State Specific Kohn–Sham Density Functional Theory

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Abstract

A generalization of the Kohn–Sham approach is derived where the correlation-energy functional depends on the one-particle density matrix of noninteracting states and on the external potential from the interacting target-state. The one-particle equations contain the exact exchange potential, a nonlocal correlation potential, and an additional operator involving the correlation density. The electronic-energy functional has multiple solutions: Any one-particle density matrix delivering the target-state density yields a solution. In order to obtain the Kohn–Sham solution, the nonlocal operators are converted into local ones using an approach developed by Sala and Görling. Since the exact exchange-potential is used, and the $N$–representability problem does not arise—in contrast to the Kohn–Sham approach—errors from Coulomb self-interactions do not occur, nor the need to introduce functionals defined by a constraint search. Furthermore, the approach does not use the Hohenberg-Kohn theorem. A density functional formalism is also derived that assumes that the one-particle density matrices of interest have $\nu$–representable (non-interacting) densities and that these density matrices can be written as an explicit functional of the electron density. For simplicity, we only consider noninteracting closed-shell states and target states that are nondegenerate, singlet ground-states.

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I. INTRODUCTION

The Kohn-Sham version of density functional theory plays a major role in both quantum chemistry and condensed matter physics [1, 2, 3, 4, 5, 6, 7]. The local density approximation [8] has been widely used for the solid state. While for molecules, by far, the most successful functional, a hybrid one [9, 10, 11, 12], is known as B3LYP [9, 13].

The Kohn–Sham approach, however, does have well known shortcomings. For example, a constraint search definition [14, 15, 16, 17] is required to treat the $\nu$–representability problem that arises in the original Kohn–Sham method [8]. Unfortunately, this formal definition is difficult to consider when deriving approximate functionals. Furthermore, in contrast to wave function based methods, the exchange-correlation functional is an unknown, implicit functional, and there is no systematic method to improve approximations. In addition, there are well known errors arising from Coulomb self-interactions that appears when using approximate functionals [1, 2, 18]. Also, the most widely used approximate functional for molecular systems, the B3LYP functional, includes a component of the exact exchange-potential, even though the Kohn–Sham approach requires the noninteracting state to come from a local potential. The optimized potential method [19, 20, 21, 22, 23, 24, 25] is an approach to convert a nonlocal operator into a local potential. Unfortunately, this method leads to potentials that are not invariant to a unitary transformation of orbitals and depend explicitly on the individual orbitals and orbital energies.

The formalism presented below uses an electronic-energy functional containing a correlation energy functional $E_{\text{co}}$ that depends on the external potential $\nu$ and on the one-particle density matrix $\rho_1$ of determinantal states. Since the $\nu$–representability problem does not appear, a constrain search definition is not needed. Also, since the approach uses the exact exchange-potential, errors from Coulomb self-interactions do not occur. The energy functionals, however, contains multiple solutions, since any one-particle density matrix $\rho_1$ delivering the density from the interacting state yields a solution. In order to obtain the Kohn–Sham solution, the nonlocal operators are converted into local ones using an approach developed by Sala and Görling [26]. In contrast to the optimized potential method [19, 20, 21, 22, 23, 24, 25], the energy functionals and local potentials are invariant to a unitary transformation of orbitals and do not depend on the individual orbital or the orbital energies. A density functional formalism is also derived that assumes that the one-particle
density matrices of interest have \(v\)-representable (non-interacting) densities and that these density matrices can be written as an explicit functional of the electron density.

Previously we have shown that the correlation energy from many body perturbation theory [27, 28, 29] can be written as an explicit functional of \(v\) and \(\rho_1\) [30]. In a similar manner, but using less restrictive energy denominators, the correlation energy functionals presented below can be shown to be an explicit functional of \(v\) and \(\rho_1\) [31]. Hence, in contrast to the Kohn–Sham method, it maybe possible to derive approximate functionals that can be improved in a systematic manner. For simplicity, we only consider noninteracting closed-shell states and target states that are nondegenerate, singlet ground-states.

II. THE ENERGY FUNCTIONALS AND TRIAL WAVE FUNCTIONS

Our interest is in finding the ground-state eigenvalue of the Hamiltonian operator,

\[
\hat{H}_{Nv} = \hat{T} + \hat{V}_{ee} + \hat{V}_v,
\]

where

\[
\hat{T} = \sum_i (-\frac{1}{2} \nabla_i^2),
\]

\[
\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}},
\]

\[
\hat{V}_v = \sum_i v(i),
\]

and \(v\) is the external potential; \(N\) is the number of electrons. Since the Hamiltonian \(\hat{H}_{Nv}\) is determined by \(N\) and \(v\), so are the ground state wave functions \(|\Psi_{Nv}\rangle\) that satisfy the Schrödinger equation:

\[
\hat{H}_{Nv}|\Psi_{Nv}\rangle = \mathcal{E}_{Nv}|\Psi_{Nv}\rangle,
\]

where, for simplicity, we only consider wave functions that are nondegenerate, singlet ground-states.

Using a second quantization approach, our spin-free Hamiltonian does not depend on \(N\), and it can be expressed by

\[
\hat{H}_v = \sum_{ij} (i|(-\frac{1}{2} \nabla^2)|j) \hat{E}_{ij} + \sum_{ij} (i|v|j) \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl} (ijkl) \hat{E}_{ijkl},
\]
where the symmetry-adapted excitation operators are given by

\[ \hat{E}_{ij} = \sum_{\sigma} a_{i\sigma}^\dagger a_{j\sigma}, \]

\[ \hat{E}_{ijkl} = \sum_{\sigma\lambda} a_{i\sigma}^\dagger a_{k\lambda}^\dagger a_{l\lambda} a_{j\sigma}, \]

and the one- and two electrons integrals are spin-free integrals written in chemist’s notation using a spatial orbital set, say \( \{\chi\} \); this set has the following form:

\[ \psi_{j\sigma}(x) = \chi_j(r)\sigma(\omega); \ \sigma = \alpha, \beta, \]

where the spatial and spin coordinates, \( r \) and \( \omega \), are denoted collectively by \( x \).

