On a Solution of the Self-Interaction Problem in Kohn-Sham Density Functional Theory

M. Däne,¹, ² A. Gonis,¹ D. M. Nicholson,³ and G. M. Stocks²

¹Physical and Life Sciences, Lawrence Livermore National Laboratory, PO Box 808, L-372, Livermore, CA 94551
²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
³Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

We report on a methodology for the treatment of the Coulomb energy and potential in Kohn-Sham density functional theory that is free from self-interaction effects. Specifically, we determine the Coulomb potential given as the functional derivative of the Coulomb energy with respect to the density, where the Coulomb energy is calculated explicitly in terms of the pair density of the Kohn-Sham orbitals. This is accomplished by taking advantage of an orthonormal and complete basis that is an explicit functional of the density that then allows for the functional differentiation of the pair density with respect to the density to be performed explicitly. This approach leads to a new formalism that provides an analytic, closed-form determination of the exchange potential. This method is applied to one-dimensional model systems and to the atoms Helium through Krypton based on an exchange only implementation. Comparison of our total energies (denoted SIF) to those obtained using the usual Hartree-Fock (HF) and optimized effective potential (OEP) methods reveals the hierarchy $E_{\text{HF}} \leq E_{\text{OEP}} \leq E_{\text{SIF}}$ that is indicative of the greater variation freedom implicit in the former two methods.

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I. INTRODUCTION

Modern calculations of the electronic structure of condensed matter rest on density functional theory (DFT), whose implementation is carried out within various forms based on the Kohn-Sham (KS) formulation of the theory.¹ While there is a vast body of work that attests to the utility of this approach, it has well documented failures in predicting electronic structure and related properties of materials where the effects of the Coulomb interaction are judged to be particularly strong. Such materials include, but are not limited to, 3$d$-transition metal oxides, 4$f$-electron rare earths and 5$f$-electron actinide systems. An important factor in this failure is the presence of the well-known unphysical self-interaction terms in the Hartree (classical) expression for the Coulomb energy as well as in the exchange and correlation energy functional. While there have been numerous attempts to correct for the presence of self-interaction, no fully satisfactory coherent scheme has yet emerged for a partial compendium of methods, see ²⁰.

Self-interaction was introduced into the theory through the original formulation of the so-called local density approximation (LDA) or local spin-density approximation (LSDA) including their gradient corrected versions (GGAs), in which the Coulomb energy of the interacting particles is expressed within the the Hartee approximation as that of a classical charge distribution, $n(r)$, with itself,

$$U_H = \frac{1}{2} \int \int \frac{n(r_1) n(r_2)}{|r_1 - r_2|} dr_1 dr_2,$$

and the exchange energy is taken from the homogeneous electron gas results. An advantage of the Hartree energy is its explicit dependence on the density that allows the functional differentiation with respect to the density and the determination of its contribution to the potential. Even though the problematic nature of the Hartree term was realized from the beginning, most of the currently used energy functionals are still based on it. The presence of self-interaction reduces not only the reliability and convincing power of results obtained in a local approximation, but also affects the formal standing of the theory as a whole.

Among the functional forms cited in some stand out as strong candidates for the development of a general theory for a self-interaction free formulation of KS-DFT. Prominent among these are the self-interaction correction (SIC) methods and the optimized effective potential (OEP) methods. The former corrects for self-interaction on an orbital by orbital basis, but cannot be shown to remove the SI error completely. The latter relies on the treatment of so-called orbital dependent functionals and attempts a functional differentiation of the Coulomb energy by means of a chain rule based on the $v$-representability of the density.

It is well known that self-interaction does not arise when the Coulomb energy is calculated in terms of the pair density, a quantity that in the KS formulation of DFT is determined through the Slater determinant of the KS orbitals. However, the dependence of the pair density on the density is only implicit. In one implementation of the OEP method, this implicit behavior is attacked through the chain rule of functional derivatives which, in turn, involves the calculation of the (inverse) susceptibility of the KS system. Alternative procedures, such as the parametrization of the potential have been formulated, where the coefficients are determined to minimize the energy.

In this paper we provide details of a new approach that is also based the pair density, thereby eliminating self-interaction effects by construction, that results in particularly simple closed form expressions for the functional derivatives. The new formalism relies on the use of mathematical procedure, first introduced by Mack and Harriman and further developed by Zumbach and Maschke, whereby a function,
e.g., the KS orbitals, that depend implicitly on the density, can be expanded in an orthonormal and complete basis of functions whose elements are expressed explicitly in terms of the density - the so called equidensity basis. As will be discussed in Section [III] by making the ansatz of only considering the explicit density dependence contained in the equidensity basis, the functional derivatives of the occupied KS orbitals can then be obtained through term by term differentiation of the expanded forms. In doing this we specifically neglect any possible implicit dependence of the expansion coefficients of the equidensity basis may have on the density - we will refer to this as the explicit equidensity basis (EEB) ansatz. The result of applying the EEB ansatz is that the final forms of the functional derivatives obtained are expressed analytically in terms of the gradients of the occupied orbitals, whose numerical evaluation is straightforward and simple to implement within existing DFT electronic structure codes. We refer to the new method as being self-interaction free (SIF) in order to emphasize the method’s primary attribute.

A short introduction of the method has been presented in previous work [25]. In the following pages, we provide complete details of the technical, i.e., algebraic, and computational, components of this method that show both the simplicity of the formalism as well as the power that derives from it. We demonstrate the characteristic features and efficacy of the new method by means of model one-dimensional calculations as well as calculations of the exchange potential and energies of the ground states of atomic systems from Helium to Krypton where it is possible to make detailed comparison with the results of calculations based on the well established OEP [27,13] and Hartree-Fock (HF) methodologies.

This is a rather long paper because of our intention of providing as complete and detailed an exposition of the method as possible. The paper takes the following form.

In Section [II], we provide a derivation of the KS equations identifying explicitly the terms corresponding to the correlation energy and potential, the exchange potential determined in a local approximation to the KS equations, and point out the difficulties associated with self-interaction. Subsection [II C] states the quantum mechanically correct form of the Coulomb energy to be used in the KS formalism. The equidensity basis, the formal and computational foundation of the methodology introduced here is set forth in Section [III]. The application of the formalism to model and realistic atomic system is presented in Section [IV]. Differences between the method provided in this paper and others are discussed in Section [V]. Section [VI] contains our conclusions.

In the interests of completeness, we also provide in the form of a set of extended appendices detailed derivations of key expressions resulting from our formulation that we used in calculating the results presented in the main part of the paper.

II. KOHN-SHAM EQUATIONS

In order to clarify the SIF methodology and its effectiveness in treating a self-interaction free Coulomb energy, we briefly review the basics of KS density functional theory [18].

We consider a finite number, $N$, of electrons interacting via a Coulomb repulsion confined in a volume, $\Omega$, and moving under the action of an external potential, $v(r)$. For simplicity, in the following we consider only non-degenerate states and in much of the development we suppress the presence of spin. Final expressions, however, are given in full spin-resolved form (see appendices).

A. Kohn-Sham Equations for Ground States

The Hamiltonian describing an interacting system of $N$ electrons in an external potential takes the usual form,

$$\hat{H}^N = \hat{V} + \hat{T}^N + \hat{U}^N,$$

with the operators $\hat{V}$, $\hat{T}^N$ and $\hat{U}^N$ corresponding, respectively, to the external field, the kinetic energy and the interparticle interaction (Coulomb repulsion). The ground-state energy of the system is given by the expectation value,

$$E_g = \langle \Psi_g^N | \hat{H}^N | \Psi_g^N \rangle, \quad \langle \Psi_g^N | \Psi_g^N \rangle = 1,$$

where $|\Psi_g^N\rangle$ denotes the many-particle ground state of $\hat{H}^N$. For electrons, $|\Psi_g^N\rangle$ leads to a wave function, $\Psi_g^N(r_1, r_2, \ldots, r_N)$, that is antisymmetric with respect to interchange of the coordinates (and spins) of individual particles, according to the requirements of Fermi statistics. We use the notation, $|\Psi_g^N\rangle \rightarrow n(r)$, and say $|\Psi_g^N\rangle$ leads to $n(r)$, to denote the property,

$$n(r) = N \int |\Psi_g^N(r_1, r_2, \ldots, r_N)|^2 dr_2 \ldots dr_N,$$

where $n(r)$ denotes the single-particle density function normalized to the total number of particles, $N$. This property is formally equivalent to taking the expectation value with respect to $\Psi_g^N(r_1, r_2, \ldots, r_N)$ of the single-particle number operator, $\hat{n}(r) = \psi^\dagger(r)\psi(r)$, where $\psi^\dagger$ and $\psi$ are field creation and destruction operators for an electron at $r$. We now write [19] in the form,

$$E_g = \int v(r)n_g(r)dr + \langle \Psi_g^N | \hat{T} + \hat{U} | \Psi_g^N \rangle$$

$$= \min_{n(r)} \left[ \int v(r)n(r)dr + F[n] \right] = \min_{n(r)} E[n],$$

in terms of the constrained search functional [22,23]

$$F[n] = \min_{|\Psi\rangle \rightarrow n(r)} \langle \Psi | \hat{T}^N + \hat{U}^N | \Psi \rangle.$$

Given a density, $n(r)$, the constrained search examines all antisymmetric $N$-particle wave functions that lead to the density and delivers the state (in the absence of degeneracy) that produces the minimum value of $\langle \Psi_g^N | \hat{T}^N + \hat{U}^N | \Psi_g^N \rangle$. Cioslowski [29] has provided a formal procedure for generating all antisymmetric wave functions leading to $n(r)$ and identifying that $\Psi_g^N(r_1, \ldots, r_N)$ (in the absence of degeneracy) that
determines \( F[n] \). For \( \nu \)-representable densities, \( F[n] \) gives the Hohenberg and Kohn functional, \( F_{\text{HK}}[n] \), and the minimizing state \( |\Psi_N^0\rangle \) coincides with \( |\Psi_g^N\rangle \).

For any other anti-symmetric state (wave function) \( |\Phi^N\rangle \neq |\Psi_g^N\rangle \) such that \(|\Phi^N\rangle \rightarrow n(r)\), we have,

\[
F[n] \leq \langle \Phi^N | \hat{T} + \hat{U} | \Phi^N \rangle,
\]

so that the exact ground-state energy, \( E_g \), forms a lower bound of the expectation values of the Hamiltonian with respect to antisymmetric \( N \)-particle states, \( |\Phi^N\rangle \rightarrow n(r) \).

As in the initial formulation of DFT by Kohn and Sham, we postulate the existence of a fictitious non-interacting \( N \)-particle system described by the Hamiltonian,

\[
\hat{H}_N^N = \hat{V}_s + \hat{T}^N,
\]

under the action of an external potential, \( \hat{V}_s \), whose ground-state density is identical to the density of the interacting system described by \( \hat{H}_N^N \). In analogy with \( \Phi \), we define the constrained search functional,

\[
T_s[n] = \min \langle \Phi^N | \hat{T}^N | \Phi^N \rangle.
\]

In the absence of degeneracy, the minimizing \( |\Phi_s^N\rangle \) is a single Slater determinant (denoted by the subscript \( s \)) of order \( N \).

