Improved method for generating exchange-correlation potentials from electronic wave functions

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Ryabinkin, Kohut, and Staroverov (RKS) [Phys. Rev. Lett. **115**, 083001 (2015)] devised an iterative method for reducing many-electron wave functions to Kohn–Sham exchange-correlation potentials, $v_{\rm XC}(\mathbf{r})$. For a given type of wave function, the RKS method is exact (Kohn–Sham-compliant) in the basis-set limit; in a finite basis set, it produces an approximation to the corresponding basis-set-limit $v_{\rm XC}(\mathbf{r})$. The original RKS procedure works very well for large basis sets but sometimes fails for commonly used (small and medium) sets. We derive a modification of the method's working equation that makes the RKS procedure robust for all Gaussian basis sets and increases the accuracy of the resulting exchange-correlation potentials with respect to the basis-set limit. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4975990]

I. INTRODUCTION

Recently, the present authors and their co-workers[1–5] developed a method for constructing Kohn–Sham (KS) exchange-correlation potentials, $v_{\rm XC}(\mathbf{r})$, from electronic wave functions for nondegenerate ground states that are pure-state v-representable.[6,7] In this method, $v_{\rm XC}(\mathbf{r})$ is generated by iterating an analytic expression that relates this potential to the interacting two-electron reduced density matrix (2-RDM) of the system. Refs. 1 and 2 describe two implementations of our technique based on slightly different but equivalent expressions for $v_{\rm XC}(\mathbf{r})$, Ref. 3 presents a general approach for deriving such expressions, while Refs. 4 and 5 elaborate on the implications. Since the two published variants[1,2] of our method are interchangeable, we will refer to them collectively as the Ryabinkin–Kohut–Staroverov (RKS) procedure, after the authors of Ref. 1. In the special case of Hartree–Fock (HF) wave functions, the RKS procedure reduces to the method of Refs. 8 and 9.

The RKS method is *not* a KS inversion technique, that is, it does not focus on finding the KS potential that reproduces a given *ab initio* electron density $\rho^{\rm WF}(\mathbf{r})$. The KS inversion problem is ill-conditioned[10] and its solution is not unique when the KS equations are solved in a finite one-electron basis set.[11–14] The objective of the RKS method is to approximate the basis-set-limit $v_{\rm XC}(\mathbf{r})$ of the system when both wave-function and KS calculations are done using a finite basis set. RKS potentials are obtained from the 2-RDM via an analytic expression for $v_{\rm XC}(\mathbf{r})$ that is exact in a complete (infinite) basis set but not in a finite one. As a consequence, they are unambiguous and uniform in appearance, but the density $\rho^{\rm KS}(\mathbf{r})$ generated by an RKS potential is exactly equal to $\rho^{\rm WF}(\mathbf{r})$ only in the basis-set limit. This is to be contrasted with KS inversion techniques,[15–23] where the requirement that $\rho^{\rm KS}(\mathbf{r})$ match $\rho^{\rm WF}(\mathbf{r})$ in *any* basis set can result in potentials that oscillate, diverge, and look nothing like the $v_{\rm XC}(\mathbf{r})$ of the basis-set limit $\rho^{\rm WF}(\mathbf{r})$ for the same system.[19,24] Thus, KS inversion and RKS methods pose different questions and give different answers in finite basis sets.

In our experience, the RKS procedure works best for large uncontracted basis sets such as the universal Gaussian basis set (UGBS).[25] For general-purpose basis sets such as cc-pVXZ,[26] cc-pCVXZ,[27] and 6-311G*, it often works well but sometimes produces deformed potentials or even fails to converge (see examples below). Here we propose a modification to the RKS method that eliminates all such problems, increases the uniformity of potentials obtained in various Gaussian basis sets, and substantially improves the accuracy of potentials generated in small basis sets with respect to the basis-set limit.

