Reduction of Electronic Wave Functions to Kohn-Sham Effective Potentials

Ilya G. Ryabinkin
Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Ontario M1C 1A4, Canada

Sviataslau V. Kohut and Viktor N. Staroverov*
Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada

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A method for calculating the Kohn-Sham exchange-correlation potential $v_{\mathrm{XC}}(\mathbf{r})$ from a given electronic wave function is devised and implemented. It requires on input one- and two-electron reduced density matrices and involves construction of the generalized Fock matrix. The method is free from numerical limitations and basis-set artifacts of conventional schemes for constructing $v_{\mathrm{XC}}(\mathbf{r})$ in which the potential is recovered from a given electron density, and is simpler than various many-body techniques. The chief significance of this development is that it allows one to directly probe the functional derivative of the true exchange-correlation energy functional and to rigorously test and improve various density-functional approximations.

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The Kohn-Sham density-functional theory [1] is the most widely used method for electronic structure calculations of molecules and solids. In this method, the ground-state energy of a system is treated as a functional of the electron density $\rho(\mathbf{r})$ and then partitioned in such a way that only one term, the exchange-correlation energy $E_{\mathrm{XC}}[\rho]$, remains unknown. Application of the variational principle to the total energy functional leads to a one-electron Schrödinger equation with an effective Hamiltonian that includes the system's electrostatic potential and the exchange-correlation potential, $v_{\mathrm{XC}}([\rho];\mathbf{r}) = \delta E_{\mathrm{XC}}[\rho]/\delta\rho(\mathbf{r})$. While the exact $E_{\mathrm{XC}}[\rho]$ can be written only in implicit form [2], its functional derivative $v_{\mathrm{XC}}([\rho];\mathbf{r})$ can in principle be computed and visualized as a *function* of $\mathbf{r}$ for any particular noninteracting v-representable density. High-quality Kohn-Sham potentials are used for testing density-functional approximations [3], accurate description of electronic excitations [4], and other purposes.

Most existing methods for generating exact exchange-correlation potentials fit the function $v_{\mathrm{XC}}(\mathbf{r})$ to a given ground-state $\rho(\mathbf{r})$ via the Kohn-Sham equations either by iterative updates [5–8] or through some constrained optimization [9–11]. The target densities are usually obtained from *ab initio* wave functions which are themselves discarded. Because small changes in $\rho(\mathbf{r})$ can induce large changes in $v_{\mathrm{XC}}(\mathbf{r})$ [12], potential-reconstruction methods that use only $\rho(\mathbf{r})$ as input suffer from numerical instabilities. Moreover, electron densities generated using ubiquitous Gaussian basis sets correspond to exchange-correlation potentials that wildly oscillate and diverge [13–16], a result that is formally correct but unwanted. Kohn-Sham potentials can be also constructed by many-body methods [17–21], but these techniques are quite elaborate and often require solving an integral equation for $v_{\mathrm{XC}}(\mathbf{r})$, which is a challenge by itself.

Here, we propose a radically different method for computing the exchange-correlation potential of a given many-electron system, which avoids the above difficulties. In this method, the functional derivative of the exact $E_{\mathrm{XC}}[\rho]$ is obtained directly from the system's electronic wave function. The approach represents a nontrivial generalization of our technique for constructing Kohn-Sham potentials corresponding to Hartree-Fock (HF) electron densities [22,23] and is conceptually related to the wave-function-based analysis of Kohn-Sham potentials developed by Baerends and co-workers [24–28].

The basic idea of our approach is to derive two expressions for the local electron energy balance, one of which originates from the Kohn-Sham equations, and the other from the Schrödinger equation. When one expression is subtracted from the other under the assumption that the Kohn-Sham and wave-function-based densities are equal, the system's electrostatic potentials cancel out and the difference gives an explicit formula for $v_{\mathrm{XC}}(\mathbf{r})$. For simplicity, the treatment presented in this Letter is restricted to electronic singlet ground states described with closed-shell Kohn-Sham determinants, and assumes that all basis functions and orbitals are real (although the notation for complex conjugate is retained).

