mathbf{s}) = \int d\underline{q}\, J(\mathbf{s},\underline{q})|\tilde{\Psi}_\lambda(\mathbf{s},\underline{q})|^2$$

$$= \int d\underline{q}\, J(\mathbf{s},\underline{q})|\overline{\Psi}_\alpha(\mathbf{s},\lambda^{1/4}\underline{q})|^2 \quad (71)$$

where $\alpha = \lambda^{-1/4}$. Using eqs (63) and (65), we find

$$\rho_\lambda(\mathbf{s}) = \int d\underline{q}\, J(\mathbf{s},\underline{q})\frac{|\Psi^{(0)}(\mathbf{s},\lambda^{1/4}\underline{q})|^2}{\alpha^{3N-3}}[1 + O(\alpha)] \quad (72)$$

In the limit $\lambda\rightarrow\infty$ when $\rho_\lambda(\mathbf{s})$ must become rigorously proportional to the electron density $\rho(\mathbf{s})$

$$\lim_{\lambda\rightarrow\infty}\rho_\lambda(\mathbf{s}) = \frac{\rho(\mathbf{s})}{N} \quad (73)$$

the terms $O(\alpha)$ in eq (72) can be dropped and eq (67) yields

$$\frac{\rho(\mathbf{s})}{N} = \lim_{\lambda\rightarrow\infty}|C^{(0)}(\mathbf{s})|^2\int d\underline{q}\, J(\mathbf{s},q)\times$$

$$\prod_{\mu=4}^{3N}\lambda^{1/4}|\Phi_{\varpi\mu(\mathbf{s})}(\lambda^{1/4}q_\mu)|^2 \quad (74)$$

Since $\Phi_\omega(u)$ is a normalized Gaussian, the μ-th factor of the product in eq (74) approaches the δ-function $\delta(q_\mu)$ as $\lambda\rightarrow\infty$. Therefore, the right-hand side of eq (74) equals $|C^{(0)}(\mathbf{s})|^2 J(\mathbf{s}, \underline{0})$, implying the result

$$|C^{(0)}(\mathbf{s})|^2 = \frac{1}{N}\frac{\rho(\mathbf{s})}{J(\mathbf{s},\underline{0})} \quad (75)$$

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Notice that the uncoupled oscillator wave function of eq (67) has the correct density to the order $\lambda^{-1/2}$ targeted here. Corrections to the density (and the coupling between the oscillators) enter $W_\lambda[\rho]$ at higher orders.

The next order in the perturbative treatment of the ground-state energy of eq (62) leads to

$$E^{(1)} = \langle \Psi^{(0)} | \hat{H}^{(1)} | \Psi^{(0)} \rangle = V^{(1)}(\underline{f}(\mathbf{s})) \quad (76)$$

The same argument used for eq (69) yields

$$V^{(1)}(\underline{f}(\mathbf{s})) = \text{const.} \quad (77)$$

independent of $\mathbf{s}$. The important point here is that the terms coming from $\hat{T}$ and $\hat{V}_{ee}$ in the Hamiltonian $\hat{H}^{(1)}$ of eq (60) have zero expectation on the ground-state of the harmonic oscillator, so that there is no contribution to this order to the large-λ expansion of $W_\lambda[\rho]$. As we shall see in the next section 7, the order $\sqrt{\lambda}\alpha = \lambda^{1/4}$ in $E_\lambda[\rho]$ of eq (61) corresponds to the order $\lambda^{-3/4}$ in the large-λ expansion of $W_\lambda[\rho]$.

Notice that, in our treatment of the strong-interaction limit of DFT, we did not consider the effect on the energy of the spin state or, more generally, of the statistics. This is because the electrons are always localized in different regions of space well separated from each other. The effect on the energy of the spin state or of statistics in the $\lambda \to \infty$ limit can be estimated as being of the order $O(e^{-\lambda^{1/4}})$, which is the order of magnitude of the overlap between two different gaussians of eq (67).