Because generally, \( |\Phi_s^N\rangle \neq |\Psi_g^N\rangle \), we have,

\[
E_s = \int v(r)n(r)\text{d}r + F_s[n] \geq E_g,
\]

where

\[
F_s[n] = \langle \Phi_s^N | \hat{T}^N + \hat{U}^N | \Phi^N \rangle \geq F[n].
\]

Defining the quantity, \( E_c[n] = F[n] - F_s[n] \), and adding and subtracting \( F_s[n] \) to \( E[n] \) in Eq. (5), we obtain,

\[
E[n] = \int v(r)n(r)\text{d}r + F_s[n] + E_c[n].
\]

The quantity \( E_c[n] \) is referred to as the correlation energy. We can view the last expression as a means of determining \( E_g \) through the states of the non-interacting system, \( |\Phi_s^N\rangle \), given the functional difference, \( E_c[n] \).

The Slater determinant, \( |\Phi_s^N\rangle \), is obtained from the solutions of a single-particle Schrödinger equation, which then also defines the potential, \( v_s(r) \).

\[
\left[-\frac{1}{2}\nabla^2 + v_s(r)\right]f_i(r) = \epsilon_i f_i(r).
\]

From (11), it follows that,

\[
n_s(r) = \sum_{j=1}^{N} |f_j(r)|^2,
\]

where the orbitals, \( f_j(r) \), correspond to the \( N \) eigenvalues of Eq. (13) that lie the lowest in energy. With respect to the same state, we also define the pair density for the non-interacting system,

\[
n_s(r_1, r_2) = \left(\frac{N}{2}\right) \int |\Phi^N(r_1, r_2, \ldots, r_N)|^2 \text{d}r_3 \ldots \text{d}r_N
\]

\[
= \frac{1}{4} \sum_{i,j} |f_i(r_1)f_j(r_2) - f_j(r_1)f_i(r_2)|^2.
\]

Now, the functional \( F_s[n] \) takes the form,

\[
F_s[n] = \int \text{d}r \int \text{d}r_1 \int \text{d}r_2 \frac{n_s(r_1, r_2)}{|r_1 - r_2|}.
\]

The form of \( F_s[n] \) is expressed in terms of the fully exchanged two-particle density and is by construction free of self-interaction effects. From Eq. (13) we obtain the expectation value of the kinetic energy operator,

\[
E_k[n] = \int \text{d}r \int \text{d}r_1 \int \text{d}r_2 \frac{n_s(r_1, r_2)}{|r_1 - r_2|} - \frac{1}{2}\sum_{i,j} \epsilon_i \epsilon_j \sum_n n_s(|r_i - r_j; n|).
\]

where a star denotes the complex conjugate of a quantity. Using these expressions, we can write

\[
\int \text{d}r \int \text{d}r_1 \int \text{d}r_2 \frac{n_s(r_1, r_2; n)}{|r_1 - r_2|} - \frac{1}{2}\sum_{i,j} \epsilon_i \epsilon_j = \int \text{d}r \int \text{d}r_1 \int \text{d}r_2 \frac{\delta n_s(r_1, r_2; n)}{|r_1 - r_2|} + v_c(r).
\]

where \( T \) denotes the exact expectation value of the kinetic energy of the interacting system and \( n(r_1, r_2) \) is the corresponding exact two-particle density.

Using the stationarity property of the KS energy for the ground state with respect to the density, \( \frac{\delta E_c[n]}{\delta n(r)} = 0 \), and

\[
\frac{\delta T_s[n]}{\delta n(r)} = -v_s(r) + \frac{\delta E_s[n]}{\delta n(r)}
\]

(where in the following the constant \( c \) is suppressed), we obtain the requirement at the ground state,

\[
v_s(r) = v(r) + \left[ \int \text{d}r_1 \int \text{d}r_2 \frac{\delta n_s(r_1, r_2)}{|r_1 - r_2|} + v_c(r) \right]_{n=n_g}
\]

where the terms in the square brackets are the sum of the Coulomb potential and the correlation potential,

\[
v_c(r) = \frac{\delta E_c[n]}{\delta n(r)}.
\]
completing the expression for $v_s$ to be used in Eq. (13). Equation \(20\) gives a unique KS potential, leaving no freedom in its determination: It is the unique (generally within a constant) potential that leads to the density.

The quantity $E_s[n]$ appearing in the previous discussion is exact, but generally unknown. For the case of systems with infinite numbers of electrons, a correlation energy functional that is consistent with the second Hohenberg-Kohn theorem in yielding energies that are no lower than their experimental counterparts can be constructed based on the properties of the homogeneous electron gas (jellium), as developed in the work of Ceperley and Alder.\(^{30}\) For finite systems, such a consistent construction of the correlation energy is still lacking. In the following, we set this term equal to zero and concentrate on the exchange-only mode of implementation of the theory, through the derivative of the Coulomb energy with respect to the density including the exchange term.

\[ E[n] = \int v(r)n(r)\,dr + E_s[n] \geq E_s. \quad (22) \]

Our aim is to develop a methodology that, with $v_s(r)$ set equal to zero, determines the potential (KS potential), $v_s(r)$, within the exchange-only mode of implementation of the theory, through the derivative of the Coulomb energy with respect to the density including the exchange term.

**B. Hartree Approximation of the Coulomb Energy**

In the Hartree approximation without self-interaction correction,\(^{29}\) the Coulomb energy of an interacting $N$-particle system, e.g., an atom, is approximated by the classical expression,

\[ U_{\text{H}} = \frac{1}{2} \int \frac{n(r_1)n(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2, \quad (23) \]

where $n(r)$ denotes the ground-state density of the interacting system, a form that lends itself immediately to functional differentiation with respect to $n(r)$, (the density appears explicitly inside the integral).

Computational ease, however, comes at a high price: the product of densities allows the simultaneous occupation of the same orbital by a single electron in violation of the Pauli exclusion principle. Alternatively, an electron at position $r_1$ is allowed to interact with itself at $r_2$, leading to a clearly unphysical self-interaction effect.

\[ U_{\text{QM}} = \int \frac{n_s(r_1,r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2, \quad (24) \]

where $n_s(r_1, r_2)$ is the pair density obtained from the KS orbitals. In general, it is convenient to define the exchange term,

\[ J_{\sigma}(r_1, r_2) = 2n_s(r_1, r_2) - n(r_1)n(r_2), \quad (25) \]

and a corresponding exchange energy,

\[ E_x[n] = \frac{1}{2} \int J_{\sigma}(r_1, r_2) \, dr_1 \, dr_2. \quad (26) \]

In this case, with $f_j(r)$ denoting an orbital in the KS determinant, the pair density takes the form ($\sigma$ denotes spin),

\[ n_s(r_1, r_2) = \frac{1}{4} \sum_{i,j} |f_i(r_1)f_j(r_2) - f_j(r_1)f_i(r_2)|^2 \]

\[ = \frac{1}{2} \sum_{i,j} \left[ f_i^*(r_1)f_j^*(r_2)f_i(r_1)f_j(r_2) - f_i^*(r_1)f_j^*(r_2)f_j(r_1)f_i(r_2) \delta_{\sigma_i, \sigma_j} \right], \quad (27) \]

and the exchange term has the form,

\[ J_{\sigma}(r_1, r_2) = \sum_{i,j} \left[ f_i^*(r_1)f_j^*(r_2)f_j(r_1)f_i(r_2) \delta_{\sigma_i, \sigma_j} \right]. \quad (29) \]

Finally, the exchange contribution to the single-particle potential arising from the Coulomb energy, called the exchange potential $v_x$, can be written as,

\[ v_x(r) = \frac{\delta E_x[n]}{\delta n(r)}, \quad (30) \]

in which the functional dependence on the density is explicitly indicated.

Written in terms of the expression in Eq. (24), the energy functional to be minimized in the exchange-only form of the KS formulation of ground-state DFT takes the form,

\[ \tilde{E}[n] = \int v(r)n(r)\,dr + T_s[n] + U_{\text{H}}[n] + E_x[n]. \quad (31) \]

This form exhibits clearly the difficulty that has been encountered in attempts to implement the KS formulation of DFT. While the functional differentiation of the Hartree term with respect to the density is straightforward (explicit dependence on density under the integral), the orbitals that enter the definition of the exchange term are only implicitly dependent on the density defying immediate differentiation with respect to $n(r)$ by analytic means. Even a brief survey of the many forms proposed for bypassing this seemingly impossible task would be exceedingly lengthy and take us too far afield of our intended purpose. At the same time, a few comments are in order.

The OEP method\(^{30}\) is the best known and most widely used procedure for the solution of the KS equations in the presence of exact exchange. The functional differentiation of the Coulomb energy in reconstructing the potential within the OEP method requires some computational effort, usually involving the calculation of the inverse susceptibility and ultimately requiring the solution of an integral equation. Alternatively, the potential can be parametrized\(^{19,28}\) where parameters
are determined in order to minimize the energy. The present SIF method avoids the need to solve the OEP equations, by using an analytic treatment in obtaining the functional derivative of the Coulomb energy with respect to the density. This is accomplished through the use of the equidensity basis formalism, introduced by Macke\cite{23} and Harriman\cite{24}. In addition to orthonormality, Zumbach and Maschke\cite{25} proved that the basis is complete. The expansion of the orbitals in this basis brings out the explicit dependence on the density allowing the straightforward differentiation using the product rule. Expressed in this way it is clear that the total variational freedom that is present in the method is the one contained in the explicit density dependence in the basis. Henceforth we shall refer to orthonormality, Zumbach and Maschke\cite{23,25}.