II. RKS METHOD AND ITS MODIFICATION

The exact expression for $v_{\rm XC}$ that lies at the heart of the RKS method was obtained[1,2] by combining two local energy balance equations derived within the KS and *ab initio* wave-function formalisms for a given N-electron system. These two equations contain the molecular electrostatic potential but differ in all other terms. The fact that both equations describe the same system is expressed by the condition

$$\rho^{\rm KS}(\mathbf{r}) = \rho^{\rm WF}(\mathbf{r}). \tag{1}$$

When one local energy balance equation is subtracted from the other, the electrostatic potential drops out and we obtain the following intermediate result:

$$v_{\rm XC} = v_{\rm XC}^{\rm hole} + \bar{\epsilon}^{\rm KS} - \bar{\epsilon}^{\rm WF} + \frac{\tau_L^{\rm WF}}{\rho^{\rm WF}} - \frac{\tau_L^{\rm KS}}{\rho^{\rm KS}}, \tag{2}$$

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

$$v_{\rm XC}^{\rm hole}(\mathbf{r}) = \int \frac{\rho_{\rm XC}(\mathbf{r},\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{r}_2 \tag{3}$$

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is the potential of the exchange-correlation hole charge[28] derived from the interacting 2-RDM and

$$\bar{\epsilon}^{\mathrm{KS}} = \frac{1}{\rho^{\mathrm{KS}}} \sum_{i=1}^{N} \epsilon_i |\phi_i|^2 \tag{4}$$

is the average local KS orbital energy, in which ϕ_i are the spatial parts of KS spin-orbitals, ϵ_i are their eigenvalues, and

$$\rho^{\mathrm{KS}} = \sum_{i=1}^{N} |\phi_i|^2. \tag{5}$$

The next quantity, defined by

$$\bar{\epsilon}^{\mathrm{WF}} = \frac{1}{\rho^{\mathrm{WF}}} \sum_{j} \lambda_j |f_j|^2, \tag{6}$$

is the *ab initio* average local electron energy,[29,30] in which f_j are the eigenfunctions of the generalized Fock operator, λ_j are their eigenvalues, and ρ^{WF} is the *ab initio* electron density. The summation in Eq. (6) extends over all eigenfunctions f_j whose number is equal to the number of one-electron basis-set functions. We choose to write the *ab initio* electron density as

$$\rho^{\mathrm{WF}} = \sum_{j} n_j |\chi_j|^2, \tag{7}$$

where χ_j are the natural orbitals and n_j are their occupation numbers. The remaining quantities are

$$\tau_L^{\mathrm{WF}} = -\frac{1}{2} \Re \left[\sum_{j} n_j \chi_j^* \nabla^2 \chi_j \right], \tag{8}$$

the Laplacian form of the interacting (*ab initio*) kinetic-energy density expressed through natural orbitals, and

$$\tau_L^{\mathrm{KS}} = -\frac{1}{2} \Re \left[\sum_{i=1}^{N} \phi_i^* \nabla^2 \phi_i \right], \tag{9}$$

the Laplacian form of the noninteracting (KS) kinetic-energy density. Note that Eq. (2) is one of an entire class of exact expressions for v_{XC}.[3,31–33]

For reasons discussed below, the RKS procedure uses *not* Eq. (2) but a different expression obtained from Eq. (2) by applying to τ_L^{WF} and τ_L^{KS} the identity

$$\tau_L = \tau - \frac{1}{4} \nabla^2 \rho, \tag{10}$$

where τ denotes the respective positive-definite form of the kinetic-energy density. The terms $\nabla^2 \rho^{\mathrm{WF}}/4\rho^{\mathrm{WF}}$ and $\nabla^2 \rho^{\mathrm{KS}}/4\rho^{\mathrm{KS}}$ cancel out because of Eq. (1), and Eq. (2) becomes

$$v_{\mathrm{XC}} = v_{\mathrm{XC}}^{\mathrm{hole}} + \bar{\epsilon}^{\mathrm{KS}} - \bar{\epsilon}^{\mathrm{WF}} + \frac{\tau^{\mathrm{WF}}}{\rho^{\mathrm{WF}}} - \frac{\tau^{\mathrm{KS}}}{\rho^{\mathrm{KS}}}, \tag{11}$$

where

$$\tau^{\mathrm{WF}} = \frac{1}{2} \sum_{j} n_j |\nabla \chi_j|^2 \tag{12}$$

and

$$\tau^{\mathrm{KS}} = \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i|^2. \tag{13}$$