7. The Functional $W'_\infty[\rho]$

From the expansion of $E_\lambda[\rho]$ of the previous section 6, we can easily compute $W_\lambda[\rho]$ using the Hellmann−Feynmann theorem

$$W_\lambda[\rho] + U[\rho] = \frac{\partial E_\lambda[\rho]}{\partial \lambda} - \int \rho(\mathbf{r}) \frac{\partial v^\lambda_{\text{ext}}(\mathbf{r})}{\partial \lambda} d^3r \quad (78)$$

From section 6, we obtain, in the $\lambda \to \infty$ limit

$$E_\lambda[\rho] - \int \rho(\mathbf{r}) v^\lambda_{\text{ext}}(\mathbf{r}) d^3r = \lambda \langle \Psi_{\text{SCE}} | \hat{V}_{ee} | \Psi_{\text{SCE}} \rangle +$$
$$+ \sqrt{\lambda} \int d^3s \frac{\rho(\mathbf{s})}{N} \sum_{\mu=4}^{3N} \frac{\omega_\mu(\mathbf{s})}{2} + O(\lambda^0) \quad (79)$$

By differentiating both sides with respect to λ, from eq (78) we obtain the expansion for $W_\lambda[\rho]$ of eq (13) with

$$W_\infty[\rho] = \int d^3s \frac{\rho(\mathbf{s})}{N} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{f}_i(\mathbf{s}) - \mathbf{f}_j(\mathbf{s})|} - U[\rho] \quad (80)$$

in agreement with the results of ref 33, and the exact expression for the next leading term

$$W'_\infty[\rho] = \frac{1}{2} \int d^3s \frac{\rho(\mathbf{s})}{N} \sum_{\mu=4}^{3N} \frac{\omega_\mu(\mathbf{s})}{2} \quad (81)$$

This result generalizes (and proves) eq (35) of ref 30 for spherical two-electron densities. As shown by eq (76), there is no $\lambda^{-3/4}$ term in $W_{\lambda \to \infty}[\rho]$. There is also no term $\propto \lambda^{-1}$,

Table 1. Comparison of the Values $W'_\infty[\rho]$ in Hartree Atomic Units Obtained with the SCE Construction and with the PC Model[32a]

	SCE (H)	PC (H)	error (mH)
He	0.62084	0.729	108
Li	1.38	1.622	240
Be	2.59	2.928	334
B	4.2	4.702	502
C	6.3	7.089	840
Ne	22	24.423	2423

[a] The absolute errors of the PC model are also reported.

which would imply a term $\propto \log(\lambda)$ in $E_\lambda[\rho]$ and thus in the kinetic energy $\langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle$. Such a term would violate the known high-density scaling of $\langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle$[35] (see also the erratum).[36]

As an example of application, we have computed $W'_\infty[\rho]$ for the same set of spherical (or sphericalized) atomic densities used in ref 33 to evaluate $W_\infty[\rho]$. For each point $(\mathbf{f}_1(\mathbf{s}),...,\mathbf{f}_N(\mathbf{s}))$ on the degenerate SCE minimum constructed in ref 33, we have evaluated the Hessian matrix, the corresponding eigenvalues $\omega^2_\mu(\mathbf{s})$, and thus $W'_\infty[\rho]$ of eq (81). In Table 1 we compare our results with the approximate PC functional[32]

$$W''^{PC}_\infty[\rho] = \int d^3r \left[C\rho(\mathbf{r})^{3/2} + D\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{7/6}} \right] \quad (82)$$

where $C = 1.535$ and $D = -0.02558$.

As explained in ref 33, the SCE minimum for spherical densities is constructed from a set of radial comotion functions and the angular minimization is done numerically. When one of the electrons is close to the nucleus, the numerical minimization displays instabilities in the smallest (but nonzero) eigenvalues of the Hessian. However, as shown by eq 81, such configurations are weighted by the density (in the spherically symmetric case by $4\pi s^2\rho(s)$) so that the error they introduce is relatively small. This error, however, increases with the number of electrons. The number of digits in our results of Table 1 is determined by this numerical error. Notice, however, that Table 1 shows that the discrepancy of the PC model with respect to our results is much larger than our estimated numerical errors on the SCE values.

While the PC model for the coefficient $W_\infty[\rho]$ makes errors of the order of 60 mH,[33] we see from Table 1 that the functional $W'_\infty[\rho]$ is much more seriously overestimated. We can reduce these errors by recalling that in the PC model for $W'_\infty[\rho]$ the coefficient D of eq (82) was fixed by the condition that the PC value for the He atom be equal to the one obtained from the MGGA functional of ref 10. Now that we have exact values, it seems natural to change D in order to make the PC model equal to the SCE result for the He atom. This gives $D = -0.028957$. The values for the other atoms obtained with the revised PC model are reported in Table 2: we see that the error is now substantially reduced.