III. EQUIDENSITY BASIS

The calculation of the Coulomb potential in Eq. (20) requires the functional derivative of the non-interacting pair density $n_s(r_1, r_2)$ with respect to the (spin) density $n^\sigma(r)$. This can be performed analytically by expressing the former in terms of an expansion that exhibits explicitly the single-particle density. Namely, for each orbital, $f^\sigma_j(r)$, we write,

$$f^\sigma_j(r) = \sum_k a^\sigma_k \phi^\sigma_k(r, [n^\sigma]),$$

$$\phi^\sigma_k(r, [n^\sigma]) = \sqrt{\frac{n^\sigma(r)}{N^\sigma}} \exp(i k \cdot R^\sigma(r, [n^\sigma])},$$

where $\phi^\sigma_k(r, [n^\sigma])$ are the elements of an orthonormal and complete basis, the equidensity basis, where $k = (k_x, k_y, k_z)$ denote a set of three signed integers, the $a^\sigma_k$ are expansion coefficients, and the vector $R^\sigma(r, [n^\sigma])$ is defined by the expressions,

$$R^\sigma_1(x, y, z, [n^\sigma]) = \frac{2\pi}{N^\sigma(y, z, [n^\sigma])} \int_{-\infty}^{\infty} dx' \ n^\sigma(x', y, z)$$

$$R^\sigma_2(y, z, [n^\sigma]) = \frac{2\pi}{N^\sigma(z, [n^\sigma])} \int_{-\infty}^{\infty} dy' \ n^\sigma(y', z, [n^\sigma])$$

$$R^\sigma_3(z, [n^\sigma]) = \frac{2\pi}{N^\sigma([n^\sigma])} \int_{-\infty}^{\infty} dz' \ n^\sigma(z', [n^\sigma])$$

with

$$N^\sigma(y, z, [n^\sigma]) = \int_{-\infty}^{\infty} dx' \ n^\sigma(x', y, z)$$

$$N^\sigma(z, [n^\sigma]) = \int_{-\infty}^{\infty} dy' \ n^\sigma(y', z, [n^\sigma])$$

$$N^\sigma([n^\sigma]) = \int_{-\infty}^{\infty} dz' \ n^\sigma(z', [n^\sigma])$$

where $0 \leq R_1, R_2, R_3 \leq 2\pi$. The transformation, $r \rightarrow R$, maps three-dimensional coordinate space onto the volume of a cube of side $2\pi$ with the points at infinity mapped onto the surface of the volume. Note that the $R$ are explicit functionals of the density. This particular choice of $R_1, R_2, R_3$ is not unique, with other choices, e.g. permuting coordinates or other coordinate systems, being possible\cite{26} as well. In the following we use the definitions given in equations (34) and (35).

The coefficients, $a^\sigma_k$, are given as the overlap integrals,

$$a^{\sigma\sigma}_k[n] = \int f^\sigma_k(r, [n]) \phi^{\sigma\sigma}_k(r, [n]) \, dr.$$  \hspace{1cm} (36)

The functional derivative of the Coulomb energy can now be carried out through the differentiation of the orbitals under the integral sign in Eq. (29). The procedure is as follows: We replace the orbitals in the exchange term with their expansions in terms of the equidensity basis, and use the property of functional derivatives,

$$\frac{\delta n^\sigma''(r')}{\delta n^\sigma(r)} = \delta_{\sigma,\sigma'} \delta(r - r'),$$

(37)

to perform the functional differentiation of the exchange term. It is clear that any density can be used to construct the equidensity basis, and the corresponding expansion of the KS orbitals. However, only the density corresponding to the KS orbitals is useful to construct the equidensity basis. This choice allows a direct functional differentiation of the basis with respect to the density at each iteration step.

A. Coulomb Potential Calculation

In general, the Coulomb potential is given by the functional derivative of the Coulomb energy with respect to the density,

$$v^{(U)}(r') = \frac{\delta}{\delta n^\sigma(r')} \left( \iint \, dr_1 \, dr_2 \, U(r_1, r_2) \, n_s(r_1, r_2) \right) = \iint \, dr_1 \, dr_2 \, U(r_1, r_2) \left[ \frac{\delta n_s(r_1, r_2)}{\delta n^\sigma(r')} \right].$$

(38)

For three-dimensional systems the interaction $U$ is given by the expression,

$$U(r_1, r_2) = \frac{1}{|r_1 - r_2|},$$

(39)

(where clearly $U$ has no functional dependence on the density).

We split the pair density into two parts, the well known Hartree and the exchange contributions (with $i$ in $f_i$ a compound index that includes spin),

$$n_s(r_1, r_2) = \frac{1}{2} \sum_{i,j \neq j} \left[ f^i_1(r_1) \, f^j_2(r_2) \, f_i(r_1) \, f_j(r_2) - f^i_1(r_1) \, f^j_1(r_2) \, f_i(r_1) \, f_j(r_2) \, \delta_{\sigma,\sigma'} \right]$$

(40)
where the exchange term has contributions from likewise spins only. In this form, the sum runs over all \(i\) and \(j\). Since the potential from the Hartree contribution is trivial, in the following we concentrate on the functional derivative of the exchange term, \(J_x(r_1, r_2)\).

Applying the product rule of functional differentiation yields the expression

\[
\frac{\delta J_x(r_1, r_2)}{\delta n^\sigma(r')} = -\sum_{ij} \left[ \delta_{\sigma_i, \sigma_j, \sigma} \left( \int dr I^{ij}(r) f_j(r) \frac{\delta f_i(r)}{\delta n^\sigma(r')} \right) + \frac{f_i^x(r_1) f_j^x(r_2)}{2} \frac{\delta f_i(r_1)}{\delta n^\sigma(r')} f_j(r_2) + f_i^x(r_1) f_j^x(r_2) \frac{\delta f_i(r_1)}{\delta n^\sigma(r')} f_j(r_2) \right]. \tag{43}
\]

In general, the integrals obtained combining (38), (42) and (43) have the form \((U\) is symmetric in \(r_1\) and \(r_2\),

\[
\int \int dr_1 dr_2 U(r_1, r_2) f_{a}^*(r_1) f_{b}^*(r_2) f_{c}^*(r_1) f_{d}^*(r_2) \frac{\delta f_{e}(r_1)}{\delta n^\sigma(r')}, \tag{44}
\]

where \(a, b, c, d \in \{i, j\}\). We define the integral \(I^{ij}\):

\[
I^{ij}(r_1) := \int dr_2 U(r_1, r_2) f_{a}^*(r_1) f_{b}^*(r_2) f_{c}^*(r_1) f_{d}^*(r_2), \tag{45}
\]

that is known to be smooth. The detailed evaluation of these integrals for three-dimensional systems is given in Appendix A.

Since \(U\) is symmetric in the spatial coordinates and \(I^{ij} = (I^{ji})^*\), equation (43) can be further simplified. We use the fact that \(r_1\) and \(r_2\) as well as the summation indices \(i\) and \(j\) can be interchanged, to obtain the expression,

\[
\psi_{\alpha}^\sigma(r') = \frac{1}{2} \int \int dr_1 dr_2 U(r_1, r_2) \frac{\delta J_x(r_1, r_2)}{\delta n^\sigma(r')},
\]

or

\[
\psi_{\alpha}^\sigma(r') = -2\Re \sum_{ij}^{N} \delta_{\sigma_i, \sigma_j, \sigma} \int dr I^{ij}(r) f_j^*(r) \frac{\delta f_i(r)}{\delta n^\sigma(r')}, \tag{47}
\]

where \(\delta_{\sigma_i, \sigma_j, \sigma}\) equals 1 when \(\sigma_i = \sigma_j = \sigma\) and vanishes otherwise. The exchange potential is always real. It becomes clear that the crucial quantity of interest is the derivative of an orbital with respect to the density, \(\frac{\delta f^\sigma_i(r)}{\delta n^\sigma(r')}\).

### B. Explicit Derivatives of Orbitals

Within SIF, the derivative of an orbital with respect to the density is straightforward. Using the expansion (32) and the definition of the equidensity basis (33) we obtain the expression,

\[
\frac{\delta f^\sigma_i(r)}{\delta n^\sigma(r')} = \sum_k \delta_{\sigma_i, \sigma} a_{i,\sigma}^k e^{ik \cdot r} \frac{\delta n^\sigma(r')}{\delta n^\sigma(r')}, \tag{48}
\]

\[
\frac{\delta f^\sigma_i(r)}{\delta n^\sigma(r')} = \sum_k \left[ \frac{1}{N^\sigma} a_{i,\sigma}^k e^{ik \cdot r} \frac{\delta n^\sigma(r')}{\delta n^\sigma(r')} \right. + \sqrt{n^\sigma(r')} i a_{i,\sigma}^k e^{ik \cdot r} \frac{1}{N^\sigma} \frac{\delta R(r, [n^\sigma])}{\delta n^\sigma(r')} + \left. \sqrt{n^\sigma(r')} i a_{i,\sigma}^k e^{ik \cdot r} k \cdot \frac{\delta R(r, [n^\sigma])}{\delta n^\sigma(r')} \right], \tag{49}
\]

For the sake of formal completeness, we include the functional derivative of the normalization integrals \(N^\sigma\) with respect to the density, that leads to the second term after the last equals sign.

\[
\frac{\delta f^\sigma_i(r)}{\delta n^\sigma(r')} = \frac{\delta (r - r')}{2N^\sigma(r')} f^\sigma_i(r) - \frac{\delta (r - r')}{2N^\sigma(r')} f^\sigma_i(r) = \frac{\delta (r - r')}{2N^\sigma(r')} f^\sigma_i(r) - \frac{\delta (r - r')}{2N^\sigma(r')} f^\sigma_i(r) + \sum_k \left[ i a_{i,\sigma}^k e^{ik \cdot r} \frac{\delta n^\sigma(r')}{\delta n^\sigma(r')} \right] \frac{\delta R(r, [n^\sigma])}{\delta n^\sigma(r')} + \left[ i a_{i,\sigma}^k e^{ik \cdot r} \frac{\delta n^\sigma(r')}{\delta n^\sigma(r')} \right] \frac{\delta R(r, [n^\sigma])}{\delta n^\sigma(r')} \tag{49}
\]
When the spin of the orbital and the spin of the density with respect to which it is differentiated coincide, the last expression reduces to the form,

\[
\frac{\delta f_\sigma^\sigma(r)}{\delta n^\sigma(r')} = \frac{\delta (r-r')}{2n^\sigma(r')} f_\sigma^\sigma(r) - \frac{\delta f_\sigma^\sigma(r)}{2N^\sigma}
\]

\[
+ \frac{\delta R(r, [n^\sigma])}{\delta n^\sigma(r')}, \sum_k i_k \alpha_k^\sigma \phi_k(r, [n^\sigma])
\]

\[
+ \sum_k \frac{\delta a_k^\sigma}{\delta n^\sigma(r')} \phi_k^\sigma(r, [n^\sigma]),
\]

(50)

where the second term (from the derivative of the normalization) leads to a constant shift in the potential and can be neglected.

Clearly, Eq. (50) has contributions to the full functional derivative of two distinctly different origins. The third term on the right side contains only terms where the dependence on the density is made explicit by use of the equidensity basis. On the other hand the final term, involving the functional derivative of the expansion coefficients of equidensity basis themselves, has only an implicit dependence on the density.

In the following we shall evaluate Eq. (50) under the ansatz that this implicit dependence can be neglected - the explicit equidensity basis (EEB) ansatz referred to in the introduction. While the algebraic consequences of making this ansatz are the subject of ongoing research, the great practical benefit is that the equations that result are of closed form and also become surprising simple to implement computationally. In addition, results presented for atoms in section IV B 2 indicate that this ansatz produces exchange only total energies of similar quality to those of HF and OEP and, furthermore, satisfy expected variational bounds. We will comment on this in more detail in section VI while here proceeding with further analysis of the remaining terms in Eq. (50).

