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2016

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Exact expressions for the Kohn–Sham exchange-correlation potential in terms of wave-function-based quantities

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(Dated: December 1, 2015)

Abstract

Several workers have deduced various exact expressions for the Kohn–Sham exchange-correlation potential in terms of quantities computable from the interacting and noninteracting wave functions of the system. We show that all these expressions can be obtained by one general method in which the interacting N-electron wave function is expanded in products of one- and $(N-1)$-electron functions. Different expressions correspond to different choices of the latter functions. Our analysis unifies and clarifies the previously proposed exact treatments of the exchange-correlation potential, and suggests new ways of expressing this quantity.

Keywords: density-functional theory, exchange-correlation potential, reduced density matrices, generalized Fock operator, Dyson orbitals

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I. INTRODUCTION

The Kohn–Sham density-functional scheme [1] involves a one-electron Schrödinger equation with the effective multiplicative potential $v_s(\mathbf{r}) = v(\mathbf{r})+v_{\mathrm{H}}(\mathbf{r})+v_{\mathrm{XC}}(\mathbf{r})$, where $v(\mathbf{r})$ is the external potential, $v_{\mathrm{H}}(\mathbf{r})$ is the electrostatic potential of the electron density $\rho(\mathbf{r})$, and $v_{\mathrm{XC}}(\mathbf{r})$ is the exchange-correlation potential. The last quantity is defined as $v_{\mathrm{XC}}(\mathbf{r}) = \delta E_{\mathrm{XC}}[\rho]/\delta\rho(\mathbf{r})$, where $E_{\mathrm{XC}}[\rho]$ is the exchange-correlation energy functional. The potential $v_{\mathrm{XC}}([\rho];\mathbf{r})$ is itself an unknown functional of $\rho(\mathbf{r})$, no less complicated than $E_{\mathrm{XC}}[\rho]$.

To develop accurate approximations to $E_{\mathrm{XC}}[\rho]$ and $v_{\mathrm{XC}}(\mathbf{r})$, it is essential to know what the exact exchange-correlation potentials look like. An accurate $v_{\mathrm{XC}}(\mathbf{r})$ can be generated numerically by fitting $v_s(\mathbf{r})$ to a given ground-state $\rho(\mathbf{r})$ for a known $v(\mathbf{r})$ [2–8] or by the optimized effective potential (OEP) method [9–11]. It is also possible to write down the exact $v_{\mathrm{XC}}(\mathbf{r})$ for a given system as a mathematical expression involving quantities that can be extracted from the interacting and the corresponding noninteracting (Kohn–Sham) wave functions. Baerends and co-workers [12–15] devised the first of such expressions and used it extensively for interpretive purposes [13–21]. The simplest formula for $v_{\mathrm{XC}}(\mathbf{r})$ obtained by the Baerends group involves one- and two-electron reduced density matrices (1- and 2-RDMs) and Dyson orbitals [19]. Other exact expressions for $v_{\mathrm{XC}}(\mathbf{r})$ involving at most the 2-RDM were devised by Ryabinkin *et al.* [22] and Cuevas-Saavedra *et al.* [23]. Either of the last two expressions enables one to generate [22, 23] accurate exchange-correlation potentials directly from many-electron wave functions in a manner that is numerically more robust than potential fitting and OEP techniques.

In this work, we show that the various exact formulas for $v_{\mathrm{XC}}(\mathbf{r})$ proposed so far are special cases of one general expression, which we derive in a transparent new way. All these formulas contain the same types of ingredients and differ only by how these ingredients are expressed. Our derivation clarifies the relationship between various exact treatments of $v_{\mathrm{XC}}(\mathbf{r})$ and suggests other possible ways of expressing this quantity.

II. PRELIMINARIES

For simplicity, we restrict our discussion to singlet ground states described with closed-shell Kohn–Sham determinants. To derive an exact formula for $v_{\mathrm{XC}}(\mathbf{r})$, we will need two

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expressions for the ground-state electron density in terms of one-electron functions: one from the Kohn–Sham scheme, the other from the wave-function method. In the Kohn–Sham scheme, the electron density is given by

$$\rho^{\mathrm{KS}}(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N} |\phi_i(\mathbf{x})|^2, \tag{1}$$

where σ is the spin variable, $\mathbf{x} = (\mathbf{r}, \sigma)$ is the collective electron coordinate, and $\phi_i(\mathbf{x})$ are solutions to the Kohn–Sham eigenvalue problem

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{XC}}(\mathbf{r})\right] \phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x}). \tag{2}$$

In the wave-function method, there are many different ways to represent the ground-state density in terms of one-electron functions. We will now derive a general formula for $\rho^{\mathrm{WF}}(\mathbf{r})$ covering a broad class of such expressions.