Wave function-based methods including perturbation theory, configuration interaction, and coupled cluster theory, use one or more reference states to express \( \Psi \) and \( E \). For closed-shell ground-state wave functions, a single determinant can be used, where closed-shell determinantal, or noninteracting, states can be constructed from a set of doubly occupied spatial-orbitals; these occupied orbitals also determine the spin-less one-particle density-matrix of the noninteracting state, given by

\[ \rho_1(r_1, r_2) = 2 \sum_{w \in \{\chi_o\}} \chi_w(r_1)\chi_w^*(r_2), \]

where the sum is over the occupied orbitals; this set of orbitals is denoted by \( \{\chi_o\} \).

For later use, we also mention that for a complete basis set we have

\[ 2\delta(r_1 - r_2) = \rho_1(r_1, r_2) + \kappa_{\rho_1}(r_1, r_2), \]

where \( \kappa_{\rho_1} \) is determined by the excited orbitals,

\[ \kappa_{\rho_1}(r_1, r_2) = 2 \sum_{r \in \{\chi_u\}} \chi_r(r_1)\chi_r^*(r_2), \]

and \( \{\chi_u\} \) denotes the set of orbitals orthogonal to the occupied set \( \{\chi_o\} \). The operator form of Eq. (11) is

\[ 2\hat{I} = \hat{\rho}_1 + \hat{\kappa}_{\rho_1}, \]

where \( \hat{I} \) is the identity operator; so, the kernels of the three operators within Eq. (13) are given by the corresponding terms within Eq. (11).
It is well known that there is a one-to-one mapping between determinantal states and their one-particle density matrices, say $\gamma$, where for a closed-shell state described by the orbitals given by Eq. (9), we have

$$\gamma(x_1, x_2) = \sum_{w \in \{\chi\}} \sum_{\sigma} \chi_w(r_1) \chi^*_w(r_2) \sigma(\omega_1) \sigma^*(\omega_2),$$  \hspace{1cm} (14)

and by using Eq. (10), we obtain

$$\gamma(x_1, x_2) = \frac{1}{2} \rho_1(r_1, r_2) \delta_{\omega_1 \omega_2}.$$  \hspace{1cm} (15)

Since our closed-shell determinantal states are determined by $\rho_1$, we denote these kets by $|\rho_1\rangle$.

According to the Hohenberg-Kohn theorem, the external potential $v$ is determined by the density, and the density also determines $N$. So, in principle, we can replace the variables $N$ and $v$ by the electronic density $n$ and, at least for nondegenerate ground-states, write

$$\hat{H}_v |\Psi_n\rangle = E_n |\Psi_n\rangle; \hspace{1cm} n \rightarrow N, v,$$

where these functions serve as density-dependent trial-wave functions for the Kohn-Sham approach. Notice we have omitted the $N$ subscript on the Hamiltonian operator, since $\hat{H}_v$ is independent of $N$ when this operator is expressed in second quantization.

As an alternative to a density-dependent wave function, we consider trial wave functions, say $|\tilde{\Psi}_{vp_1}\rangle$, that are determined by the one-body external potential $v$ and, in addition, by the spin-less one-particle density-matrix $\rho_1$ of a noninteracting state, and, as mentioned previously, these noninteracting states are denoted by $|\rho_1\rangle$.

By definition, our trial wave function $|\tilde{\Psi}_{vp_1}\rangle$ yields the exact ground-state wave function $|\Psi_n\rangle$ when the noninteracting density $\rho_s$, i.e., the density of $|\rho_1\rangle$, equals the exact density $n$ of the interacting state $|\Psi_n\rangle$, where $n$ also determines the $v$ and $N$. This state of affairs can be represented by the following:

$$|\tilde{\Psi}_{vp_1}\rangle = |\Psi_n\rangle; \hspace{0.5cm} \rho_1 \rightarrow \rho_s = n, \hspace{0.5cm} n \rightarrow N, v.$$ \hspace{1cm} (17)

In other words, $\rho_1$ determines $\rho_s$, and when $\rho_s = n$, $|\tilde{\Psi}_{vp_1}\rangle$ yields $|\Psi_n\rangle$. Letting $\rho_1$ denote the one-particle density matrix of interest, we can write

$$|\tilde{\Psi}_{\rho_1}\rangle = |\Psi_n\rangle; \hspace{0.5cm} \rho_1 \rightarrow n, \hspace{0.5cm} n \rightarrow N, v.$$  \hspace{1cm} (18)
For later use, we also mention that the density \( n \) of an interacting state can be partitioned as

\[
n = \rho_s + \rho_c,
\]

where the correlation density is given by

\[
\rho_c(r) = \frac{\langle \Psi_n | \hat{\Gamma}(r) | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} - \rho_s(r),
\]

and \( \hat{\Gamma} \) is the density operator, given by Eq. (A7).

Using our trial wave function, we introduce a variational energy functional:

\[
E_v[\rho_1] = \frac{\langle \tilde{\Psi}_{v\rho_1} | \hat{H}_v | \tilde{\Psi}_{v\rho_1} \rangle}{\langle \tilde{\Psi}_{v\rho_1} | \tilde{\Psi}_{v\rho_1} \rangle}.
\]

(21)

Our trial wave functions \( |\tilde{\Psi}_{v\rho_1}\rangle \) and energy functionals \( E_v[\rho_1] \) are assumed to be explicit functionals of \( \rho_1 \) and \( v \). However, two different one-particle density matrices, say \( \rho_1 \) and \( \rho_1' \), that yield the same density \( \rho_s \), i.e., \( \rho_1 \to \rho_s \) and \( \rho_1' \to \rho_s \), yield the same \( |\tilde{\Psi}_{v\rho_1}\rangle \) and \( E_v[\rho_1] \), so these functions are implicit functionals of \( \rho_s \), and, therefore, we can write \( |\tilde{\Psi}_{v\rho_s}\rangle \) and \( E_v[\rho_s] \). However, we will continue to consider them as functionals of their explicit variable \( \rho_1 \).