The third term of Eq. (50) involves an infinite sum over k, raising questions about convergence. This problem is circumvented through the realization that the same infinite sum occurs in the gradients of the orbitals. As shown in Appendix C comparing functional and spatial derivatives allows the replacement of the sum over k with expressions involving partial derivatives of the orbitals. For example, in the one-dimensional case we obtain the result,

\[
\sum_k a_k^\sigma i_k \phi_k^\sigma(x) = \frac{N^\sigma}{2\pi n^\sigma(x)} \left[ f' - \frac{1}{2n^\sigma(x)} f(x) n^\sigma \right]
\]

\[
= \frac{N^\sigma}{2\pi} \frac{1}{\sqrt{n^\sigma(x)}} \left( \frac{f(x)}{\sqrt{n^\sigma(x)}} \right)',
\]

(51)

where primes on functions denote spatial derivatives. The three-dimensional case follows analogously, leading to the expression,

\[
\sum_k a_k^\sigma \phi_k^\sigma(r) i_k = \left( \begin{array}{c} Q_x^\sigma \\ Q_y^\sigma \\ Q_z^\sigma \end{array} \right) = Q^\sigma =
\]

\[
\begin{bmatrix}
\frac{N^\sigma(y,z)}{2\pi n^\sigma(r)} & \frac{\nabla_x f - f(r)}{2n^\sigma} & \frac{\nabla_x n^\sigma(r)}{2n^\sigma} \\
\frac{N^\sigma(z)}{2\pi n^\sigma(y,z)} & \frac{\nabla_y f - f(r)}{2n^\sigma} & \frac{\nabla_y n^\sigma(r)}{2n^\sigma} \\
\frac{N^\sigma(x)}{2\pi n^\sigma(z)} & \frac{\nabla_z f - f(r)}{2n^\sigma} & \frac{\nabla_z n^\sigma(r)}{2n^\sigma}
\end{bmatrix},
\]

(52)

with \( \beta_{ab} \) being the partial derivatives of \( R \), defined in Eq. (34), with respect to the coordinates,

\[
\beta_{ab} := \frac{\partial R_a}{\partial b} \quad a, b \in \{ x, y, z \},
\]

(53)

given in Appendix B. In short, we can write

\[
\frac{\delta f_\sigma^\sigma(r)}{\delta n^\sigma(r')} \simeq \frac{\delta (r-r')}{2n^\sigma(r')} f_\sigma^\sigma(r) - \frac{\delta f_\sigma^\sigma(r)}{2N^\sigma}
\]

\[
+ \frac{\delta R(r, [n^\sigma])}{\delta n^\sigma(r')}, \sum_k i_k \alpha_k^\sigma \phi_k(r, [n^\sigma])
\]

\[
+ \sum_k \frac{\delta a_k^\sigma}{\delta n^\sigma(r')} \phi_k^\sigma(r, [n^\sigma]),
\]

(54)

where the Q include summations over k to infinite order.

Still to be considered is the functional derivative of \( R \) with respect to the density. The derivation is shown in detail in Appendix B. For the one-dimensional case we obtain the expression,

\[
\frac{\delta R_1(x, [n^\sigma])}{\delta n^\sigma(x')} = \frac{2\pi}{N^\sigma} \Theta(x-x')
\]

(55)

while in three-dimensions we find

\[
\frac{\delta R_1(x, y, z, [n^\sigma])}{\delta n^\sigma(x')} = \frac{\delta (y-y') \delta (z-z')}{N^\sigma(y, z)}
\]

\[
\times \left[ 2\pi \Theta(x-x') - R_1^\sigma(x, y, z) \right]
\]

\[
\frac{\delta R_2(y, z, [n^\sigma])}{\delta n^\sigma(y')} = \frac{\delta (z-z')}{N^\sigma(z)}
\]

\[
\times \left[ 2\pi \Theta(y-y') - R_2^\sigma(y, z) \right]
\]

\[
\frac{\delta R_3(z, [n^\sigma])}{\delta n^\sigma(z')} = \frac{1}{N^\sigma} \left[ 2\pi \Theta(z-z') - R_3^\sigma(z) \right],
\]

(56)

At this point we derived an analytic and closed-form expression for the functional derivative of an orbital with respect to the density, subject to the conditions imposed by the EEB ansatz described above. Through the use of the product rule, these expressions can be used to obtain the contribution, \( v_x(r) \), to the Coulomb potential. Computational details and the final expressions for the three-dimensional case are given in Appendix D.

C. Formal Summary

We summarize the discussion of the previous section. The use of spatial derivatives allows us to eliminate the explicit
evaluation of the equidensity basis and the expansion coefficients, leading to a closed-form expression for the functional derivative of an orbital with respect to the density. In the one-dimensional case we obtain the expression,

\[
\frac{\delta f^\sigma(x)}{\delta n^\sigma(x')} \simeq \frac{f^\sigma(x)}{2n^\sigma(x)} \delta(x-x') - \frac{f^\sigma(x)}{2N^\sigma} + \left( \frac{1}{n^\sigma(x)} \left[ f^\sigma(x) - \frac{f^\sigma(x) n^\sigma(x)}{2n^\sigma(x)} \right] \right) \Theta(x-x').
\]

The analogous results in three-dimensions take the form,

\[
\frac{\delta f^\sigma(r)}{\delta n^\sigma(r')} \simeq \frac{f^\sigma(r)}{2n^\sigma(r)} \delta(r-r') - \frac{f^\sigma(r)}{2N^\sigma} + \frac{Q^\sigma_y(r)}{N^\sigma(y,z)} \left[ 2\pi \Theta(x-x') - R^\sigma_1(x,y,z) \right] \delta(y-y') \delta(z-z') + \frac{Q^\sigma_y(r)}{N^\sigma(z)} \left[ 2\pi \Theta(y-y') - R^\sigma_2(y,z) \right] \delta(z-z') \]

\[
+ \frac{Q^\sigma_z(r)}{N^\sigma} \left[ 2\pi \Theta(z-z') - R^\sigma_3(z) \right],
\]

with the quantities \( R \) defined in (34), the \( N \) in (35) and the \( Q \) in (22). Computational details are given in Appendix D. The calculation of the potential becomes now straightforward using equations (47) and (45).

D. Iterative Procedure

The solution of the KS equations relies on an iterative procedure, with an updated KS potential and density determined at each iteration step. The sequence of steps in the treatment of the KS equations is summarized below:

1. At each step, \( i \), of the iteration, determine the orbitals, \( f^{(i)}(r) \), and the density, \( n^{(i)}(r) \).

2. Determine the derivatives of the orbitals with respect to the density, take the functional derivative of the Coulomb energy with respect to the density in terms of spatial gradients, and obtain the Coulomb energy contribution to the KS potential.

3. Solve the KS equation for the new potential, go back to the first step and iterate until convergence is reached within some preset tolerance.

In short, the only difference with conventional procedures is the treatment of the full Coulomb potential expressed in terms of the pair density, rather than just the Hartree term or modifications to it.

IV. EXAMPLES

In this section we present the results of applications of our method to two systems for which the exact answers are known analytically, to a one-dimensional model system, and finally on the series of atomic systems from Helium to Krypton.

A. Analytic Examples

The formalism allows the expression of the functional derivatives of the exchange energy with respect to the density by analytic means and leads to closed-form expressions in terms of the spatial gradients of the orbital functions. These expressions can be compared to exact results in cases where analytic expressions are known.

1. Two-Electron Systems

As a first example we discuss the ground state of a two-electron systems, such as the Helium atom or the Hydrogen dimer (\( H_2 \)), with two electrons of opposite spin in the same spatial orbital under the same external potential.

Assuming real, and node free orbitals we obtain

\[
n^\sigma(r) = \sum_{i=1}^{1} |f_i(r)|^2 = |f(r)|^2
\]

\[
f(r) = \sqrt{n^\sigma(r)}
\]

\[
\frac{\delta f(r)}{\delta n^\sigma(r')} = \frac{1}{2} \frac{\delta}{\delta n^\sigma(r')} \delta(r-r')
\]

\[
f \frac{\delta f}{\delta n^\sigma} = \frac{1}{2} \delta(r-r'),
\]

from which the exchange potential can be determined as follows:

\[
\nu^\sigma(r) = \frac{1}{2} \int \int dr_1 \, dr_2 \, U(r_1, r_2) \frac{\delta J_s(r_1, r_2)}{\delta n^\sigma(r)}
\]

\[
= - \int \int dr_1 \, dr_2 \, U(r_1, r_2) \left\{ f(r_1) \delta f^{(1)}(r_1) \frac{\delta f(r_2)}{\delta n^\sigma} f(r_2) + f(r_2) \delta f^{(1)}(r_2) \frac{\delta f(r_1)}{\delta n^\sigma} f(r_1) \right\}
\]

\[
= - \int dr_1 \, dr_2 \, U(r_1, r_2) \left\{ \frac{1}{2} \delta(r-r_1) f(r_2) f(r_2) + \frac{1}{2} \delta(r-r_2) f(r_1) f(r_1) \right\}
\]

\[
= - \int dr_1 \, U(r_1, r) n^\sigma(r_1)
\]

\[
\nu^\sigma(r) = - \frac{1}{2} \int dr_1 \, U(r_1, r) n(r_1)
\]

\[
= - \frac{1}{2} \nu_H(r).
\]

The exchange potential is exactly half of the Hartree potential but with the opposite sign, so that the self-interaction error is
half of the Hartree term. Using the method proposed in this paper, we write
\[ f(r) = \sum_{k=0}^{\infty} a_k \phi_k(r) \quad \text{with} \quad a_0 = 1, \quad (68) \]
where all coefficients other than \( k = 0 \) vanish. From Eq. (50) we obtain the expression,
\[ \frac{\delta f(r)}{\delta n^\sigma(r')} = \frac{\delta (r - r')}{2n^\sigma(r)} f(r) = \frac{\delta (r - r')}{2f(r)}. \quad (69) \]
Using Eq. (47) for the exchange potential yields the result,
\[ v^\sigma_x (r') = -2 \int \frac{\delta f(r)}{\delta n^\sigma(r')} dr \int \frac{\delta f(r)}{\delta n^\sigma(r')} dr' f(r) = - I^{11}(r') \quad (70) \]
\[ = - I^{11}(r') = - \int dr U(r, r') f(r) f(r) \quad (71) \]
\[ = - \int dr U(r, r') n^\sigma(r) \quad (72) \]
\[ v^\sigma_x (r') = - \frac{1}{2} \int dr U(r, r') n(x) = - \frac{1}{2} v^H(r'). \quad (73) \]
For this simple example, the SIF method reproduces the correct analytic expression for the exchange potential.

2. Hartree Potential

Our second example deals with the Hartree term. The functional derivative of the Hartree energy \( E_H \) with respect to the density is well known. From
\[ E_H = \frac{1}{2} \int \int \frac{n(r) n(r')}{|r - r'|} dr dr' \quad (74) \]
we obtain
\[ \frac{\delta E_H}{\delta n(r')} = v_H(r') = \int dr \frac{n(r)}{|r - r'|}. \quad (75) \]
It can also be shown, that
\[ \frac{\delta E_H}{\delta n(r')} = \frac{\delta E_H}{\delta n^\sigma(r')} = \frac{\delta E_H}{\delta n^{\sigma'}(r')} = v_H(r'). \quad (76) \]
We now express the density in terms of orbitals,
\[ n^\sigma(r) = \sum_{\alpha=1}^{N^\sigma} f^\sigma_\alpha(r) \phi^\sigma_\alpha(r), \quad (77) \]
and express the orbitals in terms of the equidensity basis, and take the functional derivative of \( E_H \) written in terms of the expanded forms. The results leads to \( v_H \). The detailed derivation of this result is shown in Appendix [E].