Consider the ground state of a system of N electrons described by the normalized electronic wave function Ψ^N which satisfies the stationary Schrödinger equation

$$\hat{H}^N \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E^N \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{3}$$

where the Hamiltonian is

$$\hat{H}^N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 + v(\mathbf{r}_i)\right] + \sum_{i<j}^{N} r_{ij}^{-1}. \tag{4}$$

Let $\{\theta_k^{N-1}\}$ be a full set of orthogonal (not necessarily normalized) antisymmetric $(N-1)$-electron functions, such that

$$\langle \theta_l^{N-1} | \theta_k^{N-1} \rangle = \delta_{lk} D_k. \tag{5}$$

The requirement that $\{\theta_k^{N-1}\}$ be a "full set" means that it should span the full configuration interaction (FCI) space of $(N-1)$-electron wave functions for the same system. Examples of such full sets include the set of all eigenfunctions of the $(N-1)$-electron Hamiltonian and the set of all $(N-1)$-electron Slater determinants that can be constructed from the same one-electron basis as Ψ^N. Under these conditions, Ψ^N can be expanded as

$$\begin{aligned} &\Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \\ &= \frac{1}{\sqrt{N}} \sum_k \psi_k(\mathbf{x}_1) \theta_k^{N-1}(\mathbf{x}_2, \ldots, \mathbf{x}_N), \end{aligned} \tag{6}$$

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where

$$\psi_k(\mathbf{x}_1) = \frac{\sqrt{N}}{D_k} \int \theta_k^{N-1*}(\mathbf{x}_2, \ldots, \mathbf{x}_N) \times \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \cdots d\mathbf{x}_N. \quad (7)$$

The properties of the one-electron functions $\psi_k(\mathbf{x}_1)$ are determined by the choice of $\{\theta_k^{N-1}\}$. In general, the $\psi_k(\mathbf{x}_1)$ are linearly dependent and not normalized to 1.

Recall that the density is related to the total electronic wave function by

$$\rho^{\mathrm{WF}}(\mathbf{r}_1) = N \sum_\sigma \int |\Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2\, d\mathbf{x}_2 \cdots d\mathbf{x}_N. \quad (8)$$

Substituting Eq. (6) into Eq. (8) and using Eq. (5) we obtain

$$\rho^{\mathrm{WF}}(\mathbf{r}) = \sum_\sigma \sum_l D_l |\psi_l(\mathbf{x})|^2, \quad (9)$$

where the summation is over all $\psi_l(\mathbf{x})$.

For the purposes of our derivation, we will also need an eigenvalue-type equation satisfied by the functions $\psi_k(\mathbf{x})$. To find such an equation, we draw on the work by Morrell *et al.* [24] and by Katriel and Davidson [25] and start by partitioning the Hamiltonian as

$$\hat{H}^N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = -\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) + \sum_{j>1}^{N} r_{1j}^{-1} + \hat{H}^{N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N), \quad (10)$$

where $\hat{H}^{N-1}$ is of the same type as Eq. (4). We insert Eqs. (6) and (10) into Eq. (3), multiply from the left by $\theta_l^{N-1*}(\mathbf{x}_2, \ldots, \mathbf{x}_N)$, integrate over $\mathbf{x}_2$ through $\mathbf{x}_N$ and use the orthogonality of the θ_k^{N-1} to write the result as

$$D_l \left[-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1)\right] \psi_l(\mathbf{x}_1) + \sum_k w_{lk}(\mathbf{x}_1)\psi_k(\mathbf{x}_1) = \sum_k \lambda_{lk}\psi_k(\mathbf{x}_1), \quad (11)$$

where

$$w_{lk}(\mathbf{x}_1) = \sum_{j>1}^{N} \int r_{1j}^{-1} \theta_l^{N-1*}(\mathbf{x}_2, \ldots, \mathbf{x}_N) \times \theta_k^{N-1}(\mathbf{x}_2, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (12)$$

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and

$$\lambda_{lk} = \langle \theta_l^{N-1} | E^N - \hat{H}^{N-1} | \theta_k^{N-1} \rangle. \tag{13}$$

We interpret Eq. (11) as a reduced Schrödinger equation. The solutions of this equation, $\psi_k(\mathbf{x})$, give the ground-state electron density *via* Eq. (9). Therefore, Eqs. (9) and (11) may be viewed as wave-function counterparts of the Kohn–Sham equations. We will see below that Eq. (11) can be further simplified for certain choices of the functions θ_k^{N-1}.

III. DERIVATION

The starting point for our derivation of a general formula for $v_{\mathrm{XC}}(\mathbf{r})$ is the equality

$$\rho^{\mathrm{KS}}(\mathbf{r}) = \rho^{\mathrm{WF}}(\mathbf{r}), \tag{14}$$

where $\rho^{\mathrm{KS}}(\mathbf{r})$ and $\rho^{\mathrm{WF}}(\mathbf{r})$ are given by Eqs. (1) and (9), respectively. This equality is valid by the very construction of the Kohn–Sham scheme [1].