Using Eqs. (16) and (18), we observe that our energy functional \( E_v \), given by Eq. (21), delivers the exact energy \( \mathcal{E}_n \) when the one-particle density matrix determines the exact density \( n \):

\[
E_v[\rho_1] = \mathcal{E}_n, \quad \rho_1 \to n, \quad n \to N,v,
\]

(22)

and for an arbitrary density we get

\[
E_v[\rho_1] \geq \mathcal{E}_n, \quad \rho_1 \to \rho_s \to N,
\]

(23)

where the density \( \rho_s \) from the noninteracting state \( |\rho_1\rangle \) is not necessarily \( v \)-representable.

III. TRIAL HAMILTONIANS

Our trial wave function is a ground-state eigenfunction of a Hamiltonian operator that depend explicitly on the one-particle density of a noninteracting state:

\[
\hat{H}_{v\rho_1} |\tilde{\Psi}_{v\rho_1}\rangle = \mathcal{E}_{v\rho_1} |\tilde{\Psi}_{v\rho_1}\rangle.
\]

(24)
As in our trial wave functions $|\tilde{\Psi}_{v\rho}(\rho_1)\rangle$ and energy functionals $E_v[\rho_1]$, the trial Hamiltonians $\hat{H}_{v\rho}$ are explicit functionals of $\rho_1$, but implicit functionals of $\rho_s$. So two trial Hamiltonians, say $\hat{H}_{v\rho}$ and $\hat{H}_{v\rho}'$, are equal if both $\rho_1$ and $\rho_1'$ yield the same density, i.e., $\rho_1, \rho_1' \to \rho_s$.

Our trial Hamiltonians must be chosen so that Eq. (18) is satisfied, indicating the following identity:

$$\hat{H}_{v\rho} = \hat{H}_v, \quad \rho_1 \to n, \quad n \to N, v. \quad (25)$$

There are many ways to obtain a trial Hamiltonian that satisfies Eq. (25). Consider the following trial Hamiltonian obtained by adding a term to the Hamiltonian:

$$\hat{H}_{v\rho} = \hat{H}_v + \lambda \int d\mathbf{r} g_{\rho_c}(\mathbf{r}) \left( \hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}) \right), \quad \rho_1 \to \rho_s, \quad (26)$$

where $\hat{\Gamma}(\mathbf{r})$ is the density operator, given by Eq. (A7); $(\hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}))$ is the one-body portion of $\hat{\Gamma}(\mathbf{r})$ when this operator is written in normal-ordered form [27, 40, 41, 42], given by Eq. (A6). Furthermore, $\lambda$ is an arbitrary constant, and the functional $g$ is also arbitrary, except that it vanishes when the correlation density $\rho_c$ vanishes

$$\lim_{\rho_c \to 0} g_{\rho_c}(\mathbf{r}) = 0, \quad (27)$$

where $\rho_c$ is defined by Eqs. (19) and (20).

Since $(\hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}))$ is normal-ordered, we have

$$\langle \rho_1 | \left( \hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}) \right) | \rho_1 \rangle = 0. \quad (28)$$

Therefore, the added term appearing in Eq. (26) can be considered a sort of correlation term, since it does not contribute in first order. Hence, we have

$$\langle \rho_1 | \hat{H}_{v\rho} | \rho_1 \rangle = \langle \rho_1 | \hat{H}_v | \rho_1 \rangle. \quad (29)$$

One possible choice for $g_{\rho_c}$, and presented in Appendix A, is given by

$$g_{\rho_c}(\mathbf{r}_1) = \int d\mathbf{r}_2 r_1^{-1} \rho_c(\mathbf{r}_2). \quad (30)$$

**IV. A GENERALIZATION OF THE KOHN-SHAM FORMALISM**

We now obtain a generalization of the Kohn-Sham formalism. Substituting Eq. (11) into Eq. (21) gives

$$E_v[\rho_1] = \frac{\langle \tilde{\Psi}_{v\rho} | \hat{\Gamma} | \tilde{\Psi}_{v\rho} \rangle}{\langle \tilde{\Psi}_{v\rho} | \tilde{\Psi}_{v\rho} \rangle} + \frac{\langle \tilde{\Psi}_{v\rho} | \hat{V}_{ee} | \tilde{\Psi}_{v\rho} \rangle}{\langle \tilde{\Psi}_{v\rho} | \tilde{\Psi}_{v\rho} \rangle} + \int d\mathbf{r} v(\mathbf{r}) \rho_s(\mathbf{r}) + \int d\mathbf{r} v(\mathbf{r}) \tilde{\rho}_c(\mathbf{r}), \quad (31)$$
where \( \rho_c \) is the correlation density of the trial wave function, i.e., as in Eq. (20), we have

\[
\rho_c(\mathbf{r}) = \frac{\langle \tilde{\Psi}_{v\rho_1} | \tilde{\Gamma}(\mathbf{r}) | \tilde{\Psi}_{v\rho_1} \rangle}{\langle \tilde{\Psi}_{v\rho_1} | \tilde{\Psi}_{v\rho_1} \rangle} - \rho_s(\mathbf{r}) = \tilde{n} - \rho_s(\mathbf{r}), \quad \tilde{\Psi}_{v\rho_1} \rightarrow \tilde{n}, \quad \rho_1 \rightarrow \rho_s, \tag{32}
\]

and \( \tilde{n} \) is the density of \( \tilde{\Psi}_{v\rho_1} \).