8. Revised ISI

In refs 22 and 32 an expression for $W_\lambda[\rho]$ that interpolates between the two limits of eqs (12) and (13) has been

Table 2. Comparison of the Values $W'_\infty[\rho]$ in Hartree Atomic Units Obtained with the SCE Construction and with the Revised PC Model of Section 7[a]

	SCE (H)	revPC (H)	error (mH)
Li	1.38	1.4066	26
Be	2.59	2.579	11
B	4.2	4.207	7
C	6.3	6.43	130
Ne	22	22.96	960

[a] The absolute errors of the revised PC model are also reported.

proposed and tested using the PC approximation for the functionals $W_\infty[\rho]$ and $W'_\infty[\rho]$. The interaction-strength interpolation (ISI) formula for $W_\lambda[\rho]$ of refs 22 and 32, however, contains a spurious term $\propto \lambda^{-1}$ in its $\lambda \to \infty$ expansion,[32] which, as explained after eq (81), has the wrong scaling behavior in the high-density limit. Here we propose a revised ISI functional which does not have this problem.

Instead of modeling $W_\lambda[\rho]$, we use the same ISI interpolation formula of ref 22 directly for the integral $E^\lambda_{xc}[\rho]$

$$E^\lambda_{xc}[\rho] = \int_0^\lambda d\lambda' W_{\lambda'}[\rho] \qquad (83)$$

satisfying the exact $\lambda \to 0$ and $\lambda \to \infty$ asymptotic behaviors

$$E^{\lambda,\mathrm{revISI}}_{xc}[\rho] = a[\rho]\lambda + \frac{b[\rho]\lambda}{\sqrt{1 + c[\rho]\lambda} + d[\rho]} \qquad (84)$$

The four functionals $a[\rho]$, $b[\rho]$, $c[\rho]$, and $d[\rho]$ are determined by imposing the $\lambda \to 0$ expansion of eq (12) and the $\lambda \to \infty$ expansion of eq (13), and they are thus determined by the two weak-interaction limit functionals $E_x[\rho]$ and $E^{GL2}_c[\rho]$ and the two strong-interaction limit functionals $W_\infty[\rho]$ and $W'_\infty[\rho]$

$$a[\rho] = W_\infty[\rho] \qquad (85)$$

$$b[\rho] = -\frac{8E^{GL2}_c[\rho]W'_\infty[\rho]^2}{(E_x[\rho] - W_\infty[\rho])^2} \qquad (86)$$

$$c[\rho] = \frac{16E^{GL2}_c[\rho]^2 W'_\infty[\rho]^2}{(E_x[\rho] - W_\infty[\rho])^4} \qquad (87)$$

$$d[\rho] = -1 - \frac{8E^{GL2}_c[\rho]W'_\infty[\rho]^2}{(E_x[\rho] - W_\infty[\rho])^3} \qquad (88)$$

The final formula for the revised ISI functional is obtained by putting $\lambda = 1$ in eq (84)

$$E^{\mathrm{revISI}}_{xc}[\rho] = a[\rho] + \frac{b[\rho]}{\sqrt{1 + c[\rho]} + d[\rho]} \qquad (89)$$

For the correlation energy of the neutral atoms considered here, this revised ISI gives essentially the same results of the original ISI of ref 22. This is probably due to the fact that neutral atoms are much more similar to the $\lambda = 0$ wave function than to the infinitely strongly interacting system (for an illustration from the pair-density point of view, see ref 37). We can expect to observe more sensitivity on how the $\lambda \to \infty$ limit is treated when studying more correlated systems,

like stretched bonds or low-density quantum dots. Such studies will be the object of future work.

9. Conclusions and Perspectives

We have presented a systematic treatment of the strong-interaction limit of density functional theory up to the second leading term, describing zero-point oscillations of strictly correlated electrons. We have evaluated numerically this zero-point contribution for small atoms, and we have used our results to improve a previous approximate functional for this term. A new interpolation formula for the exchange-correlation energy, satisfying more exact constraints, has been proposed, and will be tested elsewhere.