Equation (11) is the basis of the RKS method. To construct v_{XC} by this technique, one needs to compute all of the terms on the right-hand side of Eq. (11). The terms $v_{\mathrm{XC}}^{\mathrm{hole}}$, τ^{WF}, and ρ^{WF} are extracted from an *ab initio* wave function, but $\bar{\epsilon}^{\mathrm{KS}}$ and τ^{KS} are initially unknown because they depend on ϕ_i and ϵ_i, which in turn depend on v_{XC}. In Refs. 1 and 2, we showed that it is possible to simultaneously solve for v_{XC} and the associated KS orbitals by starting with a reasonable initial guess for ϕ_i and ϵ_i and iterating Eq. (11) via the KS equations until the potential v_{XC} becomes self-consistent. In a finite basis set, this potential is such that $\rho^{\mathrm{KS}} \neq \rho^{\mathrm{WF}}$ even at convergence.

Equations (2) and (11) are both exact (KS-compliant) only when all their right-hand-side ingredients are obtained in a complete basis set. This is because the two local energy balance equations leading to Eq. (2) were derived by analytically inverting the KS and generalized Fock eigenvalue problems,[1,2] and analytic inversion of operator eigenvalue problems amounts to employing a complete basis set. Refs. 19, 24, and 34 demonstrate the dramatic effect of basis-set incompleteness on the inverted KS equation, whereas Refs. 5 and 30 illustrate it for the generalized Fock eigenvalue problem.

In a finite basis set, Eqs. (2) and (11) are not even equivalent because Eq. (1), which links them, does not hold from the start of iterations. Previously we found that iterations of Eq. (2) hardly ever converge, whereas iterations of Eq. (11) converge for many, but not all, standard Gaussian basis sets. We now argue that Eq. (11) works better than Eq. (2) because in Eq. (11) the difference $\nabla^2 \rho^{\mathrm{WF}}/4\rho^{\mathrm{WF}} - \nabla^2 \rho^{\mathrm{KS}}/4\rho^{\mathrm{KS}}$ is set to its basis-set-limit value of zero even when $\rho^{\mathrm{KS}} \neq \rho^{\mathrm{WF}}$, so the resulting finite-basis-set v_{XC} can get closer to the basis-set-limit potential. Motivated by this idea, we propose the following improvement upon Eq. (11).

Let us assume for simplicity that all ϕ_i are real. Using the Lagrange identity,[35] we write

$$\begin{aligned} 2\rho^{\mathrm{KS}}\tau^{\mathrm{KS}} &= \left(\sum_{i=1}^{N} \phi_i^2 \right) \left(\sum_{i=1}^{N} |\nabla \phi_i|^2 \right) \\ &= \left| \sum_{i=1}^{N} \phi_i \nabla \phi_i \right|^2 + \sum_{i<j}^{N} |\phi_i \nabla \phi_j - \phi_j \nabla \phi_i|^2. \end{aligned} \tag{14}$$

Recognizing that $|\sum_{i=1}^{N} \phi_i \nabla \phi_i|^2 = |\nabla \rho^{\mathrm{KS}}|^2/4$ and dividing Eq. (14) through by $2\rho^{\mathrm{KS}}$, we have (cf. Ref. 36)

$$\tau^{\mathrm{KS}} = \tau_W^{\mathrm{KS}} + \tau_P^{\mathrm{KS}}, \tag{15}$$

where $\tau_W^{\mathrm{KS}} = |\nabla \rho^{\mathrm{KS}}|^2/8\rho^{\mathrm{KS}}$ is the von Weizsäcker noninteracting kinetic-energy density and

$$\tau_P^{\mathrm{KS}} = \frac{1}{2\rho^{\mathrm{KS}}} \sum_{i<j}^{N} |\phi_i \nabla \phi_j - \phi_j \nabla \phi_i|^2 \tag{16}$$

is a quantity which we call the Pauli kinetic-energy density (the name is motivated by Ref. 37). Similarly, assuming real natural orbitals and applying the Lagrange identity to the product $2\rho^{\mathrm{WF}}\tau^{\mathrm{WF}}$, we obtain

$$\tau^{\mathrm{WF}} = \tau_W^{\mathrm{WF}} + \tau_P^{\mathrm{WF}}, \tag{17}$$

where $\tau_W^{\mathrm{WF}} = |\nabla \rho^{\mathrm{WF}}|^2/8\rho^{\mathrm{WF}}$ and

$$\tau_P^{\mathrm{WF}} = \frac{1}{2\rho^{\mathrm{WF}}} \sum_{i<j} n_i n_j |\chi_i \nabla \chi_j - \chi_j \nabla \chi_i|^2. \tag{18}$$

