

4-19-2018

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Citation of this paper:

Staroverov, Viktor N., "Contracted Schrödinger equation and Kohn–Sham effective potentials" (2018).
Chemistry Publications. 307.
<https://ir.lib.uwo.ca/chempub/307>

Contracted Schrödinger equation and Kohn–Sham effective potentials

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(Dated: June 2, 2018)

The precise relationship between the exact expressions for the Kohn–Sham exchange-correlation potential, $v_{XC}(\mathbf{r})$, deduced by Buijse, Baerends, and Snijders and by Ryabinkin, Kohut, and Staroverov is clarified. These two expressions differ nontrivially by a single term which in the former method generally involves the three-electron reduced density matrix, whereas in the latter approach the same term is expressed using the two-electron reduced density matrix at most. The link between the two expressions turns out to be the 1,3-contracted Schrödinger equation. An essential feature of these and other similar expressions for $v_{XC}(\mathbf{r})$ is that they produce different results in finite-basis-set calculations and become equivalent only in the basis-set limit.

Keywords: exchange-correlation potential, reduced density matrices, contracted Schrödinger equation, generalized Fock operator

I. INTRODUCTION

Recently, we devised a method [1–5] for constructing Kohn–Sham (KS) exchange-correlation potentials, $v_{XC}(\mathbf{r})$, from ground-state *ab initio* electronic wave functions. This method is based on an exact formula for $v_{XC}(\mathbf{r})$ in terms of the interacting two-electron reduced density matrix (2-RDM) of the system, the occupied KS orbitals, and their eigenvalues. Because the KS orbital and eigenvalues are determined by $v_{XC}(\mathbf{r})$ itself, the formula is in fact an equation for $v_{XC}(\mathbf{r})$ that can be solved by iteration. In the special case of singlet two-electron systems, the KS quantities drop out and the equation becomes an explicit formula for $v_{XC}(\mathbf{r})$ in terms of the 2-RDM [6]. When applied to Hartree–Fock wave functions, the method gives essentially exact exchange potentials [7, 8].

The general method of Refs. 1–6 is conceptually different from KS inversion techniques (see, for instance, Refs. 9–15) in the following sense: when implemented for a given type of wave function using a finite basis set, it produces a $v_{XC}(\mathbf{r})$ that recovers the associated *ab initio* electron density only approximately, but otherwise is a reliable approximation to the $v_{XC}(\mathbf{r})$ of the corresponding basis-set limit. By contrast, KS inversion schemes aim to produce the $v_{XC}(\mathbf{r})$ that recovers a given finite-basis-set *ab initio* density as accurately as possible; for Gaussian basis-set densities, the fitted potential has a strong basis-set dependence and may look very different from the $v_{XC}(\mathbf{r})$ of the basis-set limit for the same type of wave function [16–18]. The problem posed by KS inversion methods is also compounded by the absence of a one-to-one mapping between $v_{XC}(\mathbf{r})$ and $\rho(\mathbf{r})$ in finite basis sets [19–21].

The exact expression for $v_{XC}(\mathbf{r})$ that forms the basis of our method is not the only such expression possible. Buijse, Baerends, and Snijders [22] deduced a differ-

ent formula involving $(N - 1)$ -electron conditional amplitudes. A third expression for $v_{XC}(\mathbf{r})$, discussed by Chong *et al.* [23], involves all Dyson orbitals and associated electron removal energies of the system. Holas and March [24] derived an integral equation for $v_{XC}(\mathbf{r})$ in terms of RDMs of up to third order, while Miao [25] gave an explicit formula for $v_{XC}(\mathbf{r})$ in terms of those RDMs. None of those earlier expressions, however, has been used to construct KS potentials for systems with more than two electrons in a manner similar to ours, possibly because of the greater complexity and/or computational cost of the ingredients involved. Differences between our formula and the two expressions of Baerends and co-workers were dealt with in our Refs. 3, 4, and 26. In this work, we show that the two key ingredients which distinguish our expression for $v_{XC}(\mathbf{r})$ from that derived by Buijse *et al.* [22] are related through the 1,3-contracted Schrödinger equation and that the formula for $v_{XC}(\mathbf{r})$ of Ref. 22 generally involves the 3-RDM, as does Miao’s result [25].