Besides the possibility of constructing an interpolation formula for $E_{xc}[\rho]$, the two functionals $W_\infty[\rho]$ of ref 33 and $W'_\infty[\rho]$ evaluated in this work, are of valuable interest for the development of Kohn–Sham DFT. They are an example of exact implicit density functionals for systems in which the electron–electron repulsion largely dominates over the kinetic energy. They can be used to test properties of the exact exchange-correlation functional like the Lieb-Oxford bound[38,39] and to test how approximate functionals perform in this limit.[40,41]

Several issues still need to be addressed and will be the object of future work. The main problem of the ISI functional is the lack of size consistency. A possible remedy is to perform the interpolation of eq (84) locally, using energy densities all defined in the same gauge (this is, at least, the standard way in which approximate DFT addresses size consistency, even if it is not always a solution in the presence of degeneracy).[42,43] A first step in our future work, thus, will be the analysis of exact energy densities for the functionals $W_\infty[\rho]$ and $W_\infty'[\rho]$ (see also ref 37) and the construction of corresponding approximations. Another important problem is the development of a reliable algorithm to solve the SCE problem for a given nonspherical density. Other promising research lines are the study of the next leading term, which is of purely kinetic origin, and the construction of approximations to describe the effect of the spin state on the energy.

A. Transformation of the Laplacian

In order to write down the components of the metric tensor G_{ik} of our local curvilinear coordinate transformation, we define the indices as follows: $\alpha, \beta, \gamma, ...$ denote the Cartesian components $1, 2, 3 \equiv x, y, z$ of **s**, the indices $\mu, \nu, \sigma, \tau, ...$ denote the normal-mode components q_μ, and the Latin indices $i, k, ...$ denote general components, either $\alpha, ...$ or $\mu, ...$ We then have to distinguish three blocks in the metric tensor G_{ik}: $\alpha\beta$, $\mu\nu$, and $\alpha\mu$

$$G_{\beta\gamma} = g_{\beta\gamma}(\mathbf{s}) - 2 \sum_{\mu=4}^{3N} q_\mu \frac{\partial^2 \underline{f}(\mathbf{s})}{\partial s_\gamma \partial s_\beta} \cdot \underline{e}^\mu(\mathbf{s}) +$$

$$\sum_{\mu,\nu=4}^{3N} \frac{\partial \underline{e}^\mu(\mathbf{s})}{\partial s_\beta} \cdot \frac{\partial \underline{e}^\nu(\mathbf{s})}{\partial s_\gamma} q_\mu q_\nu \quad (90)$$

$$G_{\beta\nu} = \sum_{\mu=4}^{3N} q_\mu \frac{\partial \underline{e}^\mu(\mathbf{s})}{\partial s_\beta} \cdot \underline{e}^\nu(\mathbf{s}) \quad (91)$$

$$G_{\mu\nu} = \delta_{\mu\nu} \quad (92)$$

where in eq (90) we have defined the 3×3 metric tensor $g_{\alpha\beta}(\mathbf{s})$ which only concerns the coordinates s_1, s_2, and s_3

$$g_{\alpha\beta}(\mathbf{s}) = \frac{\partial \underline{f}(\mathbf{s})}{\partial s_\alpha} \cdot \frac{\partial \underline{f}(\mathbf{s})}{\partial s_\beta} \quad (93)$$

When $\lambda \to \infty$, our wave function is zero everywhere except very close to Ω_0, i.e., for very small $q_\mu \propto \lambda^{-1/4}$. Introducing the scaled coordinates $u_\mu = \lambda^{1/4} q_\mu$, we see that the metric tensor G_{ik} has the λ-dependence

$$G_{ik} = G_{ik}^{(0)} + \frac{1}{\lambda^{1/4}} \sum_{\mu=4}^{3N} u_\mu \Delta_{ik}^\mu + \frac{1}{\lambda^{1/2}} \sum_{\mu,\nu=4}^{3N} u_\mu u_\nu Z_{ik}^{\mu\nu} \quad (94)$$

where Δ^μ and $Z^{\mu\nu}$ are tensors of elements

$$\Delta_{\gamma\beta}^\mu = -2 \frac{\partial^2 \underline{f}(\mathbf{s})}{\partial s_\gamma \partial s_\beta} \cdot \underline{e}^\mu(\mathbf{s}) \quad (95)$$

$$\Delta_{\beta\nu}^\mu = \frac{\partial \underline{e}^\mu(\mathbf{s})}{\partial s_\beta} \cdot \underline{e}^\nu(\mathbf{s}) \quad (96)$$

$$\Delta_{\nu\tau}^\mu = 0 \quad (97)$$

and

$$Z_{\beta\gamma}^{\mu\nu} = \frac{\partial \underline{e}^\mu(\mathbf{s})}{\partial s_\beta} \cdot \frac{\partial \underline{e}^\nu(\mathbf{s})}{\partial s_\gamma} \quad (98)$$