Next we substitute Eqs. (15) and (17) into Eq. (11). In view of Eq. (1), the terms $\tau_W^{\rm KS}/\rho^{\rm KS}$ and $\tau_W^{\rm WF}/\rho^{\rm WF}$ cancel out and we arrive at the following new expression:

$$v_{\rm XC} = v_{\rm XC}^{\rm hole} + \bar{\epsilon}^{\rm KS} - \bar{\epsilon}^{\rm WF} + \frac{\tau_P^{\rm WF}}{\rho^{\rm WF}} - \frac{\tau_P^{\rm KS}}{\rho^{\rm KS}}, \tag{19}$$

which is the main result of this work. Just like Eqs. (2) and (11), Eq. (19) is KS-compliant only in the basis-set-limit. In a finite basis set, it should give a better approximation to the basis-set-limit $v_{\rm XC}$ than Eq. (11) because it sets the quantity $\tau_W^{\rm WF}/\rho^{\rm WF} - \tau_W^{\rm KS}/\rho^{\rm KS}$ to its basis-set-limit value of zero even when $\rho^{\rm KS} \neq \rho^{\rm WF}$. We will refer to the variant of our method using Eq. (19) as the modified RKS (mRKS) procedure.

The mRKS procedure is exactly the same as the original RKS method[1,2,4] except that the former uses Eq. (19) in place of Eq. (11). Therefore, we will not describe the mRKS algorithm in detail here but only emphasize the following important points. The equality $\rho^{\rm KS} = \rho^{\rm WF}$ plays a key role in the derivation of Eqs. (11) and (19), but it is not imposed when these equations are solved by iteration. Thus, there is no such thing as a "target density" in the RKS and mRKS methods, and the extent to which $\rho^{\rm KS}$ deviates from $\rho^{\rm WF}$ at convergence is controlled implicitly through the choice of one-electron basis set. For internal consistency, the RKS and mRKS procedures use the same one-electron basis set to generate the *ab initio* wave function and to solve the KS equations in the iterative part of the algorithm. The Hartree (Coulomb) contribution to the KS Hamiltonian matrix is always computed using $\rho^{\rm KS}$ (not $\rho^{\rm WF}$); we do it analytically in terms of Gaussian basis functions. Matrix elements of $v_{\rm XC}$ are evaluated using saturated Gauss–Legendre–Lebedev numerical integration grids. We consider $v_{\rm XC}$ converged when the difference between two consecutive KS density matrices drops below 10^{-10} in the root-mean-square sense. Both the original and modified RKS procedures require direct inversion of the iterative subspace[38] to converge the potential in self-consistent-field (SCF) iterations; the mRKS procedure typically takes one or two dozen iterations, RKS up to a few dozen. The converged $v_{\rm XC}$ is independent of the initial guess; KS orbitals and orbital energies from any standard density-functional approximation are adequate as a starting point for systems with a single-reference character. For this work, we re-implemented the RKS and mRKS methods by modifying the SCF and multiconfigurational SCF links of a more recent version of the GAUSSIAN 09 program.[39]

III. COMPARISON OF THE ORIGINAL AND MODIFIED RKS METHODS

To demonstrate the practical advantages of Eq. (19) over Eq. (11), we compared exchange-correlated potentials generated by the mRKS and RKS methods from various atomic and molecular *ab initio* wave functions. The wave functions were of three types: HF, complete active space SCF (CASSCF), and full configuration interaction (FCI). Wave functions of each type were obtained using a series of standard Gaussian one-electron basis sets varying between minimal (STO-3G) and very large (UGBS). All basis sets were taken from the basis set exchange database.[40,41]