Through the first-order, the kinetic energy and electron-electron repulsion energy are given, respectively, by

\[
\langle \rho_1 | \hat{T} | \rho_1 \rangle = \int d\mathbf{r}_1 \left[ -\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2 = \mathbf{r}_1}, \tag{33}
\]

\[
\langle \rho_1 | \hat{V}_{ee} | \rho_1 \rangle = E_J[\rho_s] + E_x[\rho_1], \tag{34}
\]

where the Coulomb and exchange energies are

\[
E_J[\rho_s] = \frac{1}{2} \int \int r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2), \tag{35}
\]

\[
- E_x[\rho_1] = \frac{1}{4} \int \int r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_1). \tag{36}
\]

Adding and subtracting \( \langle \rho_1 | \hat{T} | \rho_1 \rangle \) and \( \langle \rho_1 | \hat{V}_{ee} | \rho_1 \rangle \), Eq. \( \text{(31)} \) can be written as

\[
E_v[\rho_1] = \int d\mathbf{r}_1 \left[ -\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2 = \mathbf{r}_1} + \int d\mathbf{r} v(\mathbf{r}) \rho_s(\mathbf{r}) + E_J[\rho_s] + E_x[\rho_1] + E_{co}[\rho_1, v] + \int d\mathbf{r} v(\mathbf{r}) \rho_c(\mathbf{r}), \tag{37}
\]

where the correlation-energy functional is given by

\[
E_{co}[\rho_1, v] = \frac{\langle \tilde{\Psi}_{v\rho_1} | \hat{T} | \tilde{\Psi}_{v\rho_1} \rangle}{\langle \tilde{\Psi}_{v\rho_1} | \tilde{\Psi}_{v\rho_1} \rangle} - \langle \rho_1 | \hat{T} | \rho_1 \rangle + \frac{\langle \tilde{\Psi}_{v\rho_1} | \hat{V}_{ee} | \tilde{\Psi}_{v\rho_1} \rangle}{\langle \tilde{\Psi}_{v\rho_1} | \tilde{\Psi}_{v\rho_1} \rangle} - \langle \rho_1 | \hat{V}_{ee} | \rho_1 \rangle. \tag{38}
\]

Recognizing the first four terms from Eq. \( \text{(37)} \) as the energy through the first order, \( \mathcal{E}_1 \), we can write

\[
E_v[\rho_1] = \mathcal{E}_1[\rho_1, v] + E_{co}[\rho_1, v] + \int d\mathbf{r} v(\mathbf{r}) \rho_c(\mathbf{r}), \tag{39}
\]

where

\[
\mathcal{E}_1[\rho_1, v] = \langle \rho_1 | H_v | \rho_1 \rangle = \int d\mathbf{r}_1 \left[ -\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2 = \mathbf{r}_1} \tag{40}
\]

\[
+ \int d\mathbf{r}_1 v(\mathbf{r}_1) \rho(\mathbf{r}_1) + \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \frac{1}{4} \int \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_1).
\]

Now consider the correlation energy that is obtained by wave function methods. Using the notation from Eq. \( \text{(31)} \), and a reference state \( | \rho_1 \rangle \), the correlation energy is given by

\[
\mathcal{E}_{co}[\rho_1, v] = \frac{\langle \Psi_{Nv} | \hat{H}_v | \Psi_{Nv} \rangle}{\langle \Psi_{Nv} | \Psi_{Nv} \rangle} - \mathcal{E}_1[\rho_1, v], \tag{41}
\]

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where previously we have shown that $\mathcal{E}_{co}$ can be written as an explicit functional of $v$ and $\rho_1$. In a similar manner, but using less restrictive energy denominators, our correlation energy functional $E_{co}$, given by Eq. (38), can be shown to be an explicit functional of $v$ and $\rho_1$. Therefore, by requiring the last term within Eq. (39) to be an explicit functional of $v$ and $\rho_1$, $E_v$ can also be written as an explicit functional of $v$ and $\rho_1$.

We now focus our attention on minimizing the energy functional $E_v$, subject to the constraint that the spin-less one-particle density-matrix $\rho_1$ comes from a closed-shell single-determinantal state. For the more general case of a determinantal state, say $|\gamma\rangle$, with the (spin-dependent) one-particle density matrix $\gamma$, as in Eq. (14), the two necessary conditions for $\gamma$ to satisfy are given by the following [2, 34]:

$$\int \int \gamma(x_3, x_4)\delta(x_3 - x_4) \, dx_3 dx_4 = N,$$

(42)

$$\int \gamma(x_3, x_5)\gamma(x_5, x_4) \, dx_5 = \gamma(x_3, x_4),$$

(43)

where the first relation indicates that the electron density yields the number of electrons $N$; the second relation indicates that $\gamma$ is indempotent. For our special closed-shell case, we substitute Eq. (15) into the above constrains, yielding the following conditions:

$$\int \int \rho_1(r_3, r_4)\delta(r_3 - r_4) \, dr_3 dr_4 = N,$$

(44)

$$\int \rho_1(r_3, r_5)\rho_1(r_5, r_4) \, dr_5 = 2\rho_1(r_3, r_4).$$

(45)

It is well know that the functional derivative of $\mathcal{E}_{1}$ with respect to the $\gamma$ yields the kernel of the Fock operator [2]. For the closed-shell case, we have

$$F(r_1, r_2) = \frac{\delta\mathcal{E}_{1}[\rho_1, v]}{\delta\rho_1(r_2, r_1)},$$

(46)

where, using Eq. (40), the Fock kernel is given by

$$F_{\rho_1}(r_1, r_2) = \delta(r_1 - r_2) \left( -\frac{1}{2} \nabla^2 + v(r_2) + \int dr_3 r_3^{-1} \rho(r_3) \right) + v^{\rho_1}_{x}(r_1, r_2),$$

(47)

and the exchange operator, say $\hat{v}^{\rho_1}_{x}$, has the following kernel:

$$v^{\rho_1}_{x}(r_1, r_2) = -\frac{1}{2} r_1^{-1} \rho_1(r_1, r_2).$$

(48)

