Exact exchange-correlation potentials of singlet two-electron systems

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(Received 7 September 2017; accepted 13 October 2017; published online 31 October 2017; publisher error corrected 1 November 2017)

We suggest a non-iterative analytic method for constructing the exchange-correlation potential, $v_{\rm XC}(\mathbf{r})$, of any singlet ground-state two-electron system. The method is based on a convenient formula for $v_{\rm XC}(\mathbf{r})$ in terms of quantities determined only by the system's electronic wave function, exact or approximate, and is essentially different from the Kohn–Sham inversion technique. When applied to Gaussian-basis-set wave functions, the method yields finite-basis-set approximations to the corresponding basis-set-limit $v_{\rm XC}(\mathbf{r})$, whereas the Kohn–Sham inversion produces physically inappropriate (oscillatory and divergent) potentials. The effectiveness of the procedure is demonstrated by computing accurate exchange-correlation potentials of several two-electron systems (helium isoelectronic series, H_2, H_3^+) using common *ab initio* methods and Gaussian basis sets. *Published by AIP Publishing.*
https://doi.org/10.1063/1.5003825

I. INTRODUCTION

Two-electron systems occupy a special place in electronic structure theory. On the one hand, they exhibit electron correlation effects and thus conceptually pose the same challenge as interacting many-electron systems in general. On the other hand, they are small enough that their Schrödinger equations can be solved with extremely high accuracy by *ab initio* methods.[1–8]

In the Kohn–Sham (KS) density-functional scheme,[9] the singlet ground state of a two-electron system is mapped to the singlet ground state of an auxiliary system of $N = 2$ non-interacting electrons occupying the same KS orbital. Single-orbital KS systems are also special because one can write down for them a number of exact relations that do not hold for $N > 2$. In particular, given a singlet ground-state density of a two-electron system, one can invert the KS equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\rm H}(\mathbf{r}) + v_{\rm XC}(\mathbf{r})\right]\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r}), \qquad (1)$$

where $\phi(\mathbf{r}) = \rho^{1/2}(\mathbf{r})$, and write the corresponding exchange-correlation potential as

$$v_{\rm XC}(\mathbf{r}) = \frac{\nabla^2\rho(\mathbf{r})}{4\rho(\mathbf{r})} - \frac{\tau_W(\mathbf{r})}{\rho(\mathbf{r})} - v(\mathbf{r}) - v_{\rm H}(\mathbf{r}) + \epsilon. \qquad (2)$$

Here $\tau_W(\mathbf{r}) = |\nabla\rho(\mathbf{r})|^2/8\rho(\mathbf{r})$, $v(\mathbf{r})$ is the external potential, $v_{\rm H}(\mathbf{r})$ is the Hartree (electrostatic) potential of $\rho(\mathbf{r})$, and ϵ is the KS eigenvalue which, in the exact KS scheme, is equal to the first ionization energy of the system, $\epsilon = -I$.[10–13] A generalization of Eq. (2) to $N > 2$ is easy to write (see, for instance, Ref. 14), but the result contains KS orbitals and hence cannot be used to determine $v_{\rm XC}(\mathbf{r})$ from $\rho(\mathbf{r})$ in a single step.

Equation (2) is the most obvious method for constructing exchange-correlation potentials of two-electron systems from accurate *ab initio* densities.[13,15–22] It can also be extended to the time-dependent KS scheme.[23–27] Despite its appealing simplicity, however, this method is not as sound as it may seem.

First, Eq. (2) states the result of inverting Eq. (1) analytically. This means that if the starting $\rho(\mathbf{r})$ is generated using a finite one-electron basis set and $v_{\rm XC}(\mathbf{r})$ is obtained from that $\rho(\mathbf{r})$ by Eq. (2), then one generally has to solve the KS equations with that $v_{\rm XC}(\mathbf{r})$ using a *complete* (infinite) one-electron basis set to reproduce the initial $\rho(\mathbf{r})$ exactly. The finite one-electron basis set used for generating the initial $\rho(\mathbf{r})$ simply cannot do the job.[28] Second, potentials obtained by Eq. (2) from atomic and molecular Gaussian-basis-set densities oscillate wildly and diverge as $r \to \infty$,[18,19,29–32] a result that is mathematically correct but physically inappropriate for a Coulombic $v(\mathbf{r})$. The fact that Eq. (2) can give very different potentials for exact (basis-set-limit) and approximate (finite-basis-set) densities of the same system renders it impractical for calculations employing Gaussian basis sets.

One way to obtain physically sensible potentials from reasonable densities is to restrict application of Eq. (2) to densities expanded in Slater-type basis functions.[19] Another one is to reformulate the problem so that sensible results are obtained in any reasonable basis set. We have recently developed such a reformulation.[33–38] In our approach, $v_{\rm XC}(\mathbf{r})$ is not fitted to a given $\rho(\mathbf{r})$ but is computed using a certain analytic expression that involves quantities constructed from the interacting wave function of the system and from the KS orbitals and their eigenvalues, all generated using the same one-electron basis set. Since the KS orbitals and eigenvalues are initially unknown, this expression generally needs to be iterated starting from an initial guess for $v_{\rm XC}(\mathbf{r})$. Just like Eq. (2), our method would produce potentials that recover the associated *ab initio*

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densities exactly if implemented in a complete basis set. In a finite basis set, it yields potentials that are close to the basis-set-limit $v_{\rm XC}(\mathbf{r})$, unlike Eq. (2), and can be improved systematically by increasing the basis-set size.

The definitive version of our method is the modified Ryabinkin–Kohut–Staroverov (mRKS) procedure,[38] which employs a small but crucial modification of the original expression for $v_{\rm XC}(\mathbf{r})$ derived in Ref. 33. In this work, we show that, in the special case of single-KS-orbital systems, the modified expression reduces to an exact formula for $v_{\rm XC}(\mathbf{r})$ which contains no KS quantities whatsoever. This formula allows one to reduce any singlet two-electron wave function directly to the corresponding exchange-correlation potential and in practice is much better for that purpose than Eq. (2).