For each wave function, we report three relevant properties: the total interacting kinetic energy

$$T = -\frac{1}{2}\sum_j n_j \langle \chi_j | \nabla^2 | \chi_j \rangle, \tag{20}$$

the *ab initio* exchange-correlation energy

$$E_{\rm XC}^{\rm WF} = \frac{1}{2}\int \rho^{\rm WF}(\mathbf{r}) v_{\rm XC}^{\rm hole}(\mathbf{r})\, d\mathbf{r}, \tag{21}$$

and the first ionization energy extracted from the wave function by the extended Koopmans theorem[42–47] (EKT), $I_{\rm EKT}$. For HF wave functions, $I_{\rm EKT} = -\epsilon_{\rm HOMO}^{\rm HF}$, where $\epsilon_{\rm HOMO}^{\rm HF}$ is the eigenvalue of the highest-occupied molecular orbital (HOMO). For post-HF wave functions, $I_{\rm EKT}$ was computed as the largest eigenvalue of the $\mathbf{V}'$ matrix defined in Ref. 46. The EKT ionization energies are needed to fix the constant up to which the $v_{\rm XC}$ is defined by Eqs. (11) and (19).[1,2] This is done by shifting the potential vertically so that $\epsilon_{\rm HOMO} = -I_{\rm EKT}$.

After reducing each *ab initio* wave function to a self-consistent $v_{\rm XC}(\mathbf{r})$, we evaluated the following properties: the total noninteracting kinetic energy

$$T_s = -\frac{1}{2}\sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle, \tag{22}$$

the KS exchange-correlation energy

$$E_{\rm XC}^{\rm KS} = E_{\rm XC}^{\rm WF} + T_c, \tag{23}$$

where

$$T_c = T - T_s, \tag{24}$$

and the integral

$$W = \int \left[3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})\right] v_{\rm XC}(\mathbf{r})\, d\mathbf{r}, \tag{25}$$

whose purpose will be explained shortly. The integrals in Eqs. (20), (21), and (22) were computed analytically, whereas W was evaluated numerically.

Strictly speaking, the quality of mRKS potentials should be judged by their proximity to the basis-set-limit $v_{\rm XC}$, but since exact exchange-correlation potentials are rarely available, we suggest to use weaker but feasible tests for basis-set completeness. The first test is the integrated density error

$$\Delta_\rho = \int \left|\rho^{\rm KS}(\mathbf{r}) - \rho^{\rm WF}(\mathbf{r})\right| d\mathbf{r} \geq 0, \tag{26}$$

where $\rho^{\rm KS}(\mathbf{r})$ is evaluated at convergence. For a given type of wave function, Δ_ρ is uniquely determined by the basis set used in the mRKS procedure. The premise of the test is that Δ_ρ tends to zero as the basis set approaches completeness, so the magnitude of Δ_ρ gives some indication of how close the mRKS potential is to its basis-set limit. We emphasize that Δ_ρ values have entirely different meanings in KS inversion and RKS-type methods. For instance, $\Delta_\rho \approx 0.05$ a.u. in a KS inversion procedure indicates that $v_{\rm XC}$ is not converged, whereas in the mRKS procedure it signals that the corresponding *converged* $v_{\rm XC}$ is not yet close to the basis-set-limit potential (because an insufficiently large basis set was used).

The second test is based on the fact that, for a given density functional $E_{XC}[\rho]$ and a density $\rho(\mathbf{r})$, the corresponding functional derivative $v_{XC}(\mathbf{r}) = \delta E_{XC}[\rho]/\delta\rho(\mathbf{r})$ satisfies the virial relation[48]

$$W = E_{XC}^{KS} + T_c, \tag{27}$$

where W is given by Eq. (25). The magnitude of the deviation

$$\Delta E_{vir} = W - E_{XC}^{KS} - T_c = W - E_{XC}^{WF} - 2T_c \tag{28}$$

from zero may be taken as a measure of deviation of a trial potential from $\delta E_{XC}[\rho]/\delta\rho(\mathbf{r})$. As a quality control test, $|\Delta E_{vir}|$

TABLE I. Selected characteristics of various atomic wave functions and of the exchange-correlation potentials generated from those wave functions by the RKS and mRKS methods. Δ_ρ values are in units of electron charge, the rest are in hartrees. The zeros not followed by decimal figures mean "exactly zero."