By generalizing Eq. (46), we define a generalized, or exact, Fock operator $\hat{\mathcal{F}}$, where the kernel of this operator is

$$\mathcal{F}_{\rho_1}(r_1, r_2) = \frac{\delta E_v[\rho_1]}{\delta\rho_1(r_2, r_1)} = F_{\rho_1}(r_1, r_2) + v^{\rho_1}_{co}(r_1, r_2) + v^{\rho_1}_{ec}(r_1, r_2),$$

(49)
and the correlation operator $\hat{v}_{co}^{\rho_1}$ and external-correlation operator $\hat{v}_{ec}^{\rho_1}$ are defined by their kernels:

$$v_{co}^{\rho_1}(r_1, r_2) = \frac{\delta E_{co}[\rho_1,v]}{\delta \rho_1(r_2, r_1)}, \quad (50)$$

$$v_{ec}^{\rho_1}(r_1, r_2) = \frac{\delta \left( \int dr_3 v(r_3) \tilde{\rho}_c (r_3) \right)}{\delta \rho_1(r_2, r_1)}. \quad (51)$$

Minimizing the functional $E_v$, given by Eq. (39), subject to the constraints given by Eqs. (44) and (45), is very similar to the corresponding Hartree–Fock derivation and the derivation for reference-state one-particle density matrix theory. The only difference being that the spin variable has been eliminated, and we have a factor of two appearing in Eq. (45). Therefore, we only state the main results, i.e., this minimization yields the exact electronic energy $E_n$ for the interacting state, as given by Eq. (22), where the one-particle density-matrix $\rho_1$ satisfies the following conditions:

$$\hat{\kappa}_1 \hat{\rho}_1 \hat{\kappa}_1 = 0, \quad (52)$$

$$\hat{\rho}_1 \hat{\kappa}_1 \hat{\rho}_1 = 0, \quad (53)$$

and the kernels of the operators $\hat{\rho}_1$ and $\hat{\kappa}_1$ are given by the terms on the right side of Eq. (11); also, as mentioned previously, $\rho_1$ yields the exact density $n$ of the interacting state $\Psi_n$. Using Eqs. (52) and (53), it is readily shown that $\hat{\kappa}_1$ and $\hat{\rho}_1$ commute:

$$\left[ \hat{\kappa}_1, \hat{\rho}_1 \right] = 0, \quad (54)$$

and the occupied orbitals satisfy a generalized Hartree–Fock equation:

$$\hat{F}_{\rho_1} \chi_w = \sum_{x \in \rho_1} \varepsilon_{xw} \chi_x, \quad (55)$$

where the notation $x \in \rho_1$ indicates a summation over the occupied orbitals from the determinantal state $|\rho_1\rangle$; $\chi_w$ is also an occupied orbital from $|\rho_1\rangle$. Furthermore, we can choose orbitals that diagonalize the matrix $\varepsilon_{xw}$, yielding exact, canonical Hartree–Fock equations:

$$\left( -\frac{1}{2} \nabla^2 + v + v_j^n + \hat{v}_x^{\rho_1} + \hat{v}_{co}^{\rho_1} + \hat{v}_{ec}^{\rho_1} \right) \chi_w = \varepsilon_w \chi_w, \quad \chi_w \in \rho_1, \quad (56)$$

where the Coulomb operator is defined by

$$v_j^\rho(r_1) \chi(r_1) = \int dr_2 r_{12}^{-1} \rho(r_2) \chi(r_1), \quad (57)$$
and we have

$$\varrho_1(\mathbf{r}, \mathbf{r}) = n(\mathbf{r}).$$  \hfill (58)

Equation (56) is also satisfied by the canonical excited orbitals.

For later use, we also mention that the determinantal states $|\varrho_1\rangle$ satisfy the following noninteracting Schrödinger equation:

$$\sum_{i=1}^{N} \hat{F}_{\varrho_1}(\mathbf{r}_i)|\varrho_1\rangle = 2 \left( \sum_w \varepsilon_w \right) |\varrho_1\rangle. \hfill (59)$$

Appendix B presents an alternative way of partitioning the energy functional that differs from Eq. (59).

V. CONVERSION OF THE NONLOCAL POTENTIAL INTO A LOCAL ONE

As mentioned previously, our energy functionals $E_v$ are implicit functionals of the non-interacting density $\rho_s$. Hence, any one-particle density-matrix that yields the interacting density minimizes our energy functional, i.e., we have

$$E_n = E_v[\varrho_1] = E_v[\varrho_1'] = E_v[\varrho_1''] \cdots, \hfill (60)$$

where

$$n(\mathbf{r}) = \varrho_1(\mathbf{r}, \mathbf{r}) = \varrho_1'(\mathbf{r}, \mathbf{r}) = \varrho_1''(\mathbf{r}, \mathbf{r}) \cdots, \hfill (61)$$

and there are other solutions besides Eq. (56), e.g,

$$\hat{F}_{\varrho_1'} \chi_w = \left( -\frac{1}{2} \nabla^2 + v + v^n_j + \hat{w}_{\varrho_1'} \right) \chi_w = \varepsilon_w \chi_w, \quad \chi_w \in \varrho_1', \hfill (62)$$

where the nonlocal potential $\hat{w}_{\rho_1}$ is given by

$$\hat{w}_{\rho_1} = \hat{v}_{\varrho_1}^{\rho_1} + \hat{v}_{\varrho_1'}^{\rho_1} + \hat{v}_{\varrho_1''}^{\rho_1}. \hfill (63)$$