Accomplishing the first part of this plan is easy. In the Kohn-Sham scheme, the ground-state density of a singlet N-electron system is obtained as $\rho^{\mathrm{KS}}(\mathbf{r}) = \sum_i n_i|\phi_i(\mathbf{r})|^2$, where $n_i = 0$ or 2 are occupation numbers of the corresponding Kohn-Sham orbitals ($N = \sum_i n_i$). The orbitals are obtained by solving the equation

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

where $v(\mathbf{r})$ is the electrostatic potential of the nuclei and $v_{\mathrm{H}}^{\mathrm{KS}}(\mathbf{r})$ is the electrostatic potential of $\rho^{\mathrm{KS}}(\mathbf{r})$. If we multiply Eq. (1) by $n_i\phi_i^*(\mathbf{r})$, sum over i, and divide through by $\rho^{\mathrm{KS}}(\mathbf{r})$, we obtain

$$\frac{\tau_L^{\mathrm{KS}}(\mathbf{r})}{\rho^{\mathrm{KS}}(\mathbf{r})} + v(\mathbf{r}) + v_{\mathrm{H}}^{\mathrm{KS}}(\mathbf{r}) + v_{\mathrm{XC}}(\mathbf{r}) = \bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}), \tag{2}$$

where $\tau_L^{\mathrm{KS}}(\mathbf{r}) = -\frac{1}{2}\sum_i n_i\phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})$ is the Kohn-Sham kinetic energy density and

$$\bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{KS}}(\mathbf{r})}\sum_i n_i\epsilon_i|\phi_i(\mathbf{r})|^2 \tag{3}$$

is the average local Kohn-Sham orbital energy [29].

The second part of the plan is to reduce the N-electron Schrödinger equation to a local energy balance expression analogous to Eq. (2). There is more than one way to do this. Holas and March [30] had considered a contracted Schrödinger equation for this purpose, but their proposal led to a complicated integral equation for $v_{\mathrm{XC}}(\mathbf{r})$ involving the three-electron reduced density matrix (3-RDM). The Baerends group [24–28] used an expression involving $(N-1)$-electron conditional amplitudes. The method we propose here is motivated by Löwdin's approach [31] to the problem of finding the optimal finite one-electron basis set for a configuration-interaction (CI) expansion.

Suppose we have an N-electron ground-state wave function Ψ expressed in terms of orthonormal orbitals $\{\psi_i\}$. Then the total electronic energy may be written as

$$E = \sum_{ij}\gamma_{ij}\langle\psi_j|\hat{h}|\psi_i\rangle + \sum_{ikjl}\Gamma_{ikjl}\langle\psi_j\psi_l|r_{12}^{-1}|\psi_i\psi_k\rangle, \tag{4}$$

where $\hat{h}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v(\mathbf{r})$ is the one-electron core Hamiltonian, $\gamma_{ij} = \sum_\sigma\langle\Psi|\hat{a}_{j\sigma}^\dagger\hat{a}_{i\sigma}|\Psi\rangle$ ($\sigma = \alpha, \beta$ is the spin index) are matrix elements of the spin-free 1-RDM, and $\Gamma_{ikjl} = \frac{1}{2}\sum_{\sigma\sigma'}\langle\Psi|\hat{a}_{j\sigma}^\dagger\hat{a}_{l\sigma'}^\dagger\hat{a}_{k\sigma'}\hat{a}_{i\sigma}|\Psi\rangle$ are matrix elements of the spin-free 2-RDM.

Our objective is to turn Eq. (4) into a local energy balance equation. We start by minimizing E with respect to the functions $\{\psi_i\}$, subject to the constraint $\langle\psi_j|\psi_i\rangle = \delta_{ji}$, while keeping γ_{ij} and Γ_{ikjl} fixed. The corresponding Euler-Lagrange equation is

$$\frac{\delta E}{\delta\psi_j^*(\mathbf{r})} = \sum_i\lambda_{ij}\psi_i(\mathbf{r}), \tag{5}$$

where λ_{ij} are yet undetermined Lagrange multipliers. We evaluate the functional derivative in Eq. (5), multiply the result by $\psi_j^*(\mathbf{r}')$, sum over j, and obtain