II. EXCHANGE-CORRELATION POTENTIAL

In Ref. 38, we derived the following equation for the exact exchange-correlation potential of a singlet ground-state N-electron system:

$$v_{\rm XC} = v_{\rm XC}^{\rm hole} + \bar{\epsilon}^{\rm KS} - \bar{\epsilon}^{\rm WF} + \frac{\tau_P^{\rm WF}}{\rho^{\rm WF}} - \frac{\tau_P^{\rm KS}}{\rho^{\rm KS}}, \tag{3}$$

where each quantity is a function of $\mathbf{r}$. Here

$$v_{\rm XC}^{\rm hole}(\mathbf{r}) = \int \frac{\rho_{\rm XC}(\mathbf{r},\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{r}_2 \tag{4}$$

is the potential of the exchange-correlation hole charge,[39] $\rho_{\rm XC}(\mathbf{r},\mathbf{r}_2)$, a quantity determined by the interacting two-electron reduced density matrix (2-RDM). The next term is the KS average local orbital energy

$$\bar{\epsilon}^{\rm KS}(\mathbf{r}) = \frac{1}{\rho^{\rm KS}(\mathbf{r})} \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{r})|^2, \tag{5}$$

where $\phi_i(\mathbf{r})$ are the spatial parts of the respective KS spin-orbitals, ϵ_i are the associated eigenvalues, and

$$\rho^{\rm KS}(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \tag{6}$$

is the non-interacting electron density. The analogous wave-function-based quantity, called the generalized average local electron energy,[40,41] is given by

$$\bar{\epsilon}^{\rm WF}(\mathbf{r}) = \frac{1}{\rho^{\rm WF}(\mathbf{r})} \sum_j \lambda_j |f_j(\mathbf{r})|^2, \tag{7}$$

where $f_j(\mathbf{r})$ are the spatial parts of the spin-eigenfunctions of the integral generalized Fock operator, $\hat{G}$, and λ_j are the associated eigenvalues. The kernel of $\hat{G}$ is[35,42]

$$G(\mathbf{x},\mathbf{x}') = \hat{h}(\mathbf{r})\gamma^{\rm WF}(\mathbf{x},\mathbf{x}') + 2\int \frac{\Gamma^{\rm WF}(\mathbf{x},\mathbf{x}_2;\mathbf{x}',\mathbf{x}_2)}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{x}_2, \tag{8}$$

where $\hat{h}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v(\mathbf{r})$, $\gamma^{\rm WF}(\mathbf{x},\mathbf{x}')$ is the interacting 1-RDM, and $\Gamma^{\rm WF}(\mathbf{x},\mathbf{x}_2;\mathbf{x}',\mathbf{x}_2')$ is the interacting 2-RDM. The summation in Eq. (7) is over all spin-eigenfunctions of $\hat{G}$ (their number is determined by the size of the one-electron basis set). The *ab initio* electron density is given by

$$\rho^{\rm WF}(\mathbf{r}) = \sum_j n_j |\chi_j(\mathbf{r})|^2, \tag{9}$$

where each $\chi_j(\mathbf{r})$ is the spatial part of the jth natural spin-orbital and n_j is the corresponding occupation number. The remaining quantities in Eq. (3) are the interacting Pauli kinetic-energy density[38]

$$\tau_P^{\rm WF}(\mathbf{r}) = \frac{1}{2\rho^{\rm WF}(\mathbf{r})} \sum_{i<j} n_i n_j |\chi_i(\mathbf{r})\nabla\chi_j(\mathbf{r}) - \chi_j(\mathbf{r})\nabla\chi_i(\mathbf{r})|^2 \tag{10}$$

and its KS counterpart

$$\tau_P^{\rm KS}(\mathbf{r}) = \frac{1}{2\rho^{\rm KS}(\mathbf{r})} \sum_{i<j}^{N} |\phi_i(\mathbf{r})\nabla\phi_j(\mathbf{r}) - \phi_j(\mathbf{r})\nabla\phi_i(\mathbf{r})|^2. \tag{11}$$

Note that each distinct spatial orbital appears twice, with different subscripts, in the sums of Eqs. (5)–(11).

Equation (3) determines $v_{\rm XC}(\mathbf{r})$ up to a constant. This constant is fixed by the highest-occupied molecular orbital (HOMO) condition[33,34,38]

$$\epsilon_{\rm HOMO}^{\rm KS} = -I_{\rm EKT}, \tag{12}$$

where $I_{\rm EKT}$ is the first (lowest) ionization energy determined from the interacting wave function using the extended Koopmans theorem[43–45] (EKT). In practice, we compute $I_{\rm EKT}$ by the method of Ref. 46. As the level of theory increases, $I_{\rm EKT}$ approaches[47,48] the exact first ionization energy, I, and thus attains consistency with the better-known condition[10,12,13] on the *exact* KS HOMO eigenvalue, $\epsilon_{\rm HOMO}^{\rm KS} = -I$.

Now consider a singlet ground-state two-electron system. For such a system, there is only one distinct spatial KS orbital ($\phi_1 = \phi_2$, where the subscripts label the corresponding spin-orbitals), and so Eq. (5) assumes the form

$$\bar{\epsilon}^{\rm KS}(\mathbf{r}) = \epsilon_{\rm HOMO}^{\rm KS} = -I_{\rm EKT}, \tag{13}$$

while Eq. (11) becomes

$$\tau_P^{\rm KS}(\mathbf{r}) = 0. \tag{14}$$

Thus, for $N = 2$, Eq. (3) reduces to

$$v_{\rm XC}(\mathbf{r}) = v_{\rm XC}^{\rm hole}(\mathbf{r}) + \frac{\tau_P^{\rm WF}(\mathbf{r})}{\rho^{\rm WF}(\mathbf{r})} - \bar{\epsilon}^{\rm WF}(\mathbf{r}) - I_{\rm EKT}, \tag{15}$$

where the last term is a constant. This formula contains only quantities determined by the interacting wave function (equivalently, the 2-RDM) and, therefore, allows one to compute $v_{\rm XC}(\mathbf{r})$ from that wave function without iterations. The KS orbitals corresponding to this potential can also be computed in a single step, by diagonalizing the KS Hamiltonian matrix.