Assuming $n$ is a noninteracting $v$-representable density, there exist a noninteracting state, say $|\varphi_1\rangle$, that has $n$ as its density:

$$n(\mathbf{r}) = \varphi_1(\mathbf{r}, \mathbf{r}). \hfill (64)$$
and this determinant—assuming it is a closed-shell determinant—is the ground-state solution of the following noninteracting Schrödinger equation:

\[
\sum_{i=1}^{N} \hat{f}(r_i)|\varphi_1\rangle = 2 \left( \sum_{w} \epsilon_w \right) |\varphi_1\rangle,
\]

where

\[
\hat{f} = -\frac{1}{2} \nabla^2 + v_s,
\]

and \(v_s\) is a local potential. Therefore, the canonical occupied orbitals from \(|\varphi_1\rangle\) satisfy the following one-particle Schrödinger equation:

\[
\hat{f} \phi_w = \left( -\frac{1}{2} \nabla^2 + v + v^n_j + v_{xc} \right) \phi_w = \epsilon_w \phi_w, \quad \phi_w \in \varphi_1,
\]

where with no loss of generality, we have required \(v_s\) to be defined by

\[
v_s = v + v^n_j + v_{xc}.
\]

By definition, or using Eqs. (60), (61), and (64), \(\varphi_1\) is a one-particle density matrix that minimizes our energy functional:

\[
\mathcal{E}_n = E_v[\varphi_1],
\]

and, therefore, \(\varphi_1\) also satisfies Eq. (59):

\[
\sum_{i=1}^{N} \hat{F}_{\varphi_1}(r_i)|\varphi_1\rangle = 2 \left( \sum_{w} \epsilon_w \right) |\varphi_1\rangle.
\]

Hence, it follows from Eqs. (65) and (70) that \(|\varphi_1\rangle\) is an eigenstate of two different noninteracting Hamiltonians. By comparing Eq. (62) and (67) with \(g'_1 = \varphi_1\), we see that the two operators, \(\hat{F}_{\varphi_1}\) and \(\hat{f}\), are identical, except that \(\hat{F}_{\varphi_1}\) contains the nonlocal operator \(\hat{w}_{\varphi_1}\) and \(\hat{f}\) contains the local potential \(v_{xc}\). Furthermore, the occupied orbitals from Eq. (62) and (67) with \(g'_1 = \varphi_1\) may differ by a unitary transformation, but they yield the same one-particle density matrix:

\[
\varphi_1(r_1, r_2) = 2 \sum_{w \in \varphi_1} \chi_w(r_1) \chi_w^*(r_2) = 2 \sum_{w \in \varphi_1} \phi_w(r_1) \phi_w^*(r_2).
\]

Using the approach by Sala and Görling [26], and Eqs. (65), (70), (62) and (67), but permitting the orbitals to be complex, it is readily demonstrated that \(v_{xc}\) is given by

\[
v_{xc}(r) = \frac{1}{2n(r)} \int d\mathbf{r} \left[ 2w(\mathbf{r}, \mathbf{r}) \varphi_1(\mathbf{r}, \mathbf{r}_1) - \varphi_1(\mathbf{r}, \mathbf{r}_1) \int d\mathbf{r}_2 \varphi_1(\mathbf{r}_2, \mathbf{r}) w(\mathbf{r}_1, \mathbf{r}_2) + \varphi_1(\mathbf{r}, \mathbf{r}_1) \varphi_1(\mathbf{r}, \mathbf{r}_1) v_{xc}(\mathbf{r}_1) \right].
\]

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By substituting \( v_{xc} \) repeatedly on the right side we can obtain an expansion for \( v_{xc} \):

\[
v_{xc}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})} \left[ 2w(\mathbf{r}_1, \mathbf{r})\varphi_1(\mathbf{r}, \mathbf{r}_1) - \varphi_1(\mathbf{r}, \mathbf{r}_1)\varphi_1(\mathbf{r}_2, \mathbf{r})w(\mathbf{r}_1, \mathbf{r}_2) \right]
\]

\[
+ \varphi_1(\mathbf{r}_1, \mathbf{r})\varphi_1(\mathbf{r}, \mathbf{r}_1) \left\{ \frac{1}{n(\mathbf{r}_1)} \left[ w(\mathbf{r}_2, \mathbf{r}_1)\varphi_1(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2}\varphi_1(\mathbf{r}_1, \mathbf{r}_2)\varphi_1(\mathbf{r}_3, \mathbf{r}_1)w(\mathbf{r}_2, \mathbf{r}_3) \right] \right\}
\]

\[
+ \varphi_1(\mathbf{r}_1, \mathbf{r})\varphi_1(\mathbf{r}, \mathbf{r}_1) \left[ \frac{1}{2n(\mathbf{r}_1)} \varphi_1(\mathbf{r}_2, \mathbf{r}_1)\varphi_1(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2n(\mathbf{r}_2)}w(\mathbf{r}_3, \mathbf{r}_2)\varphi_1(\mathbf{r}_2, \mathbf{r}_3) \right] \right] + \cdots \right],
\]

where there are integrations over the dummy variables \( \mathbf{r}_1, \mathbf{r}_2 \) and \( \mathbf{r}_3 \). The leading term of Eq. (73) is the Slater potential \([45, 46, 47]\); this term also appears within the Krieger–Li–Iafrate (KLI) approximation of the optimized potential method \([19, 22, 47, 48]\).

The orbitals \( \phi_w \) satisfying Eq. (67) are the Kohn–Sham orbitals \([8]\); \( |\varphi_1\rangle \) is the Kohn–Sham noninteracting state. However, \( \hat{f} \) differs from the Kohn–Sham operator, since, in addition to depending explicitly \( \varphi_1 \), instead of \( n \), \( \hat{f} \) depends explicitly on the external potential \( v \) from the interacting Hamiltonian \( \hat{H}_v \). Furthermore, the external-correlation operator \( \hat{v}_{ec}^{\rho_1} \) does not appear in Kohn–Sham formalism. In addition, unlike the original Kohn–Sham approach \([8]\), the \( N \)-representability problem does not arise, nor the need to introduce a constraint-search definition \([14, 15, 16, 17]\) to avoid this problem.