Notably, despite the use of our equidensity ansatz in Eq. (50), we still obtain the correct analytical result for this case.

B. Numerical Examples

In this section we apply our method to one-dimensional systems in terms of the particles-in-a-box problem and to realistic atomic systems.

1. One-dimensional Square Well

The work reported in this section is designed to test a simple case of non-interacting, spinless Fermions confined in an one-dimensional well of length, \( L = |x_1 - x_0| = 1 \), with infinite potential walls. We choose \( N = 6 \). This example is used for illustrating the method, deriving the potential corresponding to the energy for a given form of the inter-particle interaction. We restrict ourselves to a non-self consistent solution for a vanishing (or constant) potential. We choose an inter-particle interaction that decays exponentially with respect to inter-particle distance,
\[ U(x_1, x_2) = \Lambda e^{-\lambda |x_1 - x_2|}, \quad (78) \]
that allows us the freedom of manipulating the range of the interaction and assess its effects on the exchange potential.

For this case the orbitals corresponding to \( N \) lowest energies are known analytically and lead to an analytic expression for the density in Eq. (14) and the pair density, Eq. (42). The normalized wave functions of this system are given by the expressions,
\[ f_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n \pi x}{L} \right) \quad 0 \leq x \leq L, \quad (79) \]
with quantum numbers \( n = 1, 2, 3, \ldots \). The corresponding energies are
\[ E_n = \frac{\hbar^2}{2m} \left( \frac{n \pi}{L} \right)^2, \quad (80) \]
with the ground-state density given by \( n(x) = \sum_{n=1}^{N} |f_n(x)|^2 \).

In analogy to Eq. (44), we define the quantities \( R_{1/2/3}(x, y, z) \), that in one dimension reduce to a function \( q(x) \),
\[ q(x) = \frac{2 \pi}{N} \int_{x_0}^{x} n(x') dx'. \quad (81) \]
For the six-electron case, \( q(x) \) is shown in Fig. [I]. We see that the function \( q(x) \) is almost linear. An exact linear behavior, \( q(x) = x \), (red dashed line) would correspond to a constant density with the equidensity orbitals reduced to plane-waves. The functional derivative of \( \frac{\delta q(x)}{\delta n(x')} \) takes the form,
\[ \frac{\delta q(x)}{\delta n(x')} = \frac{2 \pi}{N} \Theta(x - x'). \quad (82) \]
We also have, neglecting terms which would contribute only to a constant shift in the potential,
\[
\frac{\delta f_n(x)}{\delta n(x'')} = \frac{f_n(x)}{2n(x)} \delta(x - x'') + \frac{\delta q(x)}{\delta n(x'')} \sum_k a_k e^{ikq[x(n)]}.
\]
In spite of the dependence on \(k\), the sum on the right-hand side converges sufficiently rapidly to be numerically stable. In this case, the equidensity basis functions, \(\phi_k(x)\), take the form,
\[
\phi_k(x) = \sqrt{\frac{n(x)}{N}} e^{ikq[x(x)]} = \sqrt{\frac{n(x)}{N}} e^{ikq[x[n]]}. \quad (83)
\]
There exist two choices for \(k\) in constructing a complete and orthonormal set of basis functions: Either signed whole integer values, \(k = 0, \pm 1, \pm 2, \pm 3, \ldots\), or half-integer values, \(k = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}, \ldots\). The rate of convergence of the expansion of the orbitals is found to depend on spatial symmetry, with those even under reflection (symmetric) about the center of the box being described more efficiently by whole integer values of \(k\), while half-integer values lead to faster convergence of the orbitals that are odd under reflection (antisymmetric). A plot of the coefficients vs. values of \(k\) is shown in Fig. 2. We find that with the choice of the faster converging expansion the error in the norm becomes smaller than \(10^{-5}\) when more than 100 basis functions are taken into account. Generally, we find that fewer than 1,000 functions are sufficient for convergence.

The ground-state density of the system, (the six electrons occupying the orbitals labeled \(n = 1, 2, \ldots, 6\), is shown in Fig. 3 while the pair density is shown in Fig. 4 with the number of basis functions indicated in the panel. Within the resolution of the figure, the two results are essentially indistinguishable. The same rate of convergence characterizes the pair density, shown in Fig. 4. We note the vanishing of the pair density along the line \(x_1 = x_2\), as expected from Eq. (40).

Another quantity to look at for convergence is the infinite sum over \(k\) appearing in Eq. (50). The result with the sums carried out to infinite order is given by the analytic expression in Eq. (51). The sums over \(k\) for the first three orbitals are shown in Fig. 5 for different numbers of expansion coefficients and basis functions taken into account, with those used chosen symmetrically around \(k = 0\). For this example, we find a rather good agreement using a few tens of coefficients in a broad range in space, between about \(x = 0.1\) and \(x = 0.9\) in Fig. 5. At the boundaries, the difference between the analytic expression and the truncated sums increases, the oscillations being a manifestation of the Gibbs phenomenon. Even though the results show convergence with the number of terms taken into account, we use the closed-form expressions of Eq. (51). This bypasses the explicit construction of the equidensity basis and the expansion coefficients.

Fig. 6 shows the potential obtained for the four values of \(\lambda = 1, 10, 50, 100\), as defined in (78), using both the Hartree expression (blue dashed curves) for the interaction energy, Eq. (23), as well as the quantum mechanically correct expression, Eq. (24) (red solid line). In all cases, convergence is well established with about 200 basis functions, although the results shown here correspond to 1,000 terms taken into account. The analytic expressions lead to the same result. An immediate effect of the quantum expression are the lower values of the potential obtained from Eq. (24), caused by the presence of the exchange term that reduces the effective region of
FIG. 3. Ground-state density of six non-interacting electrons in an one-dimensional box with infinite walls as discussed in the text. The blue dashed line marks the analytic expression, plotted below the other curve. At this scale they are almost indistinguishable.

FIG. 4. Non-interacting Ground-state pair density of six non-interacting electrons in an one-dimensional box with infinite walls as discussed in the text.

FIG. 5. Infinite sum, see Eq. (51), evaluated for the first three orbitals of the six electron example. Convergence is shown by increasing the numbers of coefficients $a_k$ (chosen symmetrically around 0) in comparison to the analytic result.

interaction of two electrons. Of interest is also the behavior of the two different expressions for the potential in the limit of short-range interaction, or large values of $\lambda$. The Hartree term yields a potential that approaches the form of the density, essentially reaching that form for $\lambda = 100$ (upper curve in panel on lower right-hand corner). In that limit, the interaction potential resembles a delta-function in two-particle space and the energy given by the Hartree term is simply proportional to the density at the point $x_1 = x_2$.

The behavior is considerably different when the pair density is used to calculate the interaction energy. Now, in the limit of short-range interaction interaction, and spinless fermions, two particles cease interacting altogether because the pair density vanishes in the region in which the interaction is noticeably non-zero and the contribution to the single-particle potential drops essentially to zero (lower curve in panel in lower right-hand corner in the figure).
FIG. 6. Single-particle potential contributed by the interaction energy in the system of six non-interacting electrons confined in a box with infinite walls as discussed in the text. The blue dashed line is calculated from Eq. (23) (Hartree), whereas the red solid line is based on Eq. (24) (pair density).

2. Atomic Calculations

In the following we apply the SIF method to realistic atomic systems. Details of the calculations, in particular of the evaluation of the Coulomb and exchange potential are given in Appendix [D]. Because the form of the correlation energy is currently unknown, the results presented are all fully self-consistent and converged within the exchange-only mode ($E_{c} = 0$). This allows us to compare SIF results with those obtained within the exchange-only OEP and the HF methods.

Fig. [7] show the results for Helium, Lithium, Beryllium, Boron, Neon and Argon obtained from a self-consistent exchange-only calculation. The left column shows the exchange potential on a logarithmic scale that allows a detailed study of the behavior close to the nucleus. To emphasize the asymptotic behavior, in the middle panel, the same exchange potential is shown on a linear scale, but multiplied by the distance to the nucleus, $r$. Finally, the density is plotted in the right column. For all examples, the corresponding full OEP results are shown for comparison. Lithium and Boron are spin-polarized, resulting in different potentials for the majority and minority spin channel.

For Helium, the exchange potential within SIF coincides with the one obtained by the OEP method, and therefore the densities are also identical. This identity is not preserved for heavier atoms. As seen in Fig. [7], the SIF potential has always a non-negative slope, whereas the OEP potentials exhibit regions where the slope becomes negative. In the OEP literature, this is referred to as the intershell structure.

Even though the potentials are different, the SIF and OEP densities are indistinguishable at the scale of the plot. All exchange potentials behave regularly near the origin, and have an $-1/r$ asymptotic behavior, as expected. For illustrative purposes, we plot the exchange potentials for the atoms Helium to Krypton in Fig. [8].

Total energies for the atom series obtained in SIF, OEP and HF are compared with experimental determined ones in Table [I] and are plotted as difference to experiment in Fig. [9] as absolute differences normalized to the atomic number, $(E - E_{\text{EXP}})/Z$. In Fig. [10] we also plot the fractional error $(E - E_{\text{HF}})/E_{\text{HF}}$, relative to the corresponding HF energies, which gives a clearer picture of the rather small relative “errors”, as compared to LDA, of both OEP and SIF.

Experimental data for the total energy can be obtained by summing all ionization potentials of the corresponding atom, a process whose difficulty increases prohibitively with atomic number, $Z$. Published results for the total energy are often characterized by a number of corrections to account for zero-point motion and relativistic effects. The resulting rather unclear situation for the total energies is discussed in Appendix [F]. In any case, the experimental values of the ground-state energies lie the lowest compared with those of HF, OEP and SIF in correspondingly increasing order. We discuss this order in more detail in the following section.

V. DIFFERENCES BETWEEN HF, OEP AND THE SIF METHODS

A. Comparison with Hartree-Fock

It has become customary in the literature to compare the results of an exchange-only implementation of DFT to those of the HF method, and we follow this practice.

The HF method relies on the direct calculation of a determinant wave function to minimize the energy of an interacting system. The single-particle orbitals defining the determinant are the basic variables of the method, and their unrestricted variation provides a path to the lowest energy obtained in this procedure. The method, however, does not provide a path to the determination of the ground state of an interacting system.

By contrast, the basic variable in DFT is the density. In order to minimize the energy the functional derivative with respect to the density is taken, and evaluated at that particular density formed by the KS orbitals. In an exchange-only implementation of the theory, the restriction of the orbitals to reproduce the total energy minimizing density energy is expected to lead to higher values of the total energy compared with those of the HF method and of course the ground state energy. This, indeed, is the case in all calculations reported here, see Table [I]. The restrictions can also be discussed in terms of the potential. Within the KS scheme, the potential, see Eq. (20), is unique to all orbitals, where in HF it is orbital-dependent. This allows HF to explore a broader space and may lead to lower energies.