Observe that for an N-electron closed-shell Hartree–Fock (HF) wave function, Eq. (15) may be written as

$$v_{\rm XC}^{\rm HF} = v_{\rm S} + \bar{\epsilon}^{\rm KS} - \bar{\epsilon}^{\rm HF} + \frac{\tau_P^{\rm HF}}{\rho^{\rm HF}} - \frac{\tau_P^{\rm KS}}{\rho^{\rm KS}}, \tag{16}$$

where $v_{\rm S}(\mathbf{r})$ is the Slater potential[49] of the HF exchange hole, while $\rho^{\rm HF}(\mathbf{r})$, $\bar{\epsilon}^{\rm HF}(\mathbf{r})$, and $\tau_P^{\rm HF}(\mathbf{r})$ are given by the same expressions as $\rho^{\rm KS}(\mathbf{r})$, $\bar{\epsilon}^{\rm KS}(\mathbf{r})$, and $\tau_P^{\rm KS}(\mathbf{r})$, only in terms of HF orbitals and orbital energies. The first EKT ionization energy

for a HF wave function is $I_{\mathrm{EKT}} = -\epsilon^{\mathrm{HF}}_{\mathrm{HOMO}}$, which implies that the vertical shift of $v^{\mathrm{HF}}_{\mathrm{XC}}(\mathbf{r})$ is fixed by the condition $\epsilon^{\mathrm{KS}}_{\mathrm{HOMO}} = \epsilon^{\mathrm{HF}}_{\mathrm{HOMO}}$.

For a closed-shell two-electron HF wave function, $\bar{\epsilon}^{\mathrm{HF}}_{\mathrm{HOMO}}(\mathbf{r}) = \epsilon^{\mathrm{HF}}_{\mathrm{HOMO}}$ and $\tau_P^{\mathrm{HF}}(\mathbf{r}) = 0$, while

$$v_{\mathrm{S}}(\mathbf{r}) = -\frac{1}{2}v_{\mathrm{H}}^{\mathrm{HF}}(\mathbf{r}) = -\frac{1}{2}\int \frac{\rho^{\mathrm{HF}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'. \tag{17}$$

Thus, for $N = 2$, Eq. (16) reduces to

$$v_{\mathrm{XC}}^{\mathrm{HF}}(\mathbf{r}) = -\frac{1}{2}v_{\mathrm{H}}^{\mathrm{HF}}(\mathbf{r}). \tag{18}$$

The exact exchange potential of *any* singlet ground-state two-electron system is given by[17]

$$v_{\mathrm{X}}(\mathbf{r}) = -\frac{1}{2}v_{\mathrm{H}}^{\mathrm{WF}}(\mathbf{r}) = -\frac{1}{2}\int \frac{\rho^{\mathrm{WF}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'. \tag{19}$$

This gives the following explicit formula for the corresponding correlation potential:

$$v_{\mathrm{C}}(\mathbf{r}) = v_{\mathrm{XC}}^{\mathrm{hole}}(\mathbf{r}) + \frac{1}{2}v_{\mathrm{H}}^{\mathrm{WF}}(\mathbf{r}) + \frac{\tau_P^{\mathrm{WF}}(\mathbf{r})}{\rho^{\mathrm{WF}}(\mathbf{r})} - \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) - I_{\mathrm{EKT}}. \tag{20}$$

Equations (15) and (20) are the main results of this work. They are nontrivially equivalent to older formulas of Buijse *et al.*,[50] namely, Eqs. (32) and (41) of Ref. 50. The difference is in how the term denoted here by $\bar{\epsilon}^{\mathrm{WF}}$ is represented and evaluated (see Appendix A).

III. NUMERICAL ILLUSTRATIONS

A. Computational details

All calculations reported below were performed with the appropriately modified GAUSSIAN 09 program[51] using Gaussian basis sets from the Environmental Molecular Sciences Laboratory (EMSL) Basis Set Library.[52,53] The u-XZ (X = D, T, Q, 5) basis sets used for the He isoelectronic series were constructed by starting with the respective cc-pVXZ basis sets for the He atom, uncontracting them, and scaling the exponents α_k of the primitive functions by the same factor according to $\exp(-\alpha_k r^2) \rightarrow \exp[-\alpha_k(\zeta r)^2]$. The optimal values of ζ for each species and basis set were obtained by minimizing the corresponding full configuration interaction (FCI) energy.

In the general mRKS procedure,[38] the Hartree part of the total KS potential is constructed in each iteration from ρ^{KS} (the density computed using the current KS orbitals) because self-consistent-field (SCF) iterations typically fail[54] to converge if v_{H} is constructed from ρ^{WF}. For $N = 2$, both methods of constructing v_{H} work but the one using ρ^{WF} does not require any SCF iterations, so it is the method we adopted here. Specifically, we constructed the electrostatic part of the KS Hamiltonian matrix by evaluating $v_{\mathrm{H}}([\rho^{\mathrm{WF}}];\mathbf{r})$ analytically and then computing matrix elements of this potential numerically using a saturated density-functional integration grid. Use of ρ^{KS} in v_{H} would not affect v_{XC} for $N = 2$ but would result in a marginally different total KS potential because ρ^{KS} and ρ^{WF} are not exactly equal in a finite basis set.[33,34,36,38]

The exchange-correlation potentials and other quantities labeled "exact" are those extracted by Umrigar and coworkers[17,55,56] from highly accurate explicitly correlated wave functions of two-electron ions. We treat those potentials as the basis-set-limit benchmarks.