II. CONTRACTED SCHRÖDINGER EQUATION

Consider the time-independent Schrödinger equation for the ground state of an N -electron system,

$$\hat{H}^N \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E_0^N \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (1)$$

where $\mathbf{x}_i \equiv \mathbf{r}_i \sigma_i$ are the space and spin coordinates and

$$\hat{H}^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \sum_{i < j}^N \frac{1}{r_{ij}}, \quad (2)$$

in which

$$\hat{h}(\mathbf{r}_i) = -\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i) \quad (3)$$

is the core Hamiltonian and $v(\mathbf{r})$ is the external potential. Cohen and Frishberg [27] and Nakatsuji [28] showed that

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if Eq. (1) is multiplied by $N\Psi^N(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N)^*$ and the product is traced over $\mathbf{x}_2, \dots, \mathbf{x}_N$, one obtains

$$\begin{aligned} & \hat{h}(\mathbf{r}_1)\gamma_1(\mathbf{x}_1; \mathbf{x}'_1) \\ & + 2 \int \left[\left(\hat{h}(\mathbf{r}_2) + \frac{1}{r_{12}} \right) \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) \right]_{\mathbf{x}'_2=\mathbf{x}_2} d\mathbf{x}_2 \\ & + 3 \int \frac{\gamma_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3; \mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3)}{r_{23}} d\mathbf{x}_2 d\mathbf{x}_3 \\ & = E_0^N \gamma_1(\mathbf{x}_1; \mathbf{x}'_1), \end{aligned} \quad (4)$$

where $\gamma_1(\mathbf{x}_1; \mathbf{x}'_1)$ is the 1-RDM, $\gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)$ is the 2-RDM, and $\gamma_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3; \mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3)$ is the 3-RDM. This particular reduction of Eq. (1) is known as the 1,3-contracted Schrödinger equation [29].

The left-hand side of Eq. (4) contains the kernel of the generalized Fock integral operator \hat{G} [30–32],

$$\begin{aligned} G(\mathbf{x}_1; \mathbf{x}'_1) &= \hat{h}(\mathbf{r}_1)\gamma_1(\mathbf{x}_1; \mathbf{x}'_1) \\ &+ 2 \int \frac{\gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)}{r_{12}} d\mathbf{x}_2. \end{aligned} \quad (5)$$

If the remaining terms are collected into the quantity

$$\begin{aligned} A(\mathbf{x}_1; \mathbf{x}'_1) &= 2 \int \left[\hat{h}(\mathbf{r}_2)\gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) \right]_{\mathbf{x}'_2=\mathbf{x}_2} d\mathbf{x}_2 \\ &+ 3 \int \frac{\gamma_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3; \mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3)}{r_{23}} d\mathbf{x}_2 d\mathbf{x}_3, \end{aligned} \quad (6)$$

then Eq. (4) may be written succinctly as

$$G(\mathbf{x}_1; \mathbf{x}'_1) + A(\mathbf{x}_1; \mathbf{x}'_1) = E_0^N \gamma_1(\mathbf{x}_1; \mathbf{x}'_1). \quad (7)$$

Let us also define the expectation value

$$E_0^{N-1} = \langle \Psi^{N-1} | \hat{H}^{N-1} | \Psi^{N-1} \rangle, \quad (8)$$

where

$$\hat{H}^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{H}^N - \hat{h}(\mathbf{r}_1) - \sum_{i=2}^N \frac{1}{r_{1i}} \quad (9)$$

and $\Psi^{N-1}(\mathbf{x}_2, \dots, \mathbf{x}_N)$ is the $(N-1)$ -electron wave function variationally optimized in the space of “hole” states $\Psi_k^{N-1} = \hat{a}_k \Psi^N$, where \hat{a}_k is the annihilation operator for the k th spin-orbital in the orthonormal one-electron basis for Ψ^N [31].