B. Comparison with OEP

Since the most widely used method for obtaining a potential from an energy functional written explicitly in terms of the
TABLE I. Total energies in Hartree for the atom series from Helium to Krypton. Two columns with experimental data are given, EXP$^a$ and EXP$^b$, for details see Appendix F. Other columns show the total energies obtained by various methods (SIF, OEP and HF) within the exchange-only mode. The data are plotted in Fig. 9. In general, the SIF energies for the atom series lie slightly above the OEP ones, and both of them are higher than the HF results. The differences are discussed in the text.

| Z | Symbol | Element | EXP$^a$ | EXP$^b$ (Ref. 32) | x-SIF | x-OEP (Ref. 33) | HF (Ref. 33) |
|---|---|---|---|---|---|---|---|
| 2 | He | Helium | -2.90339 | -2.904 | -2.862 | -2.862 | -2.862 |
| 3 | Li | Lithium | -7.47798 | -7.47806 | -7.432 | -7.433 | -7.433 |
| 4 | Be | Beryllium | -14.6685 | -14.66736 | -14.571 | -14.572 | -14.573 |
| 5 | B | Boron | -24.6582 | -24.65391 | -24.527 | -24.528 | -24.529 |
| 6 | C | Carbon | -37.8557±0.0002 | -37.8450 | -37.678 | -37.689 | -37.690 |
| 7 | N | Nitrogen | -54.6119 | -54.5892 | -54.401 | -54.403 | -54.405 |
| 8 | O | Oxygen | -75.1100±0.0001 | -75.0673 | -74.809 | -74.812 | -74.814 |
| 9 | F | Fluorine | -99.8062±0.0001 | -99.7339 | -99.406 | -99.409 | -99.411 |
| 10 | Ne | Neon | -129.0507±0.0059 | -128.9376 | -128.542 | -128.545 | -128.547 |
| 11 | Na | Sodium | -162.4283±0.0032 | -162.2546 | -161.852 | -161.857 | -161.859 |
| 12 | Mg | Magnesium | -200.3100±0.0033 | -200.053 | -199.606 | -199.612 | -199.615 |
| 13 | Al | Aluminum | -242.7121±0.0037 | -242.346 | -241.868 | -241.873 | -241.877 |
| 14 | Si | Silicon | -289.8683±0.0037 | -289.359 | -288.845 | -288.851 | -288.854 |
| 15 | P | Phosphorus | -341.9464±0.0087 | -340.709 | -340.953 | -340.980 | -340.979 |
| 16 | S | Sulfur | -399.0351±0.0050 | -397.495 | -397.502 | -397.505 | -397.506 |
| 17 | Cl | Chlorine | -461.3813±0.0051 | -459.470 | -459.478 | -459.483 | -459.483 |
| 18 | Ar | Argon | -529.1122±0.0093 | -527.540 | -526.804 | -526.812 | -526.817 |
| 19 | K | Potassium | -601.9677±0.0051 | -599.150 | -599.159 | -599.159 | -599.165 |
| 20 | Ca | Calcium | -680.1022±0.0051 | -676.743 | -676.752 | -676.756 | -676.756 |
| 21 | Sc | Scandium | -759.718 | -759.728 | -759.728 | -759.736 | -759.736 |
| 22 | Ti | Titanium | -848.375 | -848.397 | -848.397 | -848.407 | -848.407 |
| 23 | V | Vanadium | -942.852 | -942.876 | -942.876 | -942.886 | -942.886 |
| 24 | Cr | Chromium | -1043.334 | -1043.350 | -1043.350 | -1043.360 | -1043.360 |
| 25 | Mn | Manganese | -1149.848 | -1149.860 | -1149.860 | -1149.870 | -1149.870 |
| 26 | Fe | Iron | -1262.425 | -1262.440 | -1262.440 | -1262.450 | -1262.450 |
| 27 | Co | Cobalt | -1381.376 | -1381.410 | -1381.410 | -1381.420 | -1381.420 |
| 28 | Ni | Nickel | -1506.828 | -1506.860 | -1506.860 | -1506.870 | -1506.870 |
| 29 | Cu | Copper | -1638.938 | -1638.950 | -1638.950 | -1638.960 | -1638.960 |
| 30 | Zn | Zinc | -1777.820 | -1777.830 | -1777.830 | -1777.850 | -1777.850 |
| 31 | Ga | Gallium | -1923.235 | -1923.250 | -1923.250 | -1923.260 | -1923.260 |
| 32 | Ge | Germanium | -2075.335 | -2075.350 | -2075.350 | -2075.360 | -2075.360 |
| 33 | As | Arsenic | -2234.215 | -2234.230 | -2234.230 | -2234.240 | -2234.240 |
| 34 | Se | Selenium | -2399.844 | -2399.860 | -2399.860 | -2399.870 | -2399.870 |
| 35 | Br | Bromine | -2572.416 | -2572.430 | -2572.430 | -2572.440 | -2572.440 |
| 36 | Kr | Krypton | -2752.029 | -2752.040 | -2752.040 | -2752.050 | -2752.050 |

As is evident from Table I and Figs. 9 and 10, the SIF total energies are systematically higher than those of the OEP. Indeed, we find the consistent relationship $E_{HF} \leq E_{OEP} \leq E_{SIF} < E_{LDA}$. As is particularly evident from Fig. 10, the energy differences between the OEP and SIF relative to HF are small, as are the differences between OEP and SIF, particularly when judged on the scale of the energy differences between either of these and the corresponding LDA energies. In absolute terms, the root-mean-square deviations of the OEP, SIF and LDA energies from the HF energies, taken over the 36-atom set of Table I, are $8.22 \times 10^{-3}$, $2.04 \times 10^{-2}$, $1.03 \times 10^{0}$ Hartree respectively. Again, the slightly lower energies found in the OEP are indicative of some additional variational freedom contained in that approach relative to the current implementation of SIF. This despite the fact that both aim to evaluate the same functional derivative. How this difference is related to the EEB ansatz remains a matter for ongoing research.
FIG. 7. Exchange potentials for Helium, Lithium, Beryllium, Boron, Neon and Argon. The left columns depict the radial exchange potential on a logarithmic scale, the middle column the exchange potential multiplied by $r$, the distance from the nucleus, so as to exhibit its asymptotic behavior, and the third column the density. Results of this paper (referred as x-SIF) are compared to OEP calculations. The curves represent self-consistent results obtained in the absence of a correlation energy (exchange only).
FIG. 8. SIF exchange potentials multiplied by \( r \), the distance from the nucleus, for the atomic series Helium \((Z = 2)\) to Krypton \((Z = 36)\). Both figures show the same data, just at a different angle. The colored surface is for illustration, and exchange potentials are only meaningful for integer \( Z \) values, marked by the black lines.

C. Alternative Method

For special cases, e.g., closed shell atomic systems and generally spherical charge densities, Harbola and Sahni\textsuperscript{35} have shown that the exchange potential can be obtained through the use of classical electrostatics. Notably, their method does not require the calculation of the susceptibility or its inverse and is independent of both SIF and OEP. For the case of Ar, the exchange potential found using their procedure precisely matches that which we find using the SIF approach (see Figure 11). As is also evident, both curves deviate somewhat from OEP, in particular neither the Harbola and Sahni results nor SIF show the, so called, intershell structure of OEP.

In further work\textsuperscript{36}, Harbola and Sahni determined the ground-state energies of atomic systems from He to Rn. For closed shell systems, where densities are spherical and their method is applicable, their results coincide with ours as is clearly seen in Table I and Fig. 11. Of course, the SIF approach, unlike that Harbola and Sahni, can be applied quite generally to the non-spherical case.

VI. CONCLUSIONS

The developments in the paper sprang from a particularly simple observation: The functional derivative of the Hartree term with respect to the density is facilitated by the explicit appearance of the density in the integrand. The same ease would materialize were the orbitals in the exchange term given explicitly in terms of the density in a differentiable functional form. The expansion of each orbital in the equidensity basis is particularly convenient for satisfying this requirement.

Based on this expansion, we have proposed a novel treatment for the Coulomb energy to be used in implementations of the KS formulation of DFT within a local approximation. In this treatment, the Coulomb energy is expressed in terms of the pair density constructed from the single-particle orbitals arising from the solution of the KS equations, thus avoiding
by construction self-interaction effects. The pair density, in turn, is written in closed-form explicitly in terms of the density. This is accomplished through an expansion of the single-particle orbitals in terms of the equidensity basis whose elements are written explicitly in terms of the density. The resulting equations for the functional derivative of the pair density can then also be written close form. Furthermore, they can be evaluated straightforwardly provided that we neglect any possible implicit density dependence of the expansion coefficients of the equidensity basis in Eq. (50). We have then demonstrated how infinite sums appearing in the formalism can be replaced by quantities containing spatial derivatives and can thus evaluate the sums (Eqs. (51) and (52)) to infinite order leading to a computationally simple approach.

We have shown analytically that the approach recovers the exact expression for the exchange potential of two electron systems. Numerical studies of tunable interacting one-dimensional square well potential model are used to illustrate details of the inner workings of the approach and to show how it performs as a function of the interaction strength.

For real systems, we have shown results of the total energy of the atoms He through Kr and compared them with those obtained using HF, OEP, the approach of Harbola and Sahni, and standard LDA (including correlation). We find rather close agreement with the results of OEP for the total energies, charge densities and corresponding exchange potentials.

Interestingly, for systems where that method is applicable we find very precise agreement with Harbola and Sahni, with neither of these exhibiting the so called inter-shell structure seen in the exchange potential of OEP. In terms of the energy the we find the hierarchy $E_{HF} \leq E_{OEP} \leq E_{SIF}$. The fact that OEP energies are systematically slightly lower than those of SIF we attribute to the presence of additional variational freedom in that method compared with the current implementation of SIF.

The formalism presented in this paper can immediately be applied to all non-periodic systems, e.g., molecules. It is also likely that it can also be of considerable value for solids. Increasingly, DFT calculations based on exchange correlation functionals (e.g., hybrid functionals) that contain some element of exact exchange are being used to study wide classes of systems (e.g., metallic oxides) where earlier generation functionals, e.g., LDA, GGA, fail to give a good overall description of the electronic structure and bonding. Currently such “hybrid-functional” calculations are very computationally demanding which severely limits the systems sizes and complexity, and time scales in ab initio molecular dynamics, where they can be applied. Given that the approach presented in this paper yields expressions that are of closed form, they have the potential to be easily implemented and to significantly reduce the computational demands relative to existing OEP imple-
mentations. This in turn could allow hybrid-functional type methods to be applied to systems sizes currently only accessible using conventional LDA, GGA etc. Finally, we point out that the presented procedure can generally applied to any orbital dependent functional in the same way as demonstrated here on the exchange energy.