B. Results

As a first application, consider a sequence of FCI wave functions for the He atom computed using the cc-pVXZ (X = D, T, Q, 5) basis sets. The electron densities obtained from these wave functions are reasonably close to the exact (basis-set-limit FCI) density of the He atom. However, if the FCI/cc-pVXZ densities are inserted into Eq. (2), one obtains exchange-correlation potentials that have little resemblance to the basis-set-limit $v_{\mathrm{XC}}(\mathbf{r})$ (Fig. 1). By contrast, Eq. (15) produces consistent, physically correct potentials that have no oscillations anywhere and decay as $-1/r$ at large r. These potentials are visually almost indistinguishable from the exact $v_{\mathrm{XC}}(\mathbf{r})$ even for the cc-pVDZ basis set (Fig. 2).

In a similar manner, we generated exchange-correlation potentials from FCI/u-XZ wave functions for several species of the He isoelectronic series (H^-, He, Li^+, Be^{2+}, C^{4+}, and Ne^{8+}). To assess the proximity of these potentials to the basis-set limit, we substituted them into Eq. (1), solved it in the

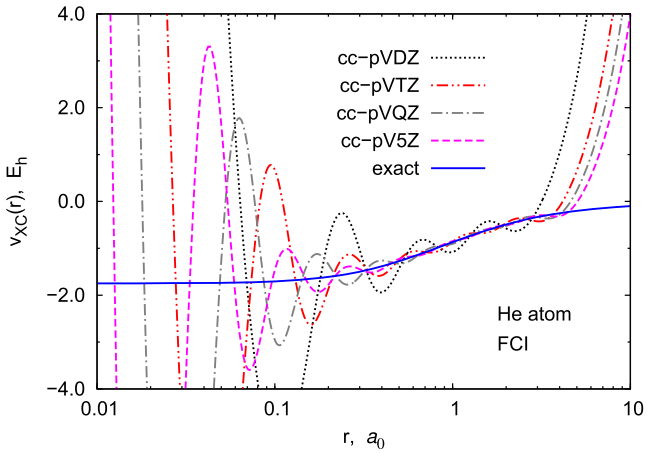


FIG. 1. Exchange-correlation potentials extracted by Eq. (2) from FCI/cc-pVXZ electron densities of the He atom.

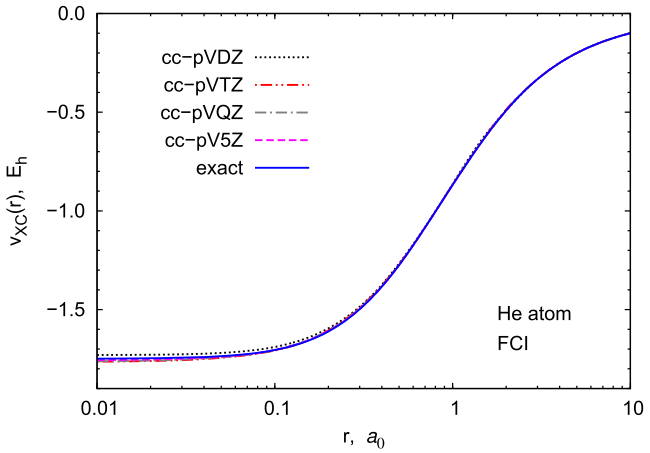


FIG. 2. Exchange-correlation potentials extracted by Eq. (15) from FCI/cc-pVXZ wave functions of the He atom.

respective basis set, and used the resulting KS orbitals to compute a number of properties which were then compared to the known exact (basis-set-limit) values. The four properties we selected include (i) the kinetic part of the correlation energy,

$$T_c = T - T_s, \tag{21}$$

where T is the interacting kinetic energy from the *ab initio* wave function and T_s is non-interacting kinetic energy computed from the KS orbitals determined by $v_{\rm XC}(\mathbf{r})$; (ii) the KS exchange-correlation energy,

$$E_{\rm XC}^{\rm KS} = E_{\rm XC}^{\rm WF} + T_c, \tag{22}$$

where

$$E_{\rm XC}^{\rm WF} = \frac{1}{2}\int \rho^{\rm WF}(\mathbf{r}) v_{\rm XC}^{\rm hole}(\mathbf{r})\, d\mathbf{r} \tag{23}$$

is the *ab initio* exchange-correlation energy (i.e., the non-Coulomb part of the electron-electron interaction energy); (iii) the integrated density discrepancy,

$$\Delta_\rho = \int |\rho^{\rm KS}(\mathbf{r}) - \rho^{\rm WF}(\mathbf{r})|\, d\mathbf{r}, \tag{24}$$

where $\rho^{\rm KS}(\mathbf{r})$ is constructed from the KS orbitals determined by $v_{\rm XC}(\mathbf{r})$; (iv) the virial-theorem[57] energy discrepancy

$$\Delta E_{\rm vir} = W - E_{\rm XC}^{\rm KS} - T_c, \tag{25}$$

where

$$W = \int \left[3\rho^{\rm KS}(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho^{\rm KS}(\mathbf{r})\right] v_{\rm XC}(\mathbf{r})\, d\mathbf{r}. \tag{26}$$

The basis-set-limit values of Δ_ρ and $\Delta E_{\rm vir}$ are zero (this remains true for any type of wave function, not just FCI). The exact (complete-basis-set FCI) values of the other properties were taken from the work of Huang and Umrigar.[56]

Table I shows that the sequence of FCI/u-XZ exchange-correlation potentials of each two-electron species steadily approaches the corresponding basis-set limit. Note that the magnitudes of Δ_ρ and $\Delta E_{\rm vir}$ are *not* indicators of any numerical deficiencies of the construction procedure (as would be the

TABLE I. Properties of selected two-electron ions computed from FCI/u-XZ wave functions and the corresponding KS potentials constructed using Eq. (15). Δ_ρ values are in units of electron charge, and the rest are in hartrees ($E_{\rm h}$). The exact (basis-set-limit) values are taken from Ref. 56.