$$Z_{\beta\tau}^{\mu\nu} = 0 \quad (99)$$

$$Z_{\tau\sigma}^{\mu\nu} = 0 \quad (100)$$

and $G_{ik}^{(0)}$ has elements $G_{\alpha\beta}^{(0)} = g_{\alpha\beta}$ and $G_{\mu\nu}^{(0)} = \delta_{\mu\nu}$ and all the off-diagonal components equal to zero. In order to compute the large-λ expansion of eq (45), we have to expand the

determinant G, and the components G^{ik} of the inverse metric tensor. Using standard formulas, we obtain

$$\sqrt{G} = \sqrt{g}\left(1 + \frac{1}{2\lambda^{1/4}} \sum_{\mu=4}^{3N} u_\mu \sum_{\alpha\beta} g^{\alpha\beta} \Delta_{\alpha\beta}^\mu\right) + O(\lambda^{-1/2}) \quad (101)$$

where g is the determinant of $g_{\alpha\beta}$, and $g^{\alpha\beta}$ are the components of its inverse. The tensor $\mathbf{G}^{-1}$ of components G^{ik} has the large-λ expansion, up to orders $\lambda^{-1/2}$

$$\mathbf{G}^{-1} = \mathbf{G}^{(0)-1} - \frac{1}{\lambda^{1/4}} \sum_{\mu=4}^{3N} u_\mu \mathbf{G}^{(0)-1} \Delta^\mu \mathbf{G}^{(0)-1} \quad (102)$$

Inserting these expansions into eq (45) we obtain eqs (48) and (49) with

$$X^\mu(\mathbf{s}) = \frac{1}{2} \sum_{\alpha\beta} g^{\alpha\beta}(\mathbf{s}) \Delta_{\alpha\beta}^\mu(\mathbf{s}) \quad (103)$$

Finally, the Jacobian of our change of coordinates is simply equal to $\sqrt{G}$ of eq (101).

B. Analytic Example

As an illustration, we consider a system of two electrons in 1D space (i.e., on the x-axis) with a given ground-state density $\rho(x)$

$$\int_{-\infty}^{\infty} dx \rho(x) = 2 \quad (104)$$

In this case, eq (17) reads $x_2 = f_2(x_1)$, with the single comotion function $f_2(s) \equiv f(s)$ which, according to ref 33, obeys the differential equation $\rho(f(s))f'(s) = \rho(s)$. For the Lorentzian density, $f(s)$ is found analytically

$$\rho(x) = \frac{2}{\pi} \frac{1}{1 + x^2} \Rightarrow f(s) = -\frac{1}{s} \quad (105)$$

In this case, the SCE external potential, fixed by the conditions $(d/dx)v_{\text{SCE}}(x) = \text{sgn}(x)|x - f(x)|^{-2}$ and $v_{\text{SCE}}(x) \to 0$ for $x \to \pm\infty$, is given by

$$v_{\text{SCE}}(x) = \left| \arctan(x) - \frac{x}{1 + x^2} \right| - \frac{\pi}{2} \quad (106)$$

In terms of $\underline{f}(s) \equiv (s, f(s))$, eq 20 now yields a 1D subset of $\Omega = \mathbb{R}^2$

$$\Omega_0 = \{\underline{f}(s) | s \in \mathbb{R}\} \subset \Omega \quad (107)$$

In the example (105), Ω_0 is given by the two branches of the hyperbola $x_2 = f(x_1) \equiv -1/x_1$ in the $x_1 x_2$-plane Ω. In the following, we focus on the branch Ω_0^+ with $x_1 > 0$ and $x_2 < 0$, $\Omega_0^+ = \{\underline{f}(s) | s \in \mathbb{R}^+\}$.

The asymptotic potential-energy function, cf. eq (19)

$$E_{\text{pot}}(\underline{x}) = \frac{1}{x_1 - x_2} + v_{\text{SCE}}(x_1) + v_{\text{SCE}}(x_2) \quad (108)$$

assumes its highly degenerate minimum for all $\underline{x} \in \Omega_0$. Consequently, the first partial derivatives

$$\frac{\partial E_{\text{pot}}(\underline{x})}{\partial x_1} = -\frac{1}{(x_1 - x_2)^2} + \frac{x_1^2}{(1 + x_1^2)^2}$$

$$\frac{\partial E_{\text{pot}}(\underline{x})}{\partial x_2} = +\frac{1}{(x_1 - x_2)^2} - \frac{x_2^2}{(1 + x_2^2)^2} \qquad (109)$$

are vanishing for $\underline{x} = \underline{f}(s)$ when the Hessian matrix of $E_{\text{pot}}(\underline{x})$ becomes

$$M(s) = \frac{2s}{(1 + s^2)^3}\begin{pmatrix} 1 & -s^2 \\ -s^2 & s^4 \end{pmatrix} \qquad (110)$$