$$\hat{h}(\mathbf{r})\gamma(\mathbf{r},\mathbf{r}') + 2\int\frac{\Gamma(\mathbf{r},\mathbf{r}_2;\mathbf{r}',\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2 = \sum_{ij}\lambda_{ij}\psi_i(\mathbf{r})\psi_j^*(\mathbf{r}'), \tag{6}$$

where

$$\gamma(\mathbf{r},\mathbf{r}') = \sum_{ij}\gamma_{ij}\psi_i(\mathbf{r})\psi_j^*(\mathbf{r}') \tag{7}$$

and

$$\Gamma(\mathbf{r},\mathbf{r}_2;\mathbf{r}',\mathbf{r}_2') = \sum_{ikjl}\Gamma_{ikjl}\psi_i(\mathbf{r})\psi_k(\mathbf{r}_2)\psi_j^*(\mathbf{r}')\psi_l^*(\mathbf{r}_2') \tag{8}$$

are the coordinate representations of the spin-free 1-RDM and 2-RDM, respectively.

We denote the left-hand side of Eq. (6) by $G(\mathbf{r},\mathbf{r}')$ and treat it as the kernel of an integral operator defined by

$$\hat{G}\psi_j(\mathbf{r}) = \int G(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{r}')d\mathbf{r}'. \tag{9}$$

Then λ_{ij} can be determined from Eqs. (6) and (9) as

$$\lambda_{ij} = \langle\psi_i|\hat{G}|\psi_j\rangle. \tag{10}$$

The operator $\hat{G}$, known as the generalized Fock operator or orbital Lagrangian, arises in various problems of quantum chemistry [31–35].

For our purposes, we need only the $\mathbf{r} = \mathbf{r}'$ part of Eq. (6), which after division by $\rho^{\mathrm{WF}}(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r})$ (the density from the wave function) becomes

$$\frac{\tau_L^{\mathrm{WF}}(\mathbf{r})}{\rho^{\mathrm{WF}}(\mathbf{r})} + v(\mathbf{r}) + \frac{2}{\rho^{\mathrm{WF}}(\mathbf{r})}\int\frac{P(\mathbf{r},\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2 = \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}), \tag{11}$$

where $\tau_L^{\mathrm{WF}}(\mathbf{r}) = -\frac{1}{2}[\nabla^2\gamma(\mathbf{r},\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}$ is the interacting kinetic energy density, $P(\mathbf{r},\mathbf{r}_2) = \Gamma(\mathbf{r},\mathbf{r}_2;\mathbf{r},\mathbf{r}_2)$ is the pair function, and

$$\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{WF}}(\mathbf{r})}\sum_{ij}\lambda_{ij}\psi_i(\mathbf{r})\psi_j^*(\mathbf{r}). \tag{12}$$

One can always write the pair function as

$$P(\mathbf{r},\mathbf{r}_2) = \frac{1}{2}\rho^{\mathrm{WF}}(\mathbf{r})[\rho^{\mathrm{WF}}(\mathbf{r}_2) + \rho_{\mathrm{XC}}^{\mathrm{WF}}(\mathbf{r},\mathbf{r}_2)], \tag{13}$$

which defines $\rho_{\mathrm{XC}}^{\mathrm{WF}}(\mathbf{r},\mathbf{r}_2)$, the exchange-correlation hole density. Substituting Eq. (13) into Eq. (11) we obtain

$$\frac{\tau_L^{\mathrm{WF}}(\mathbf{r})}{\rho^{\mathrm{WF}}(\mathbf{r})} + v(\mathbf{r}) + v_{\mathrm{H}}^{\mathrm{WF}}(\mathbf{r}) + v_S^{\mathrm{WF}}(\mathbf{r}) = \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}), \tag{14}$$

where $v_{\mathrm{H}}^{\mathrm{WF}}(\mathbf{r})$ is the electrostatic potential of $\rho^{\mathrm{WF}}(\mathbf{r})$ and

$$v_S^{\mathrm{WF}}(\mathbf{r}) = \int\frac{\rho_{\mathrm{XC}}^{\mathrm{WF}}(\mathbf{r},\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2 \tag{15}$$

is the Slater exchange-correlation-charge potential [36]. Equation (14) is the wave-function counterpart of Eq. (2).