Basis set (ζ)	$E_{\rm tot}$	T	$E_{\rm XC}^{\rm WF}$	$I_{\rm EKT}$	T_c	$E_{\rm XC}^{\rm KS}$	Δ_ρ	$\Delta E_{\rm vir}$
H^-								
u-DZ (0.36)	−0.518 824	0.520 203	−0.453 910	0.0214	0.015 723	−0.438 187	0.033 439	0.023 207
u-TZ (0.34)	−0.525 751	0.525 546	−0.452 433	0.0260	0.025 664	−0.426 769	0.007 581	0.006 161
u-QZ (0.32)	−0.526 976	0.526 868	−0.451 835	0.0271	0.027 304	−0.424 531	0.003 281	0.002 146
u-5Z (0.31)	−0.527 393	0.527 434	−0.451 475	0.0274	0.027 673	−0.423 803	0.001 704	0.000 904
Exact	−0.527 751	0.527 751	−0.450 774	0.0278	0.027 882	−0.422 892	0	0
He								
u-DZ (1.00)	−2.889 091	2.890 546	−1.091 341	0.8948	0.026 465	−1.064 876	0.002 454	0.006 948
u-TZ (1.00)	−2.900 774	2.900 937	−1.099 776	0.9012	0.034 412	−1.065 365	0.000 743	0.001 449
u-QZ (1.00)	−2.902 582	2.902 671	−1.101 945	0.9027	0.036 003	−1.065 942	0.000 298	0.000 332
u-5Z (1.00)	−2.903 183	2.903 222	−1.102 636	0.9032	0.036 390	−1.066 245	0.000 151	0.000 107
Exact	−2.903 724	2.903 724	−1.103 318	0.9037	0.036 643	−1.066 675	0	0
Li^+								
u-DZ (1.65)	−7.256 148	7.256 208	−1.717 138	2.7678	0.029 252	−1.687 887	0.000 758	0.001 152
u-TZ (1.65)	−7.275 770	7.275 910	−1.729 275	2.7767	0.037 213	−1.692 062	0.000 267	−0.000 635
u-QZ (1.65)	−7.278 301	7.278 385	−1.732 326	2.7786	0.038 944	−1.693 382	0.000 105	−0.000 449
u-5Z (1.64)	−7.279 159	7.279 167	−1.733 364	2.7793	0.039 417	−1.693 947	0.000 055	−0.000 182
Exact	−7.279 913	7.279 913	−1.734 406	2.7799	0.039 828	−1.694 578	0	0
Be^{2+}								
u-DZ (2.31)	−13.619 441	13.617 900	−2.341 620	5.6386	0.030 599	−2.311 021	0.000 360	−0.002 155
u-TZ (2.32)	−13.650 131	13.650 235	−2.356 224	5.6517	0.038 701	−2.317 523	0.000 135	−0.002 329
u-QZ (2.32)	−13.653 484	13.653 576	−2.359 841	5.6540	0.040 478	−2.319 364	0.000 056	−0.001 159
u-5Z (2.30)	−13.654 619	13.654 634	−2.361 114	5.6548	0.040 988	−2.320 126	0.000 028	−0.000 479
Exact	−13.655 566	13.655 566	−2.362 385	5.6556	0.041 483	−2.320 902	0	0
C^{4+}								
u-DZ (3.64)	−32.334 896	32.331 415	−3.589 777	14.3736	0.031 868	−3.557 909	0.000 138	−0.005 633
u-TZ (3.69)	−32.397 588	32.397 707	−3.607 850	14.4009	0.040 239	−3.567 611	0.000 058	−0.004 671
u-QZ (3.70)	−32.403 069	32.403 220	−3.612 194	14.4041	0.042 070	−3.570 123	0.000 027	−0.002 321
u-5Z (3.68)	−32.404 889	32.404 911	−3.613 769	14.4052	0.042 620	−3.571 149	0.000 012	−0.001 098
Exact	−32.406 247	32.406 247	−3.615 353	14.4062	0.043 175	−3.572 178	0	0
Ne^{8+}								
u-DZ (6.31)	−93.721 372	93.724 178	−6.085 643	43.8201	0.032 796	−6.052 847	0.000 046	−0.008 435
u-TZ (6.44)	−93.888 438	93.887 942	−6.108 643	43.8970	0.041 415	−6.067 228	0.000 023	−0.006 693
u-QZ (6.48)	−93.900 492	93.900 664	−6.113 864	43.9032	0.043 344	−6.070 520	0.000 011	−0.003 479
u-5Z (6.49)	−93.904 362	93.904 394	−6.115 786	43.9053	0.043 955	−6.071 830	0.000 006	−0.001 857
Exact	−93.906 807	93.906 807	−6.117 733	43.9068	0.044 555	−6.073 178	0	0

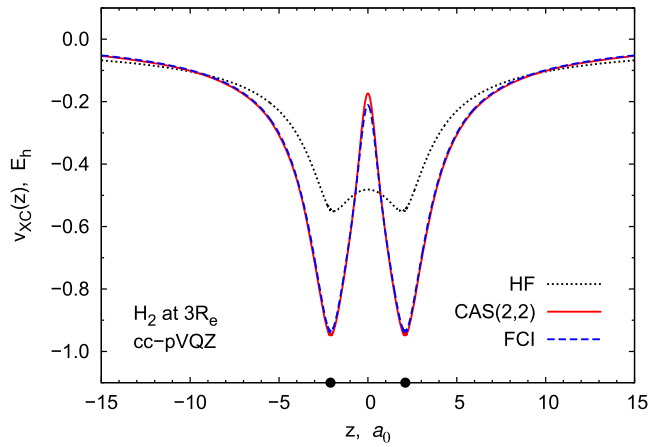


FIG. 3. Exchange-correlation potentials obtained by Eq. (15) from various wave functions of a stretched H_2 molecule.