It has the two eigenvalues

$$\omega_1(s)^2 = 0, \quad \omega_2(s)^2 = \frac{2s}{(1 + s^2)^3}(1 + s^4) > 0 \quad (111)$$

The corresponding normalized eigenvectors are

$$\underline{e}^1(s) = \frac{1}{\sqrt{1 + s^4}}\begin{pmatrix} s^2 \\ 1 \end{pmatrix}, \quad \underline{e}^2(s) = \frac{1}{\sqrt{1 + s^4}}\begin{pmatrix} 1 \\ -s^2 \end{pmatrix} \quad (112)$$

While $e^1(s)$ is tangential, $\underline{e}^2(s)$ is orthogonal to Ω_0^+ at $\underline{f}(s) \in \Omega_0^+$ and generally given by

$$\underline{e}^2(s) = \frac{1}{\sqrt{1 + f'(s)^2}}\begin{pmatrix} f'(s) \\ -1 \end{pmatrix} \equiv \underline{e}(s) \qquad (113)$$

For a point $\underline{x} = (x_1, x_2) \in \Omega_\varepsilon$, close to Ω_0^+, the curvilinear coordinates (s, q) are defined by eq (30)

$$\underline{x} = \underline{f}(s) + \underline{e}(s)q \qquad (114)$$

where s is fixed by the condition that the vector $\underline{e}(s)$ in the x_1x_2-plane is orthogonal to Ω_0^+ at $\underline{f}(s) \in \Omega_0^+$.

In terms of the partial derivatives of eq (114), the metric tensor is given by the (2×2)-matrix

$$(G_{\mu\nu}) = \begin{pmatrix} \frac{\partial \underline{x}}{\partial s} \cdot \frac{\partial \underline{x}}{\partial s} & \frac{\partial \underline{x}}{\partial s} \cdot \frac{\partial \underline{x}}{\partial q} \\ \frac{\partial \underline{x}}{\partial q} \cdot \frac{\partial \underline{x}}{\partial s} & \frac{\partial \underline{x}}{\partial q} \cdot \frac{\partial \underline{x}}{\partial q} \end{pmatrix} \qquad (115)$$

Using eqs (113) and (114), we obtain

$$\frac{\partial \underline{x}}{\partial s} = \underline{f}'(s) + q\underline{e}'(s)$$

$$= \begin{pmatrix} 1 \\ f'(s) \end{pmatrix}\left[1 + q\frac{f''(s)}{[1 + f'(s)^2]^{3/2}}\right]$$

$$\frac{\partial \underline{x}}{\partial q} = \underline{e}(s) \qquad (116)$$

and thus

$$(G_{\mu\nu}) = \begin{pmatrix} g(s, q) & 0 \\ 0 & 1 \end{pmatrix} \qquad (117)$$

where $g(s, q) = J(s, q)^2$, with the Jacobian

$$J(s, q) = \left[1 + q\frac{f''(s)}{[1 + f'(s)^2]^{3/2}}\right]\sqrt{1 + f'(s)^2} \qquad (118)$$

In the particular case of the density (105), we have

$$J(s, q) = \frac{\sqrt{1 + s^4}}{s^2} - q\frac{2s}{1 + s^4} \qquad (119)$$

and the coefficients of eq (13) are given by

$$W_\infty[\rho] + U[\rho] \equiv 2\int_0^\infty ds\frac{\rho(s)}{2}\frac{1}{s - f(s)} =$$

$$\frac{1}{\pi}\int_0^\infty \frac{ds2s}{(1 + s^2)^2} = \frac{1}{\pi} = 0.31831 \quad (120)$$

$$W_\infty'[\rho] \equiv 2\int_0^\infty ds\frac{\rho(s)}{2}\omega_2(s) =$$

$$\frac{2}{\pi}\int_0^\infty \frac{ds}{(1 + s^2)^2}\sqrt{2s\frac{1 + s^4}{1 + s^2}} = 0.633902 \quad (121)$$

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