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Appendix A: Calculation of the integrals $I^{ij}$

In spherical coordinates, the integrals $I^{ij}$ defined in Eq. (45) can be evaluated using the well known formula based on an expansion of $U$ into spherical harmonics,

$$
\frac{1}{|r - r'|} = \sum_{L=(l,m)} \frac{4\pi}{2l + 1} Y_L^{*}(\hat{r}) Y_L(\hat{r}'),
$$

(A1)

and

$$
\int_{0}^{\infty} \int_{0}^{\infty} dr' r'^2 g(r') \frac{r_<^{l'}}{r_>^{l'-1}}
\begin{cases}
1 & \text{if } l' > l \\
0 & \text{otherwise}
\end{cases}
\int_{0}^{r} dr' r'^2 g(r') + r l \int_{r}^{\infty} dr' r'^2 r'^{-l-1} g(r').
$$

(A2)

In particular for a spherically symmetric function $\bar{g}$ we get,

$$
\int \frac{\bar{g}(r')}{|r - r'|} dr' = \frac{4\pi}{r} \int_{0}^{r} \bar{g}(r') r'^2 dr' + 4\pi \int_{r}^{\infty} \bar{g}(r') r' dr'.
$$

(A3)

If the orbitals are of the form $f = R_L(r) Y_L(\theta, \phi)$ the angular part can be integrated analytically using the Gaunt coefficients,

$$
C_{LL'}^{L''} = \int d\hat{r} Y_L(\hat{r}) Y_{L'}^{*}(\hat{r}) Y_{L''}(\hat{r}) \quad L = (l, m).
$$

(A4)

Then the integrals $I^{ij}$ have the form,

$$
I^{ij}(r_1) = \sum_{L} R_L^{ij}(r_1) Y_L(\theta_1, \phi_1)
$$

(A5)

\begin{align*}
&\text{with } l_{\max} = 2 \max(l_i, l_j) \\
&R_L^{ij}(r_1) = R_L(r_1) R_{ij}(r_1) \left( C_{LL',L}^{LL''} \right)^*,
\end{align*}

(A6)

where, depending on the symmetry, some coefficients $R_L^{ij}$ might vanish. Since the functional derivatives of $R$ contain $\delta$ distributions it will be difficult to expand them into a spherical harmonics basis. We find it more useful to evaluate the integrals $I^{ij}$ in Cartesian coordinates and perform the remaining integrals to obtain the potential.

Appendix B: Derivatives of the transformed coordinates $\mathbf{R}$

1. Spatial Derivatives

For completeness, we provide all spatial derivatives of the functionals $\mathbf{R}(n(r, [n]))$ defined in Eqs. (34).

$$
\beta_{11} := \frac{\partial R_1}{\partial x} = 2\pi \frac{n(r)}{N(y, z)}
$$

(B1)

$$
\beta_{12} := \frac{\partial R_1}{\partial y} = \frac{1}{N(y, z)} \left[ 2\pi \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial y} n(x', y, z) - R_1 \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial y} n(x', y, z) \right]
$$

(B2)

$$
\beta_{13} := \frac{\partial R_1}{\partial z} = \frac{1}{N(y, z)} \left[ 2\pi \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y, z) - R_1 \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y, z) \right]
$$

(B3)

$$
\beta_{21} := \frac{\partial R_2}{\partial x} = 0
$$

(B4)

$$
\beta_{22} := \frac{\partial R_2}{\partial y} = 2\pi \frac{N(y, z)}{N(z)}
$$

(B5)

$$
\beta_{23} := \frac{\partial R_2}{\partial z} = \frac{1}{N(z)} \left[ 2\pi \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y', z) - R_2 \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y', z) \right]
$$

(B6)

$$
\beta_{31} := \frac{\partial R_3}{\partial x} = 0
$$

(B7)

$$
\beta_{32} := \frac{\partial R_3}{\partial y} = 0
$$

(B8)

$$
\beta_{33} := \frac{\partial R_3}{\partial z} = 2\pi \frac{N(z)}{N}
$$

(B9)
We see that the Jacobian is
\[
\det \beta = \det \begin{bmatrix} \frac{\partial R_1}{\partial x} & \frac{\partial R_1}{\partial y} & \frac{\partial R_1}{\partial z} \\ \frac{\partial R_2}{\partial x} & \frac{\partial R_2}{\partial y} & \frac{\partial R_2}{\partial z} \\ \frac{\partial R_3}{\partial x} & \frac{\partial R_3}{\partial y} & \frac{\partial R_3}{\partial z} \end{bmatrix} = \frac{(2\pi)^3}{N} n(r), \quad (B10)
\]
and in general \( \det \beta = \frac{(2\pi)^d}{N} n(r) \) where \( d \) is the dimension of the system.

2. Functional Derivatives of the \( R \)

Straightforward functional differentiations lead to the expressions:

\[
\frac{\delta R_1(x, y, z, [n^\sigma])}{\delta n(x'')} = 2\pi \delta n(x'') \int_{-\infty}^{\infty} dx' n(x', y, z, [n^\sigma])
\]
\[
= 2\pi \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y - y') \delta(z - z'')
\]
\[
-2\pi \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y - y') \delta(z - z'')
\]
\[
\times \left[ \int_{-\infty}^{\infty} dx' n(x', y, z, [n^\sigma]) \right]^2
\]
\[
= \frac{\delta(y - y')\delta(z - z'')}{N(y, z, [n^\sigma])} \left[ 2\pi \Theta(x - x'') - R_1(x, y, z, n[\sigma]) \right],
\]

\[
\frac{\delta R_2(y, z, [n^\sigma])}{\delta n(x'')} = 2\pi \delta n(x'') \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma])
\]
\[
= 2\pi \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y') \delta(z - z'')
\]
\[
-2\pi \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y') \delta(z - z'')
\]
\[
\times \left[ \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma]) \right]^2
\]
\[
= \frac{\delta(z - z'')}{N(z, [n^\sigma])} \left[ 2\pi \Theta(y - y') - R_2(y, z, n[\sigma]) \right],
\]

\[
\frac{\delta R_3(z, [n^\sigma])}{\delta n(x'')} = 2\pi \delta n(x'') \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma])
\]
\[
= 2\pi \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y') \delta(z' - z'')
\]
\[
-2\pi \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y') \delta(z' - z'')
\]
\[
\times \left[ \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma]) \right]^2
\]
\[
= \frac{1}{N^\sigma} \left[ 2\pi \Theta(z - z'') - R_3(z, n[\sigma]) \right].
\]

Appendix C: Spatial Derivatives and their Connection to Infinite Sums

The use of the equidensity basis requires the evaluation of the rather difficult infinite sum in Eq. (50) whose value de-
ing considerations allow the sum to be carried out to infinite order.

First, we discuss the one-dimensional case. We are interested in evaluating the sum,

\[ \sum_k a_k i k \phi_k(x, [n^\sigma]) = \sum_k a_k i k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}, \]  

(C1)

where the orbitals \( f(x) \) are expressed in the form (where for simplicity of notation we omit the spin superscript on the orbitals),

\[ f(x) = \sum_k a_k \phi_k = \sum_k a_k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}. \]  

(C2)

From the definition,

\[ q(x, [n^\sigma]) = \frac{2\pi}{N^\sigma} \int_{x_0}^x n^\sigma(x') dx' \]  

(C3)

we have,

\[ \frac{\delta q(x, [n^\sigma])}{\delta n^\sigma(x')} = \frac{2\pi}{N^\sigma} \Theta(x - x'), \]  

(C4)

and

\[ \frac{d q(x, [n^\sigma])}{d x} = \frac{2\pi}{N^\sigma} n^\sigma(x). \]  

(C5)

The spatial derivative is given by

\[ f' = \frac{df(x)}{dx} = \sum_k a_k \frac{d}{dx} \left( \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \right) \]  

(C6)

\[ = \sum_k \left[ \frac{1}{\sqrt{N^\sigma}} a_k \frac{1}{2\sqrt{n^\sigma(x)}} \frac{dn^\sigma(x)}{dx} e^{i k q(x, [n^\sigma])} \right] + i k a_k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \frac{dq(x)}{dx} \]  

\[ = \frac{n^\sigma(x)}{2n^\sigma(x)} \sum_k a_k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \frac{f(x)}{q'} \]  

(C7)

\[ + \frac{2\pi}{N^\sigma} n^\sigma(x) \sum_k a_k i k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}, \]

from which it follows that

\[ \sum_k a_k i k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \]  

\[ = \frac{N^\sigma}{2\pi n^\sigma(x)} \left( \frac{df(x)}{dx} - \frac{N^\sigma}{4\pi |n^\sigma(x)|^2} f(x) \frac{dn^\sigma(x)}{dx} \right) \]  

\[ = \frac{N^\sigma}{2\pi n^\sigma(x)} \left[ f' - \frac{1}{2 n^\sigma(x)} f(x) n^\sigma \right] \]  

(C8)

\[ = \frac{N^\sigma}{2\pi n^\sigma(x)} \left[ \sqrt{n^\sigma(x)} \left( \frac{f(x)}{\sqrt{n^\sigma(x)}} \right)' \right] \]  

(C9)

\[ = \frac{N^\sigma}{2\pi \sqrt{n^\sigma(x)}} \left( \frac{f(x)}{\sqrt{n^\sigma(x)}} \right)' \]  

(C10)

The spatial derivatives with respect to \( x \) (marked by primes) of the orbitals and the density can be calculated numerically.

It now follows that it is no longer necessary to construct explicitly the equidensity basis, or the expansion coefficients, \( a_k \). The three-dimensional generalization of the one-dimensional results is straightforward. The components of the gradient of an orbital, \( f \), decomposed into the equidensity basis are given by

\[ \nabla_\alpha f = \sum_k a_k^\alpha \frac{\partial}{\partial \alpha} \left( \sqrt{\frac{n^\sigma(r)}{N^\sigma}} e^{i k R(r, [n^\sigma])} \right) \]  

(C11)

\[ = \frac{1}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial \alpha} f(r) \]

\[ + i \sum_k a_k^\alpha \phi_k^\sigma(r, [n^\sigma]) \left( \frac{\partial R(r, [n^\sigma])}{\partial \alpha} \cdot k \right) \]  

(C12)

with \( \alpha = \{x, y, z\} \).