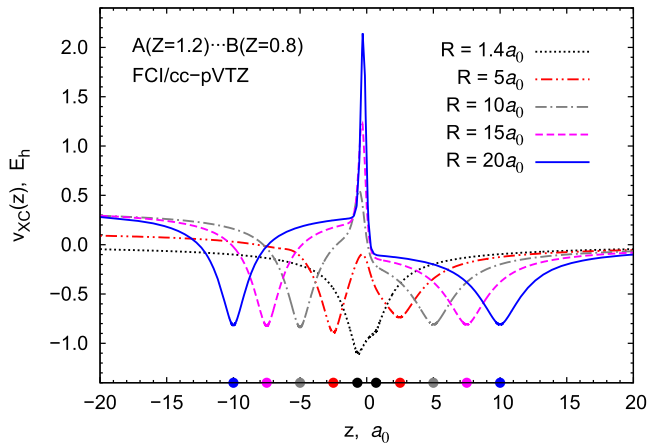


FIG. 5. Exchange-correlation potentials computed by Eq. (15) from FCI/cc-pVTZ wave functions of the two-electron diatomic molecule AB with nuclear charges $Z_A = 1.2$ a.u. and $Z_B = 0.8$ a.u. for various internuclear separations.

case with the KS inversion technique) because the construction is analytic. Rather, the non-zero values of Δ_ρ and ΔE_{vir} are properties of the resulting potentials, uniquely determined by the wave function and the basis set.

Our next application involves the H_2 molecule ($R_e = 1.401a_0$). A 2-electron/2-orbital complete active space (CAS) SCF wave function, abbreviated (2,2)CAS, is a compact approximation that has all of the qualitative features of the exact wave function for this system. Equation (15) is convenient for illustrating the well-known effect that, as the H_2 molecule is stretched, the exact $v_{XC}(\mathbf{r})$ develops a peak at the bond midpoint,[50,58,59] a feature that comes from the τ_P^{WF}/ρ^{WF} term and is absent in KS potentials obtained from the HF wave function (Fig. 3). The height of this peak for H_2 tends to 0.5 E_h in the $R \to \infty$ limit[50] (Fig. 4).

Consider now a fictitious heteronuclear molecule AB consisting of two electrons and two nuclei with charges $Z_A = 1.2$ and $Z_B = 0.8$ a.u. At large internuclear separation, the exact $v_{XC}(\mathbf{r})$ for this system should have a step Δv equal[60] to the difference of the ionization energies of the isolated one-electron atoms A and B, $\Delta v = (Z_A^2 - Z_B^2)/2 = 0.4\ E_h$. KS potentials for this system generated from multireference wave functions such as FCI/cc-pVTZ indeed exhibit such steps: the potential well of atom A is upshifted relative to the potential well of atom B by a constant approaching 0.4 E_h as $R \to \infty$, and the wells are separated by a peak whose height increases with R (Fig. 5). Similar steps and peaks in exchange-correlation potentials of heteronuclear diatomics have been previously reported for model and real systems.[13,20,61,62] A partitioning analysis of the potential for $R = 20a_0$ shows (Fig. 6) that the step stems from the term $\bar{\epsilon}^{WF}(\mathbf{r})$, while the peak arises from the kinetic-energy term, as was noted in a number of previous studies.[20,37,50,61] We stress that exchange-correlation potentials of the quality seen in Figs. 3–6 would be impossible to obtain from Gaussian-basis-set densities by KS inversion without some sort of post-processing because Eq. (2) would produce severely corrupted curves.[18,19]

Our final illustration of the capabilities of Eq. (15) involves a multicenter two-electron ion, H_3^+,[63] at its symmetrically stretched geometry, an equilateral triangle with a side of $R_{HH} = 2R_e = 3.300a_0$. We have generated the exchange-correlation potential for this system from the FCI/cc-pVTZ wave function and visualized the result in the form of a contour plot in the molecular plane (Fig. 7). It is interesting

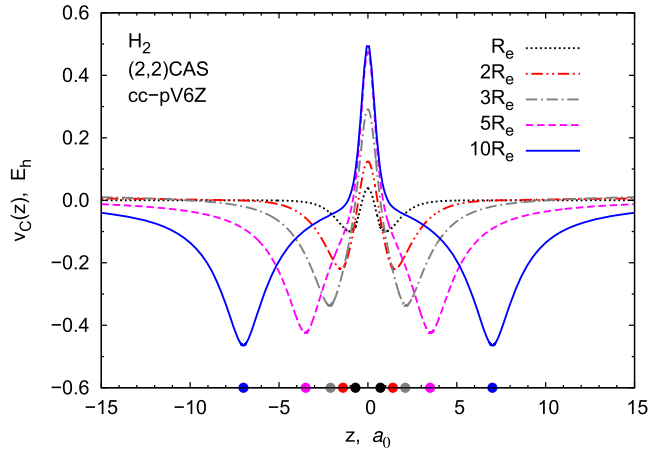


FIG. 4. Correlation potentials obtained by Eq. (20) from (2,2)CAS wave functions of the H_2 molecule for various internuclear separations.