From now on, we will specialize to spin-compensated systems for simplicity. Returning to Eq. (7), we set $\mathbf{x}_1 = \mathbf{x}'_1 = \mathbf{x}$, sum all terms over the spin variable σ , divide the result by

$$\rho(\mathbf{r}) \equiv \sum_{\sigma} \gamma_1(\mathbf{x}; \mathbf{x}), \quad (10)$$

and subtract E_0^{N-1} from both sides. Introducing the notation

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) = \frac{\sum_{\sigma} G(\mathbf{x}; \mathbf{x})}{\rho(\mathbf{r})} \quad (11)$$

and

$$v^{N-1}(\mathbf{r}) = \frac{\sum_{\sigma} A(\mathbf{x}; \mathbf{x})}{\rho(\mathbf{r})} - E_0^{N-1} \quad (12)$$

we write the diagonal part of Eq. (7) as

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) + v^{N-1}(\mathbf{r}) = -I, \quad (13)$$

where

$$I = E_0^{N-1} - E_0^N. \quad (14)$$

Note that, in the basis-set limit, E_0^{N-1} would be equal to the exact ground-state energy of the $(N-1)$ -electron system for the external potential $v(\mathbf{r})$ and I would be the exact first vertical ionization energy—the result known as the extended Koopmans theorem [33–37].

The quantity $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ defined by Eq. (11) is the generalized average local ionization energy [38, 39]. As we emphasized elsewhere [4, 39], in practical calculations using finite basis sets, the numerator $G(\mathbf{x}; \mathbf{x})$ of Eq. (11) should be evaluated not by Eq. (5) but by using the spectral representation

$$G(\mathbf{x}; \mathbf{x}) = \sum_j \lambda_j |f_j(\mathbf{x})|^2, \quad (15)$$

where $f_j(\mathbf{x})$ are the spin-eigenfunctions of the \mathbf{G} matrix and λ_j are the associated eigenvalues. This is because the spectral representation of $G(\mathbf{x}; \mathbf{x})$ by Eq. (15) is more appropriate than Eq. (5) in situations where the domain of \hat{G} has a finite dimension. Unlike Eq. (5), Eq. (15) does not produce nonphysical oscillations even in finite Gaussian basis sets [39].

The quantity $v^{N-1}(\mathbf{r})$ was introduced by Buijse *et al.* [22] in their partitioning analysis of exact exchange-correlation potentials, although those workers wrote it in terms of $(N-1)$ -electron quantities. We will now show that the definition of $v^{N-1}(\mathbf{r})$ given by Buijse *et al.* [22] can be simplified to Eq. (12).

III. EXCHANGE-CORRELATION POTENTIALS

Consider the KS description [40] of the ground state of the system defined by Eq. (1). The KS (noninteracting) wave function Ψ_s^N is the solution of the equation

$$\hat{H}_s^N \Psi_s^N = E_{s,0}^N \Psi_s^N, \quad (16)$$

where

$$\hat{H}_s^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N \hat{h}_{\text{KS}}(\mathbf{r}_i), \quad (17)$$

in which

$$\hat{h}_{\text{KS}}(\mathbf{r}_i) = -\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i) + v_{\text{H}}(\mathbf{r}_i) + v_{\text{XC}}(\mathbf{r}_i) \quad (18)$$

is the one-electron KS Hamiltonian, $v_H(\mathbf{r})$ being the Hartree (electrostatic) potential of $\rho(\mathbf{r})$, and

$$E_{s,0}^N = \langle \Psi_s^N | \hat{H}_s^N | \Psi_s^N \rangle = \sum_{i=1}^N \epsilon_i, \quad (19)$$

where ϵ_i are the eigenvalues of the N lowest-energy KS spin-orbitals whose spatial parts are obtained by solving

$$\hat{h}_{\text{KS}}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}). \quad (20)$$

Buijse *et al.* [22] showed that the KS exchange-correlation potential associated with the ground-state interacting wave function Ψ^N may be written exactly as

$$v_{\text{XC}}(\mathbf{r}) = v_{\text{XC}}^{\text{hole}}(\mathbf{r}) + v_{\text{c,kin}}(\mathbf{r}) + v_{\text{resp}}(\mathbf{r}), \quad (21)$$

where the first term,

$$v_{\text{XC}}^{\text{hole}}(\mathbf{r}_1) = \int \frac{\rho_{\text{XC}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_2, \quad (22)$$

is the potential of the exchange-correlation hole charge, a quantity defined by

$$\rho_{\text{XC}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{2 \sum_{\sigma_1, \sigma_2} \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2). \quad (23)$$