Let us apply the Laplacian operator to both sides of Eq. (14),

$$\nabla^2 \rho^{\mathrm{KS}}(\mathbf{r}) = \nabla^2 \rho^{\mathrm{WF}}(\mathbf{r}). \tag{15}$$

Substituting Eqs. (1) and (9) into Eq. (15) we have, after dividing the result by 4,

$$\begin{aligned} &\frac{1}{2}\Re\left[\sum_\sigma \sum_{i=1}^N \phi_i^*(\mathbf{x}) \nabla^2 \phi_i(\mathbf{x})\right] + \tau^{\mathrm{KS}}(\mathbf{r}) \\ &= \frac{1}{2}\Re\left[\sum_\sigma \sum_l D_l \psi_l^*(\mathbf{x}) \nabla^2 \psi_l(\mathbf{x})\right] + \tau^{\mathrm{WF}}(\mathbf{r}), \end{aligned} \tag{16}$$

where

$$\tau^{\mathrm{KS}}(\mathbf{r}) = \frac{1}{2}\sum_\sigma \sum_{i=1}^N |\nabla \phi_i(\mathbf{x})|^2 \tag{17}$$

and

$$\tau^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{2}\sum_\sigma \sum_l D_l |\nabla \psi_l(\mathbf{x})|^2. \tag{18}$$

The quantity $\tau^{\mathrm{KS}}(\mathbf{r})$ is the electronic kinetic energy density of the noninteracting Kohn–Sham system, and $\tau^{\mathrm{WF}}(\mathbf{r})$ is the electronic kinetic energy density of the real (interacting) system.

Now from Eq. (2)

$$-\frac{1}{2}\nabla^2 \phi_i(\mathbf{x}) = \left[\epsilon_i - v(\mathbf{r}) - v_{\mathrm{H}}(\mathbf{r}) - v_{\mathrm{XC}}(\mathbf{r})\right] \phi_i(\mathbf{x}) \tag{19}$$

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and from Eq. (11)

$$-\frac{D_l}{2}\nabla^2\psi_l(\mathbf{x}) = \sum_k \lambda_{lk}\psi_k(\mathbf{x}) - D_l v(\mathbf{r})\psi_l(\mathbf{x}) - \sum_k w_{lk}(\mathbf{x})\psi_k(\mathbf{x}). \quad (20)$$

Insert Eqs. (19) and (20) into Eq. (16) and use Eqs. (1) and (9) to simplify the result. After dividing by $\rho^{\text{WF}} = \rho^{\text{KS}}$ and rearranging the terms we obtain

$$v_{\text{XC}}(\mathbf{r}) = v_{ee}(\mathbf{r}) - v_{\text{H}}(\mathbf{r}) + \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}) + \frac{\tau^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})}, \quad (21)$$

where

$$v_{ee}(\mathbf{r}) = \frac{1}{\rho^{\text{WF}}(\mathbf{r})}\sum_\sigma\sum_{kl} w_{lk}(\mathbf{x})\psi_l^*(\mathbf{x})\psi_k(\mathbf{x}), \quad (22)$$

$$\bar{\epsilon}^{\text{KS}}(\mathbf{r}) = \frac{1}{\rho^{\text{KS}}(\mathbf{r})}\sum_\sigma\sum_{i=1}^{N}\epsilon_i|\phi_i(\mathbf{x})|^2, \quad (23)$$

and

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) = \frac{1}{\rho^{\text{WF}}(\mathbf{r})}\sum_\sigma\sum_{kl}\lambda_{lk}\psi_l^*(\mathbf{x})\psi_k(\mathbf{x}). \quad (24)$$

Observe that by using Eqs. (6) and (12) we can rewrite Eq. (22) as

$$\begin{aligned} v_{ee}(\mathbf{r}_1) &= \frac{N}{\rho^{\text{WF}}(\mathbf{r}_1)}\sum_{\sigma_1}\sum_{j>1}^{N}\int r_{1j}^{-1}|\Psi^N|^2\,d\mathbf{x}_2\cdots d\mathbf{x}_N \\ &= \frac{N(N-1)}{\rho^{\text{WF}}(\mathbf{r}_1)}\sum_{\sigma_1}\int r_{12}^{-1}|\Psi^N|^2\,d\mathbf{x}_2\cdots d\mathbf{x}_N \\ &= \frac{2}{\rho^{\text{WF}}(\mathbf{r}_1)}\int\frac{P(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\,d\mathbf{r}_2, \end{aligned} \quad (25)$$

where the quantity

$$P(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\sigma_1\sigma_2}\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2), \quad (26)$$

called the pair function, is the spin-free diagonal part of the 2-RDM

$$\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \frac{N(N-1)}{2}\int\Psi^N(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N) \times \Psi^{N*}(\mathbf{x}_1',\mathbf{x}_2',\mathbf{x}_3,\ldots,\mathbf{x}_N)\,d\mathbf{x}_3\cdots d\mathbf{x}_N. \quad (27)$$

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Moreover, one can always write the pair function as

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho^{\mathrm{WF}}(\mathbf{r}_1)\left[\rho^{\mathrm{WF}}(\mathbf{r}_2) + \rho^{\mathrm{WF}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2)\right], \tag{28}$$

which defines $\rho^{\mathrm{WF}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2)$, the exchange-correlation hole. Then Eq. (25) becomes

$$v_{ee}(\mathbf{r}_1) = v_{\mathrm{H}}(\mathbf{r}_1) + v^{\mathrm{WF}}_{\mathrm{S}}(\mathbf{r}_1), \tag{29}$$

where

$$v^{\mathrm{WF}}_{\mathrm{S}}(\mathbf{r}_1) = \int \frac{\rho^{\mathrm{WF}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_2 \tag{30}$$

is the Slater exchange-correlation-charge potential. Substituting Eq. (29) into Eq. (21) we obtain

$$v_{\mathrm{XC}}(\mathbf{r}) = v^{\mathrm{WF}}_{\mathrm{S}}(\mathbf{r}) + \bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}) - \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) + \frac{\tau^{\mathrm{WF}}(\mathbf{r})}{\rho^{\mathrm{WF}}(\mathbf{r})} - \frac{\tau^{\mathrm{KS}}(\mathbf{r})}{\rho^{\mathrm{KS}}(\mathbf{r})}. \tag{31}$$