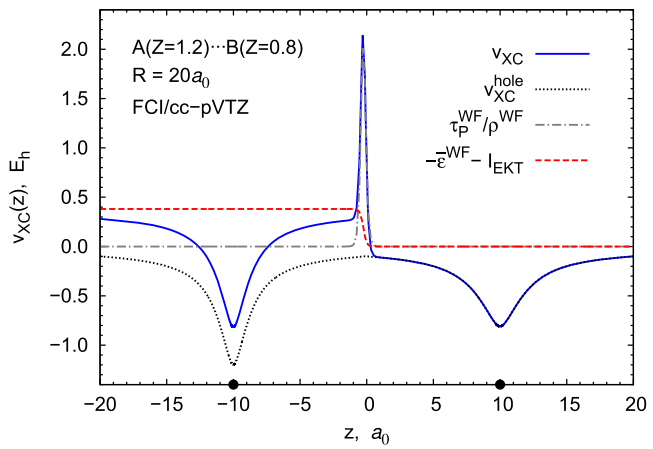


FIG. 6. Partitioning of one of the exchange-correlation potentials of Fig. 5. Here $I_{EKT} = 0.3291\ E_h$.

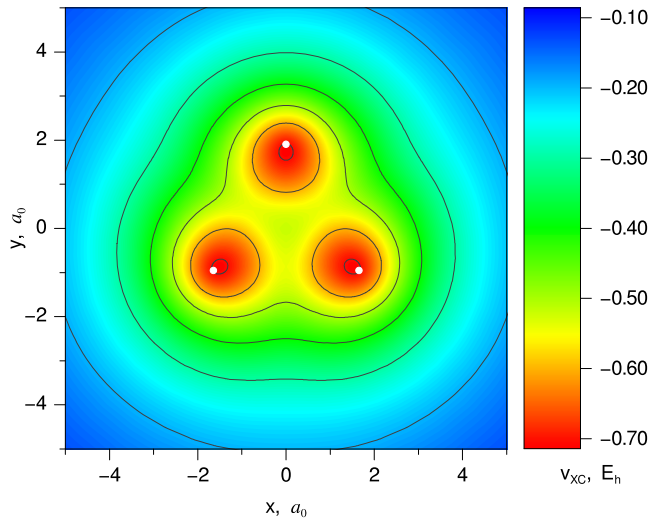


FIG. 7. Exchange-correlation potential computed by Eq. (2) from the FCI/cc-pVTZ wave function of a stretched H_3^+ ion (D_{3h}, $R_{HH} = 3.300a_0$). The plot is for the molecular plane. The white dots mark the nuclear positions.

to note that the minima of this v_{XC} do not coincide with the nuclear positions.

IV. CONCLUDING REMARKS

We have shown that Eq. (3), which is generally not a closed-form expression for $v_{XC}(\mathbf{r})$, becomes an explicit formula for $v_{XC}(\mathbf{r})$ in the case of singlet ground-state two-electron systems. This formula, Eq. (15), enables one to construct the exchange-correlation and correlation potentials of such systems directly from interacting wave functions. Note that triplet two-electron systems involve two spatial KS orbitals so that construction of exchange-correlation potentials for triplet states would require the general (iterative) method of Ref. 38. We deliberately chose small to moderately large basis sets for our illustrative applications of Eq. (15) in order to emphasize that it can routinely produce potentials of high quality. If one wishes to generate even more accurate potentials, all one has to do is to use a better basis set.

Exchange-correlation potentials associated with finite-basis-set densities by Eq. (15) do not recover those densities exactly (analogously, solutions of the Roothaan equations[64] do not satisfy exactly the Hartree–Fock integro-differential equations). Nevertheless, potentials obtained by Eq. (15) are consistent and physically appropriate for Coulombic systems, in contrast to potentials obtained from Gaussian-basis-set densities by Eq. (2). The two methods serve entirely different purposes: Eq. (2) gives the potential that recovers a given density, provided that the KS equations with that potential are solved using a complete basis set, whereas Eq. (15) gives a finite-basis-set approximation to the system's $v_{XC}(\mathbf{r})$ corresponding to the basis-set limit of the chosen level of *ab initio* theory.

In a comment[65] on Refs. 33–35, Baerends and Gritsenko argued that the method proposed in those papers "does not allow to compute the KS potential from wave-function quantities... since those quantities cancel in the expression for $v_{XC}(\mathbf{r})$" and that it does not "progress" beyond Eq. (2). Equation (15) and comparison of Figs. 1 and 2 refute those arguments even more explicitly than the evidence presented in our response.[41]

Previously, Helbig *et al.*[61] derived an exact formula for the KS potential of a simplified two-electron diatomic molecule in which each electron is tightly bound to its nucleus (a similar model had been employed by Perdew[13]). Another separated-atom, two-electron model for studying the exact KS potential was developed by Tempel *et al.*[20] Equation (15), derived for two-electron systems with no restrictions on the type of wave function, represents a nontrivial generalization of all such formulas (see Appendix B). It would be not difficult to extend Eq. (15) to non-integer electron numbers ($0 < N \leq 2$), as was done for the model potential of Ref. 61 by Benítez and Proetto.[62] Extension to time-dependent wave functions is another possibility.

ACKNOWLEDGMENTS

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

APPENDIX A: FORMULA OF BUIJSE AND CO-WORKERS

Buijse *et al.*[50] devised an exact expression for the KS potential which generally involves both interacting and non-interacting wave functions, as Eq. (3), but for singlet two-electron systems reduces to a simpler formula which involves the interacting wave function alone, as Eq. (15). The purpose of this section is to explain how Eq. (15) differs from the result of Buijse *et al.* (The general expressions for v_{XC} are compared in Ref. 35.)