The second term,

$$v_{\text{c,kin}}(\mathbf{r}) = \frac{\tau^{\text{WF}}(\mathbf{r}) - \tau^{\text{KS}}(\mathbf{r})}{\rho(\mathbf{r})}, \quad (24)$$

is the kinetic correlation potential [41] in which

$$\tau^{\text{WF}}(\mathbf{r}) = \frac{1}{2} \left[\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'} \sum_{\sigma, \sigma'} \gamma_1(\mathbf{x}, \mathbf{x}') \right]_{\mathbf{r}=\mathbf{r}'} \quad (25)$$

is the positive-definite interacting kinetic energy density and $\tau^{\text{KS}}(\mathbf{r})$ is its noninteracting counterpart. The third term,

$$v_{\text{resp}}(\mathbf{r}) = v^{N-1}(\mathbf{r}) - v_s^{N-1}(\mathbf{r}), \quad (26)$$

is the “response potential” [41], defined in terms of the noninteracting (Ψ_s^N) and interacting (Ψ^N) N -electron wave functions of the system. Specifically [22],

$$\begin{aligned} v_s^{N-1}(\mathbf{r}_1) &= \frac{N}{\rho(\mathbf{r}_1)} \sum_{\sigma_1} \int \Psi_s^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)^* \\ &\quad \times \hat{H}_s^{N-1} \Psi_s^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N - E_{s,0}^{N-1}, \end{aligned} \quad (27)$$

where

$$\hat{H}_s^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{H}_s^N - \hat{h}_{\text{KS}}(\mathbf{r}_1) = \sum_{i=1}^{N-1} \hat{h}_{\text{KS}}(\mathbf{r}_i) \quad (28)$$

and

$$E_{s,0}^{N-1} = \langle \Psi_s^{N-1} | \hat{H}_s^{N-1} | \Psi_s^{N-1} \rangle = \sum_{i=2}^N \epsilon_i, \quad (29)$$

in which Ψ_s^{N-1} is the Slater determinant built from the lowest-energy KS spin-orbitals ϕ_i , $i = 1, 2, \dots, N-1$. Since ϕ_i are eigenfunctions of \hat{h}_{KS} , the integral in Eq. (27) may be evaluated using general rules for matrix elements between Slater determinants to give [41]

$$v_s^{N-1}(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \sum_{i=1}^N \epsilon_i |\phi_i(\mathbf{r})|^2 + \epsilon_N. \quad (30)$$

The quantity $v^{N-1}(\mathbf{r})$ was defined by Buijse *et al.* [22] as

$$\begin{aligned} v^{N-1}(\mathbf{r}_1) &= \frac{N}{\rho(\mathbf{r}_1)} \sum_{\sigma_1} \int \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)^* \\ &\quad \times \hat{H}^{N-1} \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N - E_0^{N-1}. \end{aligned} \quad (31)$$

Now if we substitute Eq. (9) into Eq. (31), integrate over $\mathbf{x}_2, \dots, \mathbf{x}_N$, and use the fact that

$$N \int \Psi^{N*} \hat{H}^N \Psi^N d\mathbf{x}_2 \cdots d\mathbf{x}_N = G(\mathbf{x}_1; \mathbf{x}_1) + A(\mathbf{x}_1; \mathbf{x}_1), \quad (32)$$

while

$$N \int \Psi^{N*} \left[\hat{h}(\mathbf{r}_1) + \sum_{i=2}^N \frac{1}{r_{1i}} \right] \Psi^N d\mathbf{x}_2 \cdots d\mathbf{x}_N = G(\mathbf{x}_1; \mathbf{x}_1), \quad (33)$$

then Eq. (12) follows. The latter shows that the expression for $v_{\text{XC}}(\mathbf{r})$ of Buijse *et al.* [22] as written does require more than the 2-RDM, specifically, the 3-RDM.