In our derivation we have assumed that \( |\varphi_1\rangle \) is a ground state solution of Eq. (65). However, the results may also be valid if \( |\varphi_1\rangle \) is an excited state solution, since the Sala and Görling approach may also be valid in this case.

VI. CONVERSION OF THE ONE-PARTICLE DENSITY-MATRIX FUNCTIONALS INTO DENSITY FUNCTIONALS

For noninteracting states, the wave function is determined by the one-particle density matrix. For certain closed-shell determinantal states, we can write \( \rho_1[\rho_s] \), where this functional includes all densities that are noninteracting \( v \)-representable, but it is also defined for all \( N \)-representable densities. Using the constraint search approach \([14, 15, 16, 17]\), for a given density, say \( \rho' \), the functional \( \rho_1[\rho'] \) yields the one-particle density matrix that minimizes the expectation value of the kinetic energy:

\[
\text{Min}_{\rho_1 \to \rho'} \langle \rho_1|\hat{T}|ho_1\rangle = \langle \rho_1[\rho']|\hat{T}|ho_1[\rho']\rangle,
\]

where the search is over all determinantal states that have a density of \( \rho' \).
Substituting $\rho_1[\rho]$ into $E_{co}$ of Eq. (37) gives

$$E_v[\rho_1] = \int d\mathbf{r}_1 \left[ -\frac{1}{2} \nabla^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2=\mathbf{r}_1} + \int d\mathbf{r} v(\mathbf{r}) \rho_1(\mathbf{r})$$

$$+ E_J[\rho_1] + E_X[\rho] + E_{co}[\rho, v] + \int d\mathbf{r} v(\mathbf{r}) \tilde{\rho}_c(\mathbf{r}), \ \rho \rightarrow \rho_1, (75)$$

where, using $\rho_1[\rho]$, the last term is also a functional of $v$ and $\rho$. This equation differs from the Kohn–Shan density functional, since the correlation-energy functional depends on the external potential $v$, and the last term does not appear in the Kohn–Sham approach. However, mathematically speaking, the minimization of Eq. (75) follows the same procedure as in the Kohn–Sham method, yielding

$$\hat{f}\phi_w = \left( -\frac{1}{2} \nabla^2 + v + v^n_x + v^n_{co} + v^n_{ec} \right) \phi_w = \epsilon_w \phi_w, \ \phi_w \in \varphi_1,$$

where the local potentials are given by

$$v^n_x(\mathbf{r}) = \frac{\delta E_x[\rho, v]}{\delta \rho(\mathbf{r})}, \quad (77)$$

$$v^n_{co}(\mathbf{r}) = \frac{\delta E_{co}[\rho, v]}{\delta \rho(\mathbf{r})}, \quad (78)$$

$$v^n_{ec}(\mathbf{r}) = \frac{\delta \left( \int d\mathbf{r}_1 v(\mathbf{r}_1) \tilde{\rho}_c(\mathbf{r}_1) \right)}{\delta \rho(\mathbf{r})}. \quad (79)$$

Assuming the density $n$ from the interacting state is noninteracting $v$-representable, we have

$$E_v[n] = \mathcal{E}_n, \ n \text{ is noninteracting } v\text{-representable}. \quad (80)$$

Note that Eq. (75) is a valid energy functional only when the one-particle density matrix that enters the first term is the same one generated by the functional $\rho_1[\rho]$; this is the case, at least when $\rho$ is non-interacting $v$-representable.

**APPENDIX A: A POSSIBLE CHOICE FOR $g_{\rho C}$**

The electron-electron repulsion operator is spin-free and can be written as

$$\hat{V}_{ee} = \frac{1}{2} \sum_{ij} (ij|_{12}^{-1}|kl) \hat{E}_{ijkl}. \quad (A1)$$
where the two-electron integral is written in chemist’s notation \[32\] and the two-electron spin-adapted excitation-operator is given by Eq. \([8]\). This operator can also be written as

\[
\hat{V}_{ee} = \int \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \hat{\Gamma}_2(\mathbf{r}_2, \mathbf{r}_1),
\]

(A2)

where the pair-function operator is given by

\[
\hat{\Gamma}_2(\mathbf{r}_2, \mathbf{r}_1) = \frac{1}{2} \sum_{ijkl} \chi_j(\mathbf{r}_1) \chi_i(\mathbf{r}_1) \chi_l(\mathbf{r}_2) \chi_k(\mathbf{r}_2) \hat{E}_{ijkl},
\]

(A3)

and this operator yields the diagonal elements of the spinless two-particle density matrix as the expectation value. Writing this operator in normal-ordered form \([27, 40, 41, 42]\) with respect to the vacuum state \(|\rho_1\rangle\), we have

\[
\hat{V}_{ee} = \int \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \rho_2(\mathbf{r}_2, \mathbf{r}_1)\rho_1 + \int \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \rho_s(\mathbf{r}_2)\hat{\Gamma}(\mathbf{r}_1)\rho_s
\]

\[
- \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \rho_1(\mathbf{r}_2, \mathbf{r}_1)\hat{\Gamma}(\mathbf{r}_1, \mathbf{r}_2)\rho_1 + \int \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} \hat{\Gamma}_2(\mathbf{r}_2, \mathbf{r}_1)\rho_1,
\]

(A4)

where, examining each term in turn, from the first term we have

\[
\rho_2(\mathbf{r}_2, \mathbf{r}_1)\rho_1 = \frac{1}{2}\rho_s(\mathbf{r}_2)\rho_s(\mathbf{r}_1) - \frac{1}{4}\rho_1(\mathbf{r}_2, \mathbf{r}_1)\rho_1(\mathbf{r}_1, \mathbf{r}_2),
\]

(A5)

and this function is the diagonal elements of the spinless second-order density matrix of the determinantal state \(|\rho_1\rangle\). From the second term, we have

\[
\hat{\Gamma}(\mathbf{r})_{\rho_s} = \sum_{ij} \chi_j(\mathbf{r})\chi_i(\mathbf{r})\{\hat{E}_{ij}\}_{\rho_1} \rightarrow \rho_s,
\]

(A6)

and this operator is the one-body portion of the density operator, where the density operator is given by

\[
\hat{\Gamma}(\mathbf{r}) = \sum_{ij} \chi_j(\mathbf{r})\chi_i(\mathbf{r})\hat{E}_{ij}.
\]

(A7)

Note that we can write

\[
\hat{\Gamma}(\mathbf{r})_{\rho_s} = \hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}),
\]

(A8)

indicating that \(\hat{\Gamma}(\mathbf{r})_{\rho_s}\) is determined by \(\rho_s\) and not by \(\rho_1\); two different one-particle density matrices that yield the same density have the same \(\hat{\Gamma}(\mathbf{r})_{\rho_s}\).