Equation (31) is the desired exact expression for $v_{\mathrm{XC}}(\mathbf{r})$. Next we consider several variants of this general formula.

IV. SPECIAL CASES

Here we show that it is the choice of the functions θ_k^{N-1} that distinguishes the previously derived expressions for the exchange-correlation potential.

A. Expression in terms of Dyson orbitals

If θ_k^{N-1} are chosen as the exact normalized eigenfunctions of the $(N-1)$-electron Hamiltonian, that is,

$$\theta_k^{N-1} = \Psi_k^{N-1}, \tag{32}$$

where

$$\hat{H}^{N-1}\Psi_k^{N-1} = E_k^{N-1}\Psi_k^{N-1}, \tag{33}$$

then the one-electron functions $\psi_k(\mathbf{x})$ are the Dyson orbitals [25],

$$\psi_k(\mathbf{x}_1) = d_k(\mathbf{x}_1) = \sqrt{N}\int \Psi_k^{N-1*}(\mathbf{x}_2, \ldots, \mathbf{x}_N) \times \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \cdots d\mathbf{x}_N. \tag{34}$$

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The Dyson orbitals are neither orthogonal nor normalized [25]. But the Ψ_k^{N-1} are normalized,

$$\langle \Psi_l^{N-1} | \Psi_k^{N-1} \rangle = \delta_{lk}, \tag{35}$$

so $D_k = 1$, and the *ab initio* expression for the electron density given by Eq. (9) becomes

$$\rho^{\mathrm{WF}}(\mathbf{r}) = \sum_{\sigma} \sum_{k} |d_k(\mathbf{x})|^2, \tag{36}$$

and the kinetic energy density of Eq. (18)

$$\tau^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{2} \sum_{\sigma} \sum_{k} |\nabla d_k(\mathbf{x})|^2. \tag{37}$$

Equation (13) simplifies to

$$\lambda_{lk} = \delta_{lk}(E^N - E_k^{N-1}) = -\delta_{lk} I_k, \tag{38}$$

where

$$I_k = E_k^{N-1} - E^N \tag{39}$$

is the ionization energy corresponding to the kth state of the ion, and then Eq. (24) assumes the form

$$\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = -\frac{1}{\rho^{\mathrm{WF}}(\mathbf{r})} \sum_{\sigma} \sum_{k=1} I_k |d_k(\mathbf{x})|^2, \tag{40}$$

where the summation is over all Dyson orbitals.

Equation (31), in which the wave-function-based quantities other than $v_{\mathrm{S}}^{\mathrm{WF}}(\mathbf{r})$ are given by Eqs. (36)–(40), is an exact formula for $v_{\mathrm{XC}}(\mathbf{r})$ in terms of the 2-RDM and Dyson orbitals. This expression was first derived by Chong *et al.* [19] using a different method. The method of Chong and co-workers and its relation to our technique will be explained in Section V.

We note that the expression for $v_{\mathrm{XC}}(\mathbf{r})$ in terms of Dyson orbitals is not practical for direct construction of exchange-correlation potentials from wave functions because Eq. (40) involves *all* Dyson orbitals of the system, computing which is not an easy task. However, the formula in terms of Dyson orbitals proves very useful for interpreting the Kohn–Sham orbital eigenvalues as approximations to vertical ionization energies [19–21].

B. Expression in terms of natural orbitals

A simpler exact expression for $v_{\mathrm{XC}}(\mathbf{r})$ containing only quantities that can be extracted from the 1- and 2-RDMs was devised recently by Cuevas-Saavedra *et al.* [23]. Recall that

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the 1-RDM is defined by

$$\gamma^{\mathrm{WF}}(\mathbf{x}_1,\mathbf{x}_1') = N \int \Psi^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) \times \Psi^{N*}(\mathbf{x}_1',\mathbf{x}_2,\ldots,\mathbf{x}_N)\, d\mathbf{x}_2 \cdots d\mathbf{x}_N, \tag{41}$$

and that the eigenfunctions of the integral operator with the kernel $\gamma^{\mathrm{WF}}(\mathbf{x}_1,\mathbf{x}_1')$ are the natural spin-orbitals,

$$\int \gamma^{\mathrm{WF}}(\mathbf{x},\mathbf{x}')\chi_k(\mathbf{x}')\, d\mathbf{x}' = n_k \chi_k(\mathbf{x}), \tag{42}$$

n_k being the natural orbital occupation numbers.