Observe that the sum in Eq. (12) does not change if we replace every λ_{ij} with λ_{ji}^*. This means that $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ is determined by the Hermitian (symmetric) part of $\hat{G}$. If desired, one can define the self-adjoint operator $\hat{F} = (\hat{G} + \hat{G}^\dagger)/2$ and solve the Hermitian eigenvalue problem $\hat{F}f_i(\mathbf{r}) = \lambda_i f_i(\mathbf{r})$. This optional step allows one to cast Eq. (12) as

$$\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{WF}}(\mathbf{r})} \sum_i \lambda_i |f_i(\mathbf{r})|^2, \tag{16}$$

which is formally analogous to Eq. (3). The quantity $\bar{\epsilon}^{\mathrm{WF}}(\mathbf{r})$ as given by Eq. (16) was introduced by us earlier under the name of "average local electron energy" [37].

Now let us subtract Eq. (14) from Eq. (2), substitute the identity $\tau_L = \tau - \nabla^2\rho/4$ for τ_L^{KS} and for τ_L^{WF} with $\tau^{\mathrm{KS}} = \frac{1}{2}\sum_i n_i |\nabla\phi_i|^2$ and $\tau^{\mathrm{WF}}(\mathbf{r}) = \frac{1}{2}[\nabla_{\mathbf{r}'}\nabla_{\mathbf{r}}\gamma(\mathbf{r},\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}$, and apply the condition $\rho^{\mathrm{KS}}(\mathbf{r}) = \rho^{\mathrm{WF}}(\mathbf{r})$. This yields the central equation of this work:

$$v_{\mathrm{XC}}(\mathbf{r}) = v_S^{\mathrm{WF}}(\mathbf{r}) + \bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}) - \bar{\epsilon}^{\mathrm{WF}}(\mathbf{r}) + \frac{\tau^{\mathrm{WF}}(\mathbf{r})}{\rho^{\mathrm{WF}}(\mathbf{r})} - \frac{\tau^{\mathrm{KS}}(\mathbf{r})}{\rho^{\mathrm{KS}}(\mathbf{r})}. \tag{17}$$

Since τ^{KS} and $\bar{\epsilon}^{\mathrm{KS}}$ are initially unknown, Eq. (17) must be solved iteratively in conjunction with the Kohn-Sham equations. The transition from τ_L to τ is not strictly necessary but beneficial for numerical calculations because τ does not diverge at the nuclei as does τ_L.

Note that as $r \to \infty$, the term v_S^{WF} vanishes, but the other ingredients remain nonzero: $\bar{\epsilon}^{\mathrm{KS}}$, $\tau_L^{\mathrm{KS}}/\rho^{\mathrm{KS}}$, and $-\tau^{\mathrm{KS}}/\rho^{\mathrm{KS}}$ approach ϵ_{HOMO} [38], while $\bar{\epsilon}^{\mathrm{WF}}$, $\tau_L^{\mathrm{WF}}/\rho^{\mathrm{WF}}$, and $-\tau^{\mathrm{WF}}/\rho^{\mathrm{WF}}$ approach $-I_{\mathrm{min}}$ [37], where I_{min} is the first ionization energy of the system as determined by the extended Koopmans theorem [39]. To ensure that $v_{\mathrm{XC}}(\mathbf{r})$ as given by Eq. (17) properly vanishes at infinity, we shift all current values of ϵ_i in each Kohn-Sham iteration to satisfy the condition

$$\epsilon_{\mathrm{HOMO}} = -I_{\mathrm{min}}, \tag{18}$$

which also imparts $\rho^{\mathrm{KS}}(\mathbf{r})$ with proper asymptotic decay.

The proposed algorithm is as follows. (1) Obtain a wave function for the system of interest. Calculate ρ^{WF}, τ^{WF}, v_S^{WF}, $\bar{\epsilon}^{\mathrm{WF}}$, and I_{min}. (2) Generate an initial guess for the occupied Kohn-Sham orbitals $\{\phi_i\}$ and their eigenvalues $\{\epsilon_i\}$. (3) Using the current guess for $\{\phi_i\}$ and shifted $\{\epsilon_i\}$, construct the potential v_{XC} by Eq. (17). (4) Solve the Kohn-Sham equations using the current v_{XC} and the same basis as in step 1. This gives new sets $\{\phi_i\}$ and $\{\epsilon_i\}$. (5) Return to step 3 and iterate until the potential v_{XC} is self-consistent.