The exact expression for $v_{\text{XC}}(\mathbf{r})$ derived by Ryabinkin *et al.* [1] (see also Refs. 2 and 3) has the same form as Eq. (21) except that the response potential is written as

$$v_{\text{resp}}(\mathbf{r}) = \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}), \quad (34)$$

where

$$\bar{\epsilon}^{\text{KS}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^N \epsilon_i |\phi_i(\mathbf{r})|^2, \quad (35)$$

and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ uses the spectral representation of $G(\mathbf{x}; \mathbf{x})$,

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_j \lambda_j |f_j(\mathbf{r})|^2, \quad (36)$$

where $f_j(\mathbf{r})$ are spatial parts of the spin-eigenfunctions of \hat{G} . The analytic representations of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ by Eqs. (11) and (36) are equivalent in a complete (infinite) basis set but not in a finite basis set because KS orbitals are eigenfunctions of the KS Hamiltonian only in the discretized

(matrix) form but not in the operator form. For the same reason, representations of $v_s^{N-1}(\mathbf{r})$ by Eqs. (27) and (30) are equivalent only in the basis-set limit.

Note that if Ψ^N is an exact eigenfunction of \hat{H}^N , then Eq. (31) can also be manipulated [42] into

$$v^{N-1}(\mathbf{r}) = -\frac{\tau_L(\mathbf{r})}{\rho(\mathbf{r})} - v(\mathbf{r}) - v_H(\mathbf{r}) - v_{XC}^{\text{hole}}(\mathbf{r}) - I, \quad (37)$$

where

$$\tau_L(\mathbf{r}) = \left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 \sum_{\sigma, \sigma'} \gamma_1(\mathbf{x}; \mathbf{x}') \right]_{\mathbf{r}'=\mathbf{r}}. \quad (38)$$

This representation is nothing but

$$v^{N-1}(\mathbf{r}) = -\frac{\sum_{\sigma} G(\mathbf{x}; \mathbf{x})}{\rho(\mathbf{r})} - I, \quad (39)$$

that is, the combination of Eqs. (11) and (13), where $G(\mathbf{x}; \mathbf{x})$ is given by Eq. (5). Equation (37) also requires at most the 2-RDM but is not useful for computing $v^{N-1}(\mathbf{r})$ in Gaussian basis sets because it results in nonphysical oscillations (as discussed above). Nor is it useful for constructing $v_{XC}(\mathbf{r})$ by Eq. (21) because substitution of Eq. (37) into Eq. (21) reverses the derivation of the latter and leads back to the inverted KS eigenvalue equation [4, 42], which contains no wave-function quantities.

IV. CONCLUSION

Equation (13), which connects the formulas for $v_{XC}(\mathbf{r})$ derived by Buijse *et al.* [22] and by us [1, 2], was previ-

ously [3] deduced by indirect means. Here we established that, apart from a factor of $\rho(\mathbf{r})$, Eq. (13) is precisely the diagonal part of the 1,3-contracted Schrödinger equation.

It is probable that Eq. (21) with $v^{N-1}(\mathbf{r})$ evaluated by Eq. (12) could be used to generate exchange-correlation potentials as in our iterative method. This would generally require the 3-RDM, as would the closely related formula for $v_{XC}(\mathbf{r})$ deduced by Miao [25]. The exception is two-electron systems, for which the three-electron part of $v^{N-1}(\mathbf{r})$ vanishes and Eq. (12) reduces [6] to

$$\begin{aligned} v^{N-1}(\mathbf{r}) &= \frac{2}{\rho(\mathbf{r})} \sum_{\sigma} \int \left[\hat{h}(\mathbf{r}_2) \gamma_2(\mathbf{x}, \mathbf{x}_2; \mathbf{x}, \mathbf{x}'_2) \right]_{\mathbf{x}'_2=\mathbf{x}_2} d\mathbf{x}_2 - E_0^{N-1}. \end{aligned} \quad (40)$$

For such systems, Eq. (21) involves the 2-RDM at most. By contrast, the expression for $v_{XC}(\mathbf{r})$ derived in Refs. 1–3, using the spectral representation of $\epsilon^{\text{WF}}(\mathbf{r})$ by Eq. (36), involves at most the 2-RDM for all N . Thus, the expressions for $v_{XC}(\mathbf{r})$ derived by Buijse *et al.* [22] and by Ryabinkin *et al.* [1] are distinct for all $N > 1$.

Acknowledgments

The work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Discovery Grant (Application No. RGPIN-2015-04814) and a Discovery Accelerator Supplement (RGPAS 477791-2015).

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