In the language of this work, the derivation of Ref. 23 amounts to setting

$$\theta_k^{N-1} = \eta_k^{N-1}, \tag{43}$$

where η_k^{N-1} are $(N-1)$-electron functions defined by

$$\eta_k^{N-1}(\mathbf{x}_2,\ldots,\mathbf{x}_N) = \sqrt{N}\int \chi_k^*(\mathbf{x}_1)\Psi^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\, d\mathbf{x}_1. \tag{44}$$

Carlson and Keller [26] studied such functions and showed that they are related to the eigenfunctions X_k^{N-1} of the $(N-1)$-electron RDM by

$$\eta_k^{N-1} = n_k^{1/2} X_k^{N-1}, \tag{45}$$

and are orthogonal,

$$\langle \eta_l^{N-1} | \eta_k^{N-1} \rangle = \delta_{lk} n_k. \tag{46}$$

The eigenfunctions X_k^{N-1} span the FCI space of $(N-1)$-electron functions if eigenfunctions with zero eigenvalues are included. The eigenfunctions X_k^{N-1} with zero eigenvalues, however, do not contribute to the expansion of Ψ^N, which is why the set of η_k^{N-1} is sufficient for expanding Ψ^N [24–26]. Thus, one can also say that the derivation of Ref. 23 amounts to choosing θ_k^{N-1} to be the eigenfunctions X_k^{N-1} scaled by $n_k^{1/2}$.

For $\theta_k^{N-1} = \eta_k^{N-1}$, we have $D_k = n_k$. Substitution of Eq. (44) into Eq. (7) then gives

$$\psi_k(\mathbf{x}_1) = \frac{1}{n_k}\int \gamma^{\mathrm{WF}}(\mathbf{x}_1,\mathbf{x}_1')\chi_k(\mathbf{x}_1')\, d\mathbf{x}_1' = \chi_k(\mathbf{x}_1). \tag{47}$$

Because the natural spin-orbitals are orthonormal,

$$\langle \chi_l | \chi_k \rangle = \delta_{lk}, \tag{48}$$

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by Eq. (9) we have

$$\rho^{\mathrm{WF}}(\mathbf{r}) = \sum_\sigma \sum_k n_k |\chi_k(\mathbf{x})|^2, \tag{49}$$

where the summation is over all natural orbitals. By Eq. (18),

$$\tau^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{2} \sum_\sigma \sum_k n_k |\nabla \chi_k(\mathbf{x})|^2, \tag{50}$$

and by Eq. (24),

$$\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{WF}}(\mathbf{r})} \sum_\sigma \sum_{kl} \lambda_{lk} \chi_l^*(\mathbf{x}) \chi_k(\mathbf{x}), \tag{51}$$

where now

$$\lambda_{lk} = \langle \eta_l^{N-1} | E^N - \hat{H}^{N-1} | \eta_k^{N-1} \rangle. \tag{52}$$

To construct $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ by Eq. (51) one needs the matrix elements λ_{lk}. Instead of using the awkward Eq. (52) for computing λ_{lk}, the method of Ref. 23 employed an alternative expression which we derive here as follows.

Observe that for $\psi_k = \chi_k$, Eq. (11) may be written as

$$\begin{aligned} & n_l \left[-\frac{1}{2} \nabla_1^2 + v(\mathbf{r}_1) \right] \chi_l(\mathbf{x}_1) \\ & + 2 \int \frac{\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2) \chi_l(\mathbf{x}_1')}{r_{12}} \, d\mathbf{x}_1' d\mathbf{x}_2 = \sum_k \lambda_{lk} \chi_k(\mathbf{x}_1), \end{aligned} \tag{53}$$

because

$$\sum_k w_{lk}(\mathbf{x}_1) \chi_k(\mathbf{x}_1) = 2 \int \frac{\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2) \chi_l(\mathbf{x}_1')}{r_{12}} \, d\mathbf{x}_1 d\mathbf{x}_2', \tag{54}$$

which can be verified by expanding the 2-RDM in natural spin-orbitals and using their orthonormality. Equation (53), which was previously derived by Löwdin [27] and by Morrell *et al.* [24], may be cast compactly as

$$\int G(\mathbf{x}, \mathbf{x}') \chi_l(\mathbf{x}') \, d\mathbf{x}' = \sum_k \lambda_{lk} \chi_k(\mathbf{x}), \tag{55}$$

where

$$\begin{aligned} G(\mathbf{x}_1, \mathbf{x}_1') = & \left[-\frac{1}{2} \nabla_1^2 + v(\mathbf{r}_1) \right] \gamma^{\mathrm{WF}}(\mathbf{x}_1, \mathbf{x}_1') \\ & + 2 \int \frac{\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2)}{r_{12}} \, d\mathbf{x}_2 \end{aligned} \tag{56}$$

with $\gamma^{\mathrm{WF}}(\mathbf{x}_1, \mathbf{x}_1') = \sum_k n_k \chi_k(\mathbf{x}_1) \chi_k^*(\mathbf{x}_1')$. Equation (55), which is a transformed version of Eq. (52), implies that

$$\lambda_{lk} = \langle \chi_l | \hat{G} | \chi_k \rangle, \tag{57}$$

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where $\hat{G}$ is an integral operator with the kernel defined by Eq. (56).