From Eqs. (C12), (B1), (B4) and (B7) we obtain

\[ \nabla_x f = \frac{1}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial x} f(r) \]

\[ + \sum_k a_k^\sigma \phi_k^\sigma(r)(ik_1) \left( \frac{2\pi}{N^\sigma(y, z)} \right) \]  

(C13)

and

\[ Q_x^\sigma = \sum_k a_k^\sigma \phi_k^\sigma(r)(ik_1) = \frac{n^\sigma(y, z)}{2\pi n^\sigma(r)} \times \left[ \nabla_x f - \frac{f(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial x} \right]. \]  

(C14)

In the same way, using Eqs. (C12), (B2), (B5) and (B8)

\[ \nabla_y f = \frac{1}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial y} f(r) \]

\[ + \sum_k a_k^\sigma \phi_k^\sigma(r)(ik_2) \beta_{12}^\sigma \]

\[ + \sum_k a_k^\sigma \phi_k^\sigma(r)(ik_2) 2\pi N^\sigma(y, z) \]  

(C15)

\[ = \frac{N^\sigma}{2\pi n^\sigma(r)} \left( \frac{f(r)}{\sqrt{n^\sigma(r)}} \right)' \]  

(C16)
Finally using Eqs. (C12), (B3), (B6) and (B9), we find,
\[
\nabla \mathbf{v} = \frac{1}{2\eta^2(r)} \frac{\partial n^\sigma(r)}{\partial z} f(r) \\
+ \sum_k a_k^r \phi_k^r(r)(ik_1) \beta^r_{13} \\
+ \sum_k a_k^r \phi_k^r(r)(ik_2) \beta^r_{23} \\
+ \sum_k a_k^r \phi_k^r(r)(ik_3) \left[ \frac{2\pi N^\sigma(z)}{N^\sigma} \right] \beta^r_{33},
\]
(C17)

and
\[
Q_z^\sigma = \sum_k a_k^r \phi_k^r(r)(ik_3) = \frac{N^\sigma}{2\pi N^\sigma(z)} \\
\times \left[ \nabla \mathbf{v} - \frac{f(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial z} - Q_z^\sigma \beta^r_{13} - Q_y^r \beta^r_{23} \right].
\]
(C18)

These results can be summarized in vector form,
\[
\sum_k a_k^r \phi_k^r(r)(ik) = \begin{pmatrix}
\frac{Q_x^\sigma}{Q_y^\sigma} \\
\frac{Q_y^\sigma}{Q_z^\sigma}
\end{pmatrix} \\
\left( \begin{array}{c}
\frac{N^\sigma(x,y,z)}{2\pi n^\sigma(r)} \\
\frac{N^\sigma(x)}{2\pi N^\sigma(y,z)} \\
\frac{N^\sigma(z)}{2\pi N^\sigma(y,z)}
\end{array} \right) \\
\left( \begin{array}{c}
\nabla \frac{f(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial z} \\
\nabla \frac{f(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial y} \\
\nabla \frac{f(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial x} - Q_z^\sigma \beta^r_{13} - Q_y^r \beta^r_{23}
\end{array} \right). \tag{D1}
\]

\section*{Appendix D: Numerical Evaluation of the Exchange Potential Components}

We split the exchange potential into different components with regard to Eqn. (54) and (47),
\[
v_x^\sigma(r') = v_x^\sigma[1](r') + v_x^\sigma[Qx](r') + v_x^\sigma[Qy](r') + v_x^\sigma[Qz](r'). \tag{D1}
\]
In the following we show how to evaluate the different integrals to obtain the exchange potential, in cartesian coordinates, which makes it easy to deal with integrals over Theta functions.

The contribution from the first term of Eq. (54) takes the form,
\[
v_x^\sigma[1](r') = -2 \Re \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} \\
\times \int d\mathbf{r}_1 I^{ij}(\mathbf{r}_1) f_j^*(\mathbf{r}_1) f_i(\mathbf{r}_1) \frac{\delta(\mathbf{r}_1 - \mathbf{r}')}{{n^\sigma}^2(\mathbf{r}_1)} \\
= -\frac{1}{2n^\sigma(\mathbf{r})} \Re \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} I^{ij}(r') f_j^*(r') f_i(\mathbf{r}).
\]

The contribution that includes \( \frac{\partial n^\sigma}{\partial \sigma} Q_x \) in the last term of Eq. (54), reads as follows
\[
v_x^\sigma[Qx](r') = -2 \Re \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} \int d\mathbf{r} I^{ij}(\mathbf{r}) f_j^*(\mathbf{r'}) \frac{\delta(y - y') \delta(z - z')}{N^\sigma(y, z, [\mathbf{n}^\sigma])} \times \\
\left[ 2\pi \Theta(x - x') - R_1(x, y, z, [\mathbf{n}^\sigma]) \right] \times \frac{N^\sigma(y, z)}{2\pi n^\sigma(r)} \times \\
\left[ \nabla \frac{f_i(\mathbf{r})}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial x} \\
\times \left( \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_i^j(x, y, z)}{N^\sigma(y, z)} \right) \right] \\
\delta(y - y') \delta(z - z'). \tag{D2}
\]

The integrals over \( y \) and \( z \) are trivial. Left over are two simple integral over \( x \).

We can define:
\[
A_x^\sigma(x, y, z) := \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_i^j(x, y, z)}{N^\sigma(y, z)}
\]
\[
A_y^\sigma(x, y, z) := \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_i^j(x, y, z)}{N^\sigma(z)}
\]
\[
A_z^\sigma(x, y, z) := \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_i^j(x, y, z)}{N^\sigma(z)}
\]
that leads to
\[
v_x^\sigma[Qx](r') = v_x^\sigma[Qx](x', y', z') \\
= -2 \Re \int_{x'}^{x} dx \left( A_x^\sigma(x, y', z') \\
- \int_{-\infty}^{x} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \right) R_1(x, y', z', [\mathbf{n}^\sigma]) A_x^\sigma(x, y', z'). \tag{D3}
\]

The contribution from the term that includes \( \frac{\partial n^\sigma}{\partial \sigma} Q_y \) in the last term of equation (54), reads as follows
\[
v_x^\sigma[Qy](r') = v_x^\sigma[Qy](y', z') \\
= -2 \Re \int_{x'}^{x} dx \int_{y'}^{y} dy \int_{-\infty}^{\infty} dz \left( 2\pi \Theta(y - y') - R_2(y, z, [\mathbf{n}^\sigma]) \right) \times \left[ \sum_{ij} \delta_{\sigma,\sigma_j,\sigma} I^{ij}(x, y, z) f_j(x, y, z) \frac{Q_i^j(x, y, z)}{N^\sigma(z)} \right] \\
\delta(z - z') \tag{D4}
\]
\[
= -2 \Re \int_{y'}^{y} dy \int_{x'}^{x} dx \int_{y'}^{y} dy \int_{-\infty}^{\infty} dz 2\pi A_y^\sigma(x, y, z')
\]
\[
- \int_{-\infty}^{\infty} \, dy \int_{-\infty}^{\infty} \, dx \, R_2(y, z', [n^\sigma]) A_\alpha^\sigma(x, y, z') = (D5)
\]

The contribution from the term that includes \( \frac{\partial R_3}{\partial n} Q_z \) in the last term of equation (53), reads as follows
\[
v_\alpha^\sigma [Q\tilde{E}](r') = v_\alpha^\sigma [Q\tilde{E}](z') = -2 \Re \int \, dx \, dy \, dz \left\{ \left[ 2 \pi \Theta(z - z') - R_3(z, [n^\sigma]) \right] \times \left[ \sum_{ij} \delta_{\sigma,\sigma'} f_J^i(x, y, z) f_J^i(x, y, z) Q_i(x, y, z) \frac{N^\sigma}{N^\sigma} \right] \right\}
\]

\[
= -2 \Re \left[ \int_{z'}^{\infty} \, dz \int_{-\infty}^{\infty} \, dy \int_{-\infty}^{\infty} \, dx \, 2 \pi A_\alpha^\sigma(x, y, z) \right. \left[ \int_{-\infty}^{\infty} \, dz \int_{-\infty}^{\infty} \, dy \int_{-\infty}^{\infty} \, dx \, R_3(z, [n^\sigma]) A_\alpha^\sigma(x, y, z) \right],
\]

this is a constant, spin dependent

\[
(D6)
\]

**Appendix E: Functional Derivative of the Hartree term**

For the Hartree term it is easy to show that
\[
\frac{\delta E_H}{\delta n^\sigma(r)} = \frac{\delta E_H}{\delta n^\sigma(r)} = \frac{\delta E_H}{\delta n^\sigma(r)} = v_H(r).
\]

Nevertheless, it still needs to be proven that the proposed procedure calculating the functional derivative with respect to the density leads to the exact same result, namely the Hartree potential.

For the spin density we have
\[
n^\sigma(r) = \sum_{i} n^\sigma_i(r) f_i^\sigma(r)
\]
\[
\nabla_\alpha n^\sigma(r) = \sum_{i} \left[ f_i^\sigma(r) \nabla_\alpha f_i^\sigma(r) + f_i^\sigma(r) \nabla_\alpha f_i^\sigma(r) \right] = \frac{\partial n^\sigma}{\partial \alpha} - \frac{\partial n^\sigma}{\partial \alpha} = 0
\]

(E6)

This leads directly to:
\[
\sum_{i} f_i^\sigma Q_i^\sigma + f_i^\sigma Q_i^\sigma = 0
\]
\[
\sum_{i} f_i^\sigma Q_i^\sigma + f_i^\sigma Q_i^\sigma = 0,
\]

showing that there is no contribution to the potential from the term appearing in the functional derivative of an orbital with respect to the density \( \frac{\delta H[n(r)]}{\delta n^\sigma(r)} \). The remaining four terms used to calculate the potential contribution have the same structure,
\[
\frac{1}{2} \int \, dr_1 \, dr_2 \, U(r_1, r_2) \times f_i^\sigma(r_2) f_i^\sigma(r_1) f_i^\sigma(r_2) \frac{f_i^\sigma(r_1)}{2n^\sigma(r')} \delta(r_1 - r') \delta_{\sigma,\sigma'}
\]
\[
= \frac{1}{2} \int \, dr_2 \, U(r', r_2) n(r_2) = \frac{1}{4} v_H(r').
\]

(E8)

(E9)

Due to the product rule during the functional differentiation this term appears four times so that the contribution to the potential is exactly the Hartree potential. One should note that taking the functional derivative with respect to the spin-up or spin-down density leads to the same result. All the above relationships apply in the same way in the non-spin-polarized case.

We have now proven that the proposed procedure to calculate the functional derivative of the Hartree term leads exactly to the Hartree potential.

**Appendix F: Experimental Data for the Atom Series**

In practice, it is not easy and in most cases impossible to measure quantities corresponding to the total energy of calculations. In principle, one has to ionize all electrons and measure the energy. The total energy is then the sum of all ionization energies. For the first few atoms of the periodic table this seems to be possible, but with larger \( Z \) it becomes harder and harder to ionize all of the electrons. A complete set of wavelength corresponding to all of the ionization potentials from Hydrogen to Calcium \( (Z = 20) \) has been published \cite{37} quite some time ago. One can now use the CODATA \cite{38,39} containing the latest values of physical constants and their errors, to convert the measured wavelength to energies. The second column of Table \[I\] labeled EXP(\alpha) contains these data, with the estimated error bars.
Based on the experimental data, some effort has been made to try to calculate non-relativistic correlation energies and relativistic corrections to the ionization potential. The data from reference seems to be widely used in the literature. But since they were determined by calculations rather than measurements, or only partially, we have doubts that these energies can be quoted as experimental data. Because it is not clear which data set should be used, we decided to quote both in this paper.

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