The method was implemented in the GAUSSIAN09 suite of programs [40], which already contains subroutines for constructing the generalized Fock matrix as a part of the multiconfigurational self-consistent-field (MCSCF) module. The values of I_{min} were computed as in Ref. [34], while ρ^{WF} and τ^{WF} were assembled from natural orbitals. Any reasonable density-functional approximation may be used to generate an initial guess for $\{\phi_i\}$ and $\{\epsilon_i\}$. The potential was considered converged when all Kohn-Sham density matrix elements from consecutive iterations differed by less than 10^{-10} in the root-mean-square sense. The method works best with basis sets that are not heavily contracted in the core region.

An added benefit of generating $v_{\mathrm{XC}}(\mathbf{r})$ from a wave function is that one can readily obtain the corresponding exchange-correlation energy $E_{\mathrm{XC}}^{\mathrm{KS}}$, which is inaccessible when only the electron density is known. We computed this energy as $E_{\mathrm{XC}}^{\mathrm{KS}} = E_{\mathrm{XC}}^{\mathrm{WF}} + T_c$, where $E_{\mathrm{XC}}^{\mathrm{WF}}$ is the *ab initio* exchange-correlation energy defined as $E_{\mathrm{XC}}^{\mathrm{WF}} = \frac{1}{2}\int \rho^{\mathrm{WF}}(\mathbf{r}) v_S^{\mathrm{WF}}(\mathbf{r}) d\mathbf{r}$ and $T_c = T - T_s$ is the difference between the *ab initio* and Kohn-Sham total kinetic energies, evaluated analytically. Also of interest is the integrated density difference $\Delta\rho = \int |\rho^{\mathrm{KS}}(\mathbf{r}) - \rho^{\mathrm{WF}}(\mathbf{r})| d\mathbf{r}$, evaluated for the self-consistent $v_{\mathrm{XC}}(\mathbf{r})$. Because the condition $\rho^{\mathrm{KS}}(\mathbf{r}) = \rho^{\mathrm{WF}}(\mathbf{r})$ is imposed in our approach only in the derivation of Eq. (17), $\Delta\rho$ strictly vanishes only in the basis-set limit. Insistence on reproducing $\rho^{\mathrm{WF}}(\mathbf{r})$ *exactly* in Gaussian basis sets would be misplaced because (i) it brings out unwanted oscillations and divergences of $v_{\mathrm{XC}}(\mathbf{r})$ and (ii) the potential that yields a given density in a finite basis is not unique anyway [41,42].

To test the method, we computed exchange-correlation potentials for the three atoms (He, Be, and Ne) for which exact potentials are available in the literature [43,44] using full CI (FCI) and complete active space (CAS) self-consistent-field (SCF) wave functions and standard Gaussian basis sets [45]. For He, already the potential extracted from the FCI wave function in the cc-pVTZ basis set is very close to the exact $v_{\mathrm{XC}}(\mathbf{r})$, and the cc-pVQZ and cc-pV5Z FCI exchange-correlation potentials are visually indistinguishable from the benchmark (Fig. 1 and Table I). Even the correlation potential for He, $v_{\mathrm{C}}(\mathbf{r}) = v_{\mathrm{XC}}(\mathbf{r}) - v_{\mathrm{H}}(\mathbf{r})/2$, which is almost 2 orders of magnitude smaller than $v_{\mathrm{XC}}(\mathbf{r})$, is very accurate at the FCI cc-pV5Z level (Fig. 1). For Be, the sequence of potentials from CAS(2,4) wave functions quickly approaches the exact $v_{\mathrm{XC}}(\mathbf{r})$ with increasing basis set size (Fig. 2), as do the corresponding T_s values (Table I). By contrast, T_c and $E_{\mathrm{XC}}^{\mathrm{KS}}$ converge slowly because they depend not only on $v_{\mathrm{XC}}(\mathbf{r})$ but