Since the kernel of $\hat{G}$ depends on the 2-RDM at most, Eq. (57) is more convenient for computing λ_{lk} than Eq. (52). The formula for $v_{\mathrm{XC}}(\mathbf{r})$ derived in Ref. 23 is a particular version of Eq. (31) in which the wave-function-based quantities are given by Eqs. (49)–(51) and (57).

There exists a connection between the expansions of Ψ^N in terms of Dyson orbitals and in terms of natural orbitals. Goscinski and Lindner [28] showed that the natural orbitals can be obtained by canonical orthonormalization of the Dyson orbitals. The set of all Dyson orbitals is overcomplete. The dimension of the space spanned by the Dyson orbitals is equal to the number of natural spin-orbitals with nonzero eigenvalues, which is equal [26] to the number of eigenfunctions X_k^{N-1} with nonzero eigenvalues, which in turn is the same as the number of η_k^{N-1}. This is why the expansion of Ψ^N in terms of η_k^{N-1} contains fewer terms than the expansion in terms of Ψ_k^{N-1}.

C. Expression in terms of energy orbitals

The approach used by Ryabinkin *et al.* [22] to derive another exact expression for $v_{\mathrm{XC}}(\mathbf{r})$ deviates considerably from the present method. However, their final result has the same structure as Eq. (31) and differs from the previously discussed formulas only in how $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ is represented.

The central quantity in derivation of Ryabinkin *et al.* [22] is the integral operator $\hat{G}$. This operator naturally arises in many problems of electronic structure theory and is known as the generalized Fock operator, extended Hartree–Fock operator, or orbital Lagrangian [27, 29–34]. The generalized Fock operator is in general non-Hermitian and becomes Hermitian for variational methods. Ryabinkin *et al.* [22] observed that

$$\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = \frac{\sum_\sigma G(\mathbf{x},\mathbf{x})}{\rho^{\mathrm{WF}}(\mathbf{r})}. \tag{58}$$

Therefore, expressions for $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ in terms of matrix elements of $\hat{G}$ such as Eqs. (24) and (51) do not change if every λ_{lk} is replaced with λ_{kl}^*. This means that $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ is determined by the Hermitian (symmetric) part of $\hat{G}$ and remains real even for nonvariational methods. The Hermitian part of the matrix of λ_{lk} can always be diagonalized by solving the eigenvalue

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problem

$$\hat{F} f_j(\mathbf{x}) = \lambda_j f_j(\mathbf{x}), \tag{59}$$

where $\hat{F} = (\hat{G} + \hat{G}^\dagger)/2$. The eigenfunctions $f_j(\mathbf{x})$, which we called "energy orbitals" [35], form a complete orthonormal set and span the same space as $\{\psi_j\}$, $\{d_k\}$, and $\{\chi_j\}$. The expression for the average local electron energy in terms of energy orbitals is

$$\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{WF}}(\mathbf{r})} \sum_\sigma \sum_j \lambda_j |f_j(\mathbf{x})|^2, \tag{60}$$

where the summation is over all energy orbitals.

The formula for $v_{\mathrm{XC}}(\mathbf{r})$ proposed in Ref. 22 is a special case of Eq. (31) in which $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ is expressed by Eq. (60) and the remaining wave-function-based quantities are as in Section IV B. One could also write $\rho^{\mathrm{WF}}(\mathbf{r})$ and $\tau^{\mathrm{WF}}(\mathbf{r})$ in terms of energy orbitals, but these expressions would have a nondiagonal form and offer no conceptual or computational advantage over the corresponding expressions in terms of natural orbitals.

For Hartree–Fock (HF) wave functions, energy orbitals coincide with the natural and canonical HF orbitals, the eigenvalues of these orbitals are related through $\lambda_k^{\mathrm{HF}} = n_k^{\mathrm{HF}} \epsilon_k^{\mathrm{HF}}$ [35], and $v_{\mathrm{S}}^{\mathrm{WF}}(\mathbf{r})$ reduces the Slater exchange-charge potential [36]. Therefore, for HF wave functions, Eq. (60) simplifies to

$$\bar{\epsilon}^{\mathrm{HF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{HF}}(\mathbf{r})} \sum_\sigma \sum_{i=1}^{N} \epsilon_i^{\mathrm{HF}} |\phi_i^{\mathrm{HF}}(\mathbf{x})|^2. \tag{61}$$

Exchange-correlation potentials constructed by Eq. (31) for Hartree–Fock wave functions are excellent approximations to exact exchange potentials [37, 38].