Returning to Eq. \((A4)\), from the third term we have

\[
\hat{\Gamma}(\mathbf{r}_1, \mathbf{r}_2)\rho_1 = \sum_{ij} \chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\{\hat{E}_{ij}\}_{\rho_1},
\]

(A9)
and this operator is the one-body portion of the one-particle density-matrix operator, given by

$$\hat{\Gamma}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} \chi_j(\mathbf{r}_1)\chi_i^*(\mathbf{r}_2) \hat{E}_{ij} = \rho_1(\mathbf{r}_1, \mathbf{r}_2) + \hat{\Gamma}(\mathbf{r}_1, \mathbf{r}_2)_{\rho_1}. \quad (A10)$$

And from the last term, we have

$$\hat{\Gamma}_2(\mathbf{r}_2, \mathbf{r}_1)_{\rho_1} = \frac{1}{2} \sum_{ijkl} \chi_j(\mathbf{r}_1)\chi_i^*(\mathbf{r}_1)\chi_l^*(\mathbf{r}_2)\chi_k^*(\mathbf{r}_2) \{\hat{E}_{ijkl}\}_{\rho_1}, \quad (A11)$$

and this operator is the two-body portion of the pair-function operator, Eq. (A3).

To obtain a slight modification of $\hat{V}_{ee}$, we replace the determinantal state density $\rho_s$, that appears in Eq. (A4), with the exact density $n$, giving

$$\hat{V}^{\rho_1}_{ee} = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_2(\mathbf{r}_2, \mathbf{r}_1)_{\rho_1} + \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_2(\mathbf{r}_2, \mathbf{r}_1)_{\rho_1} \hat{\Gamma}(\mathbf{r}_1)_{\rho_s}$$

$$- \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_1(\mathbf{r}_2, \mathbf{r}_1)\hat{\Gamma}(\mathbf{r}_1, \mathbf{r}_2)_{\rho_1} + \int \int d\mathbf{r}_1 d\mathbf{r}_2 \hat{\Gamma}_2(\mathbf{r}_2, \mathbf{r}_1)_{\rho_1}, \quad (A12)$$

and this operator can also be written as

$$\hat{V}^{\rho_1}_{ee} = \hat{V}_{ee} + \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_c(\mathbf{r}_2) \left(\hat{\Gamma}(\mathbf{r}_1) - \rho_s(\mathbf{r}_1)\right), \quad (A13)$$

Replacing $\hat{V}_{ee}$ by $\hat{V}^{\rho_1}_{ee}$ within the Hamiltonian operator, we have obtain a trial Hamiltonian:

$$\hat{H}_{v\rho_1} = \hat{H}_v + \lambda \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_c(\mathbf{r}_2) \left(\hat{\Gamma}(\mathbf{r}_1) - \rho_s(\mathbf{r}_1)\right), \quad (A14)$$

where $\lambda$ is unity, but it can be permitted to be any constant value. Comparing this equation with Eq. (26) yields Eq. (30).

**APPENDIX B: ENERGY FUNCTIONAL USING INTERMEDIATE NORMALIZATION**

Using Eq. (26), our energy functional $E_v$, Eq. (21), can be also be written as

$$E_v[\rho_1] = \frac{\langle \tilde{\Psi}_{\rho_1} | \hat{H}_{v\rho_1} | \tilde{\Psi}_{\rho_1} \rangle}{\langle \tilde{\Psi}_{\rho_1} | \tilde{\Psi}_{\rho_1} \rangle} - \lambda \int d\mathbf{r} g_{\rho_c}(\mathbf{r}) \left(\hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r})\right). \quad (B1)$$

By requiring our trial wave functions to satisfy intermediate normalization,

$$\langle \rho_1 | \tilde{\Psi}_{\rho_1} \rangle = 1, \quad (B2)$$
we have

\[ E_v[\rho_1] = \langle \rho_1 | \hat{H}_{vp_1} | \tilde{\Psi}_{vp_1} \rangle - \lambda \int d\mathbf{r} \, g_{\rho_c}(\mathbf{r}) \left( \hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}) \right). \]  

(B3)

This form suggests the following partitioning:

\[ E_v[\rho_1] = \mathcal{E}_1[\rho_1, v] + \tilde{E}_{co}[\rho_1, v] - \lambda \int d\mathbf{r} \, g_{\rho_c}(\mathbf{r}) \left( \hat{\Gamma}(\mathbf{r}) - \rho_s(\mathbf{r}) \right), \]  

(B4)

where \( \tilde{E}_{co} \) is the correlation-energy (functional) of the trial wave function:

\[ \tilde{E}_{co}[\rho_1, v] = \langle \rho_1 | \hat{H}_{vp_1} | \tilde{\Psi}^Q_{vp_1} \rangle, \]  

(B5)

and the correlation function \( \tilde{\Psi}^Q_{vp_1} \) is defined by

\[ |\tilde{\Psi}_{vp_1}\rangle = |\rho_1\rangle + |\tilde{\Psi}^Q_{vp_1}\rangle. \]  

(B6)

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