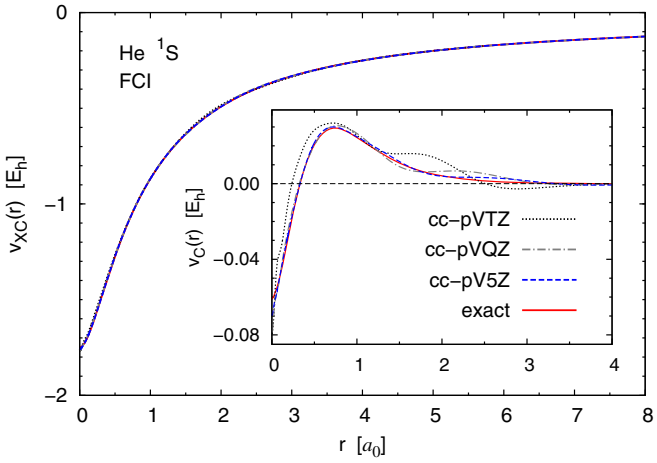

FIG. 1 (color online). Exchange-correlation and correlation (inset) potentials for the He atom calculated from FCI wave functions using various basis sets.

TABLE I. Characteristics of selected wave functions and the corresponding Kohn-Sham effective potentials (in atomic units).

System	Wave function	E_{tot}	I_{min}	T_s	$T_c = T - T_s$	$E_{\mathrm{XC}}^{\mathrm{KS}}$	$\Delta\rho$
He	FCI/cc-pVTZ	−2.900 232	0.9013	2.8571	0.0435	−1.0550	0.002 51
	FCI/cc-pVQZ	−2.902 411	0.9026	2.8652	0.0370	−1.0645	0.000 65
	FCI/cc-pV5Z	−2.903 152	0.9032	2.8668	0.0364	−1.0662	0.000 13
	Exact[a]	−2.903 724	0.9037	2.8671	0.0366	−1.0667	
Be	CAS(2,4)/cc-pCVDZ	−14.615 45	0.3485	14.4901	0.1333	−2.6146	0.017 29
	CAS(2,4)/cc-pCVTZ	−14.616 53	0.3489	14.5538	0.0619	−2.6866	0.004 93
	CAS(2,4)/cc-pCVQZ	−14.616 77	0.3490	14.5910	0.0258	−2.7232	0.005 47
	FCI/u-cc-pCVTZ	−14.663 70	0.3421	14.5956	0.0654	−2.7715	0.002 15
	Exact[a]	−14.667 36	0.3426	14.5942	0.0732	−2.7701	

[a]Accurate estimates from Ref. [43] (He) and Ref. [44] (Be).

also on the accuracy of the wave function through the value of T. Potentials for the Ne atom constructed from CAS(8,8) wave functions also improve rapidly with the size of the basis set (Fig. 2). Thus, even compact correlated wave functions can produce accurate Kohn-Sham potentials, provided that the basis set is of good quality.

The method works equally well for molecules. It is known that, in molecules, the onset of strong correlation induced by bond stretching manifests itself in characteristic midbond peaks of $v_{\mathrm{XC}}(\mathbf{r})$ [27,46–48]. Using our method, we readily reproduced these peaks in a number of stretched diatomics exemplified by N_2 (Fig. 3). Exchange-correlation potentials for polyatomic molecules can also be generated by our method (Fig. 4).

It is remarkable that Kohn-Sham potentials computed from wave functions are always well defined and free from spurious features. Conventional methods for extracting $v_{\mathrm{XC}}(\mathbf{r})$ from densities, when implemented in matrix form, would not deliver such unambiguous results because there is no one-to-one correspondence between densities and potentials in finite basis sets [41]. Furthermore, when density-to-potential mapping techniques are rigorously applied to electron densities generated in Gaussian basis sets, one obtains unphysical potentials [13–16]. Neither of these complications affects our approach.