V. COMPARISON WITH THE METHOD OF BAERENDS AND CO-WORKERS

The earliest exact expression for $v_{\mathrm{XC}}(\mathbf{r})$ in terms of wave-function and Kohn–Sham quantities was derived by Baerends and co-workers [12–14, 19, 20]. Their approach is similar in spirit to our method in that it also involves a factorization of Ψ^N, but differs in essential details. Baerends and co-workers start by writing Ψ^N as a *single* product,

$$\Psi^N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = a(\mathbf{x}_1)\Phi(\mathbf{x}_2, \ldots, \mathbf{x}_N; \mathbf{x}_1), \tag{62}$$

where

$$a(\mathbf{x}_1) = \sqrt{\frac{\rho^{\mathrm{WF}}(\mathbf{x}_1)}{N}} \tag{63}$$

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and

$$\Phi(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1)=\frac{\Psi^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)}{a(\mathbf{x}_1)}, \tag{64}$$

which has the property

$$\int|\Phi(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1)|^2\,d\mathbf{x}_2\cdots d\mathbf{x}_N=1\quad\text{for all }\mathbf{x}_1. \tag{65}$$

This formal factorization of Ψ^N was originally proposed by Hunter [39, 40] who interpreted $a(\mathbf{x}_1)$ as a marginal probability amplitude and Φ as a conditional probability amplitude. The Kohn–Sham determinant Ψ_s^N is factorized similarly as

$$\Psi_s^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)=a_s(\mathbf{x}_1)\Phi_s(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1), \tag{66}$$

where

$$a_s(\mathbf{x}_1)=\sqrt{\frac{\rho^{\mathrm{KS}}(\mathbf{x}_1)}{N}}=a(\mathbf{x}_1) \tag{67}$$

and

$$\Phi_s(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1)=\frac{\Psi_s^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)}{a_s(\mathbf{x}_1)}. \tag{68}$$

Buijse and Baerends [12] showed that if Eq. (62) is inserted into the N-electron Schrödinger equation with $\hat{H}^N$ partitioned as in Eq. (10) and if the result is multiplied from the left by Φ^* and integrated over $\mathbf{x}_2\cdots\mathbf{x}_N$, one obtains the reduced one-electron Schrödinger equation for the marginal probability amplitude. By using this reduced Schrödinger equation and a similar equation derived from Eqs. (66)–(68), Gritsenko *et al.* [13] arrived at the following expression,

$$v_{\mathrm{XC}}(\mathbf{r})=v_{\mathrm{XC}}^{\mathrm{hole}}(\mathbf{r})+v_{c,\mathrm{kin}}(\mathbf{r})+v_{\mathrm{resp}}(\mathbf{r}), \tag{69}$$

which is equivalent to our Eq. (31), as we will now show.

The first term on the right-hand side of Eq. (69), the exchange-correlation hole potential, is identical to our generalized Slater potential,

$$v_{\mathrm{XC}}^{\mathrm{hole}}(\mathbf{r})=v_{\mathrm{S}}^{\mathrm{WF}}(\mathbf{r}). \tag{70}$$

The second term is given by [19]

$$v_{c,\mathrm{kin}}(\mathbf{r})=\frac{\left[\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}\rho^{\mathrm{WF}}(\mathbf{r},\mathbf{r}')-\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}\rho^{\mathrm{KS}}(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}'=\mathbf{r}}}{2\rho(\mathbf{r})}, \tag{71}$$

where $\rho(\mathbf{r})=\rho^{\mathrm{KS}}(\mathbf{r})=\rho^{\mathrm{WF}}(\mathbf{r})$,

$$\rho^{\mathrm{KS}}(\mathbf{r},\mathbf{r}')=\sum_{\sigma}\sum_{i=1}^{N}\phi_i(\mathbf{x})\phi_i^*(\mathbf{x}') \tag{72}$$

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is the spin-free Kohn–Sham 1-RDM, and

$$\rho^{\mathrm{WF}}(\mathbf{r},\mathbf{r}') = \sum_{\sigma} \gamma^{\mathrm{WF}}(\mathbf{x},\mathbf{x}') \tag{73}$$

is the spin-free 1-RDM from the wave function. Clearly,

$$v_{c,\mathrm{kin}}(\mathbf{r}) = \frac{\tau^{\mathrm{WF}}(\mathbf{r})}{\rho^{\mathrm{WF}}(\mathbf{r})} - \frac{\tau^{\mathrm{KS}}(\mathbf{r})}{\rho^{\mathrm{KS}}(\mathbf{r})}. \tag{74}$$

The third term in Eq. (69) is defined as

$$v_{\mathrm{resp}}(\mathbf{r}) = v^{N-1}(\mathbf{r}) - v_s^{N-1}(\mathbf{r}), \tag{75}$$

where [19]

$$\begin{aligned} v^{N-1}(\mathbf{r}) = &- E_0^{N-1} + \sum_{\sigma_1} \int \Phi^*(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1) \\ &\times \hat{H}^{N-1}\Phi(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1)\, d\mathbf{x}_2\cdots d\mathbf{x}_N, \end{aligned} \tag{76}$$

in which E_0^{N-1} is the ground-state energy of the $(N-1)$-electron system, and

$$\begin{aligned} v_s^{N-1}(\mathbf{r}) = &- E_{s,0}^{N-1} + \sum_{\sigma_1} \int \Phi_s^*(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1) \\ &\times \hat{H}_s^{N-1}\Phi_s(\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1)\, d\mathbf{x}_2\cdots d\mathbf{x}_N, \end{aligned} \tag{77}$$

in which $E_{s,0}^{N-1}$ is the ground-state energy of the noninteracting $(N-1)$-electron system.