Buijse *et al.* showed that for a singlet two-electron system [see Eq. (32) of Ref. 50],

$$v_{HXC}(\mathbf{r}) = v_{cond}(\mathbf{r}) + v_{kin}(\mathbf{r}) + v^{N-1}(\mathbf{r}), \tag{A1}$$

where each term is determined by the interacting wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$. The first term is[50,65]

$$v_{cond}(\mathbf{r}) = v_H(\mathbf{r}) + v_{XC}^{hole}(\mathbf{r}). \tag{A2}$$

The second term is given by[50]

$$v_{kin}(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau_W(\mathbf{r})}{\rho(\mathbf{r})}, \tag{A3}$$

where $\tau(\mathbf{r}) = \frac{1}{2}\left[\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'} \gamma^{WF}(\mathbf{r}, \mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'}$. Since $\tau_P = \tau - \tau_W$ in any basis set, we identify v_{kin} as our τ_P/ρ term. The quantity v^{N-1} is defined in Ref. 50 by Eq. (18) which involves the $(N-1)$-electron Hamiltonian, $\hat{H}^{N-1}$, and the entire interacting wave function. To compute v^{N-1} by definition, one actually needs no more than the 2- and 3-RDMs, a fact that is not obvious from Ref. 50 but can be deduced by the method of Ref. 66. For $N = 2$, however, $\hat{H}^{N-1}$ becomes the one-electron bare-nucleus Hamiltonian $\hat{h}(\mathbf{r}_2)$, so v^{N-1} reduces to

$$v^{N-1}(\mathbf{r}) = \frac{2}{\rho(\mathbf{r})}\sum_{\sigma}\int \Psi^*(\mathbf{x},\mathbf{x}_2)\hat{h}(\mathbf{r}_2)\Psi(\mathbf{x},\mathbf{x}_2)\,d\mathbf{x}_2 - E_0^{N-1}, \tag{A4}$$

where E_0^{N-1} is the ground-state energy of the ionized (i.e., corresponding one-electron) system. The right-hand side of Eq. (A4) can be evaluated using the 2-RDM alone. Evaluation of $\bar{\epsilon}^{\mathrm{WF}}$ by Eq. (7) also requires no more than the 2-RDM (but for all N) and is arguably more convenient than that of v^{N-1} by Eq. (A4) even for $N = 2$ because the generalized Fock matrix is readily available in most *ab initio* electronic structure codes as part of analytic energy gradient subroutines and multiconfigurational SCF modules.

It can be shown[35] that, in a complete basis set, v^{N-1} and $\bar{\epsilon}^{\mathrm{WF}}$ are related by

$$v^{N-1}(\mathbf{r}) + \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = -I. \tag{A5}$$

This identity does not mean that $\bar{\epsilon}^{\mathrm{WF}}$ is given by the same expression as v^{N-1} up to a constant, but rather that the functions $\bar{\epsilon}^{\mathrm{WF}}$ and v^{N-1} are such that their sum is a constant. It remains to be seen whether Eq. (A5) holds pointwise in finite-basis-set implementations.

Note that if Ψ is an eigenfunction of the all-electron interacting Hamiltonian, then the integral in Eq. (A4) can be evaluated[65] to give

$$v^{N-1}(\mathbf{r}) = -\frac{\tau_L(\mathbf{r})}{\rho(\mathbf{r})} - v_{\mathrm{cond}}(\mathbf{r}) - v(\mathbf{r}) - I, \tag{A6}$$

where $I = E_0^{N-1} - E_0^N = -\epsilon$ and $\tau_L = \tau - \nabla^2\rho/4$. Substituting Eqs. (A2), (A3), and (A6) into Eq. (A1) and subtracting out v_{H}, one reverts to Eq. (2). However, Eq. (A6) is *not* true when its ingredients are evaluated using a finite basis set (i.e., when Ψ is not an eigenfunction). If one ignores that and evaluates v^{N-1} by Eq. (A6) anyway, then Eq. (A1) proves to be no different from the KS inversion of Eq. (2).[65] This illustrates our key point[36] that different expressions for v_{XC} which are equivalent on paper may not be equivalent when implemented using a finite basis set.

Buijse *et al.*[50] did use Eqs. (A1)–(A4) to compute exchange-correlation potentials for He and H_2 from FCI wave functions but did not investigate the KS electron densities recovered by those potentials. As far as we know, Ref. 50 remains the only work where KS potentials were constructed using Eq. (A4) as written.

APPENDIX B: SPECIAL CASES OF EQ. (15)

Helbig and co-workers[61] studied a model two-electron system that is mathematically equivalent to a singlet system of two non-interacting electrons occupying the first two lowest-energy eigenstates of the one-electron Hamiltonian with an external potential v,

$$\left(-\frac{1}{2}\nabla^2 + v\right)\psi_k = e_k\psi_k. \tag{B1}$$

For such a system,

$$\rho^{\mathrm{WF}} = |\psi_1|^2 + |\psi_2|^2 \tag{B2}$$

and the generalized Fock operator reduces to the actual one-electron Hamiltonian of Eq. (B1), so $f_k = \psi_k$ and $\lambda_k = e_k$ ($k = 1, 2$). Thus,

$$\bar{\epsilon}^{\mathrm{WF}} = \frac{1}{\rho^{\mathrm{WF}}}(e_1|\psi_1|^2 + e_2|\psi_2|^2). \tag{B3}$$

Moreover, $v_{\mathrm{H}} = v_{\mathrm{XC}}^{\mathrm{hole}} = 0$,

$$\tau_P = \frac{1}{2\rho^{\mathrm{WF}}}|\psi_1\nabla\psi_2 - \psi_2\nabla\psi_1|^2, \tag{B4}$$

and $I_{\mathrm{EKT}} = e_2$. Substitution of these expressions into Eq. (15) gives the three-dimensional version of Eq. (11) of Ref. 61—the exact exchange-correlation potential for the model system of Helbig *et al.*

Tempel and co-workers[20] derived an analytic expression for the total KS potential, v_s, starting from a Heitler–London-type two-electron wave function [Eq. (25) of Ref. 20]. Their expression also has an explicit connection to Eq. (15): in the interatomic region of a highly stretched molecule, $v + v_{\mathrm{H}} \approx 0$, so $v_s \approx v_{\mathrm{XC}}$ and Eq. (25) of Ref. 20 reduces to Eq. (11) of Ref. 61, a special case of our Eq. (15).

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