In conclusion, we have developed a practical method for folding a many-electron wave function into the corresponding exchange-correlation potential. The key ingredient of our approach is the generalized Fock matrix which is commonly available in *ab initio* codes as a byproduct of computing MCSCF wave functions, nuclear gradients, and first-order properties. The method possesses several advantages over existing techniques for constructing exchange-correlation potentials: it delivers $v_{\mathrm{XC}}(\mathbf{r})$ in a simple analytic form, avoids the ambiguity of associating a given electron density with a Kohn-Sham potential in a finite basis set, is stable with respect to changes in basis sets, convergence thresholds, and other details of the calculation, and produces potentials without oscillations and divergences when using Gaussian basis sets. Further exploration of the capabilities of our approach is under way.

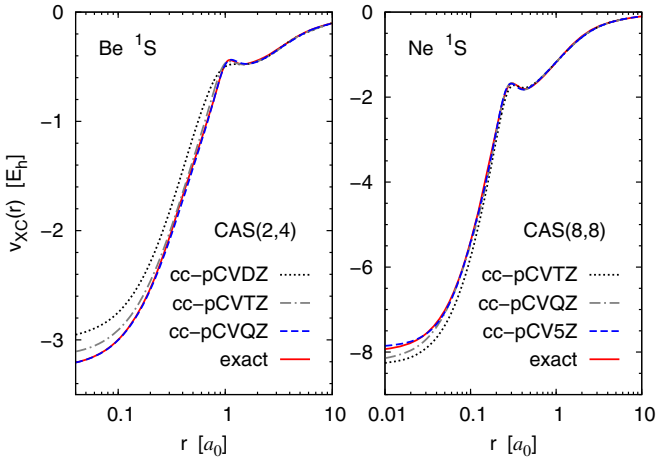

FIG. 2 (color online). Exchange-correlation potentials for the Ne and Be atoms calculated from compact CASSCF wave functions using various basis sets.

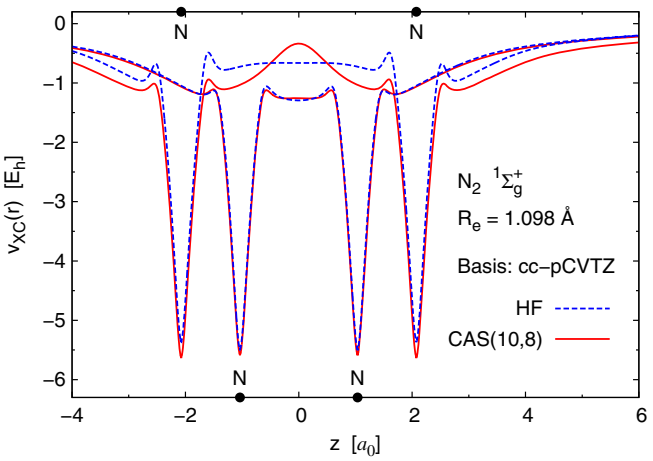

FIG. 3 (color online). Exchange-correlation potentials for the N_2 molecule obtained from HF and valence CASSCF wave functions at the experimental equilibrium bond length and at $2R_e$.

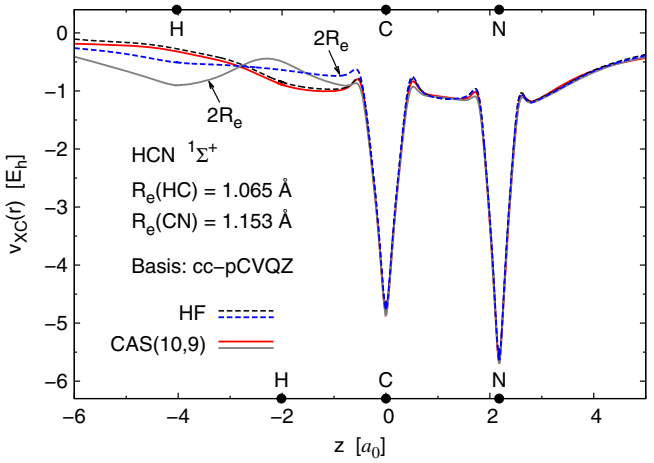

FIG. 4 (color online). Exchange-correlation potentials for HCN obtained from HF and valence CASSCF wave functions at the experimental equilibrium geometry and with $R(\mathrm{HC}) = 2R_e(\mathrm{HC})$.

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*vstarove@uwo.ca

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