Chong *et al.* [19] showed that if Ψ^N is expanded in Dyson orbitals, then $v^{N-1}(\mathbf{r})$ becomes

$$v^{N-1}(\mathbf{r}) = -I_0 + \frac{1}{\rho^{\mathrm{WF}}(\mathbf{r})} \sum_{\sigma} \sum_{k=1} I_k |d_k(\mathbf{x})|^2, \tag{78}$$

where I_0 is the first ionization energy of the system, while Gritsenko *et al.* [13] showed that

$$v_s^{N-1}(\mathbf{r}) = \epsilon_N - \frac{1}{\rho^{\mathrm{KS}}(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{x})|^2, \tag{79}$$

where ϵ_N is the eigenvalue of the highest occupied Kohn–Sham orbital. The connection between these and our quantities is, therefore,

$$v^{N-1}(\mathbf{r}) = -\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) - I_0 \tag{80}$$

and

$$v_s^{N-1}(\mathbf{r}) = -\bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}) + \epsilon_N. \tag{81}$$

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Since in the exact Kohn-Sham scheme [41],

$$I_0 = -\epsilon_N, \tag{82}$$

we conclude that

$$v_{\mathrm{resp}}(\mathbf{r}) = \bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}) - \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}). \tag{83}$$

Equation (83) also follows from the equality of the right-hand sides of Eqs. (31) and (69) together with the identities expressed by Eqs. (70) and (74).

VI. CONCLUSION

We have devised a unified method for deriving various exact expressions for the exchange-correlation potential of the Kohn–Sham density-functional theory. The starting point of our derivation is the expansion of the interacting N-electron wave function in products of one- and $(N-1)$-electron functions. Depending on how the $(N-1)$-electron functions are chosen, the method produces different formulas for $v_{\mathrm{XC}}(\mathbf{r})$ which all have the same analytic structure given by Eq. (31) but differ in how individual terms are expressed.

The expressions for $v_{\mathrm{XC}}(\mathbf{r})$ derived by the Baerends group [13, 19] and by Staroverov and co-workers [22, 23] are particular cases of Eq. (31). The main difference between those formulas is in how one particular term, $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$, is represented. Baerends and co-workers gave two analytic expressions for $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$—one in terms of conditional probability amplitudes, Eq. (76), the other in terms of Dyson orbitals, Eq. (40). Conditional probability amplitudes are as complicated objects as Ψ^N itself, while Dyson orbitals require the knowledge of all Ψ_k^{N-1} or at least the system's single-particle Green's function. Our expressions for $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$, Eqs. (51) or Eq. (60), are simpler in that they require the 2-RDM at most.

Another way to describe the difference between the existing formulas for $v_{\mathrm{XC}}(\mathbf{r})$ is to state which ingredients have a diagonal representation and which do not. In the expression involving natural orbitals, $\rho^{\mathrm{WF}}(\mathbf{r})$ and $\tau^{\mathrm{WF}}(\mathbf{r})$ have a diagonal form in terms of one-electron functions, whereas $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ does not. In the expression involving energy orbitals, it is the other way around. In the expression in terms of Dyson orbitals, all three quantities $\rho^{\mathrm{WF}}(\mathbf{r})$, $\tau^{\mathrm{WF}}(\mathbf{r})$, and $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ are in diagonal form.

Our key finding is that each variant of Eq. (11) gives rise to a distinct expression for $v_{\mathrm{XC}}(\mathbf{r})$. In this work, we have analyzed the cases where Eq. (11) defines the natural spin-

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orbitals, Dyson orbitals, and energy orbitals. Other exact expressions for $v_{\mathrm{XC}}(\mathbf{r})$ can be generated by using some other reduced one-electron form of the Schrödinger equation.

Acknowledgement

This article is dedicated to Andreas Savin on the occasion of his 65th birthday.

Funding

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Postdoctoral Fellowship Program and the Discovery Grants Program, Application No. RGPIN-2015-04814.

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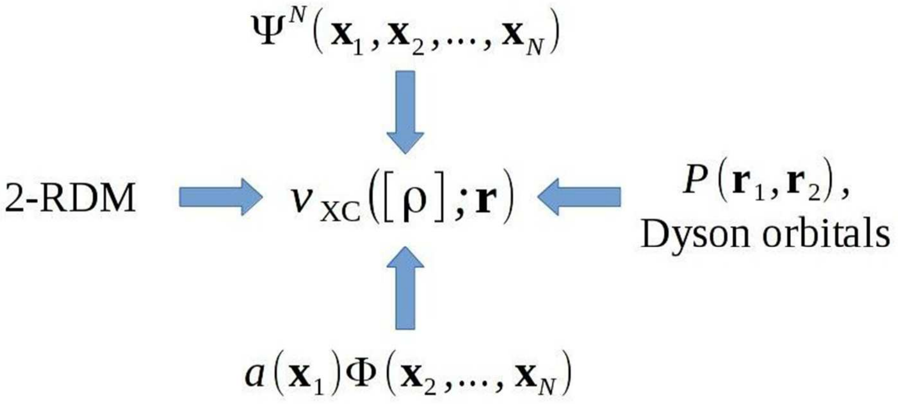

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