				RKS			mRKS		
Basis set	T	E_{XC}^{WF}	I_{EKT}	T_s	ΔE_{vir}	Δ_ρ	T_s	ΔE_{vir}	Δ_ρ
Be, HF SCF									
STO-3G	14.844185	–2.768067	0.2540	14.844185	0.003001	0	14.844185	0.003001	0
cc-pCVDZ	14.571730	–2.667161	0.3091	SCF fails to converge			14.583020	0.026191	0.0096
cc-pCVTZ	14.572722	–2.666932	0.3093	14.549079	–0.016873	0.0123	14.574235	0.003444	0.0112
cc-pCVQZ	14.572929	–2.666929	0.3093	14.582472	0.009668	0.0047	14.572859	0.001138	0.0043
UGBS	14.573022	–2.666914	0.3093	14.572575	0.000138	0.0013	14.572484	0.000045	0.0014
Numerical grid[a]	14.573023	–2.666914	0.3093				14.572462	6.4×10^{-12}	2.4×10^{-12}
Be, FCI									
cc-pCVDZ	14.647784	–2.815393	0.3410	14.634247	0.036533	0.0238	14.584365	0.012058	0.0159
cc-pCVTZ	14.659118	–2.834119	0.3419	14.554768	–0.025476	0.0052	14.586875	0.000927	0.0052
cc-pCVQZ[b]	14.663862	–2.839342	0.3423	14.595868	0.005482	0.0047	14.591807	0.001910	0.0054
Basis-set limit[c]	14.66736	–2.8433	0.3426	14.5942			14.5942		
Ne, (8,8)CASSCF									
3-21G	127.526022	–12.331354	0.7418	127.146953	–0.317862	0.0242	127.259455	–0.235164	0.0269
6-31G	128.368644	–12.299273	0.7701	128.074403	–0.057903	0.0343	128.207015	0.070006	0.0419
6-311G	128.643794	–12.310115	0.7889	128.368172	0.054083	0.0119	128.551997	0.152103	0.0100
cc-pVDZ	128.379168	–12.295050	0.7712	128.091704	–0.065663	0.0354	128.217811	0.073355	0.0429
cc-pVTZ	128.699598	–12.313278	0.7972	SCF fails to converge			128.319831	–0.440787	0.0154
cc-pVQZ	128.679046	–12.310777	0.8017	128.401283	–0.166744	0.0119	128.527364	–0.055301	0.0115
cc-pV5Z	128.681107	–12.308871	0.8036	SCF fails to converge			128.544494	–0.038485	0.0127
cc-pV6Z	128.680330	–12.308590	0.8038	129.471075	0.850616	0.0275	128.568158	–0.011267	0.0129
cc-pCVDZ	128.449457	–12.299356	0.7719	128.585448	0.305618	0.0337	128.447270	0.233908	0.0339
cc-pCVTZ	128.694070	–12.315890	0.7978	128.991030	0.391687	0.0110	128.624258	0.044520	0.0099
cc-pCVQZ	128.682785	–12.311376	0.8019	128.639121	0.054117	0.0079	128.583579	0.000298	0.0088
cc-pCV5Z	128.680478	–12.308899	0.8036	128.573403	–0.005645	0.0022	128.578853	–0.000630	0.0025
cc-pCV6Z	128.680103	–12.308582	0.8038	128.579759	0.000595	0.0009	128.579291	0.000100	0.0010
UGBS	128.679971	–12.308530	0.8039	128.579178	0.000069	0.0004	128.579203	0.000089	0.0005
Ar, HF SCF									
STO-3G	512.489655	–30.273170	0.4959	512.489655	–0.925101	0	512.489655	–0.925101	0
6-31G	526.813061	–30.189268	0.5889	526.566956	–0.285033	0.0238	526.598840	–0.027741	0.0343
6-311G	526.800338	–30.186097	0.5901	528.020941	0.260067	0.0495	526.131112	–0.942386	0.0413
cc-pVDZ	526.799649	–30.189363	0.5880	526.499343	–0.366185	0.0259	526.552243	–0.118648	0.0386
cc-pVTZ	526.813176	–30.186281	0.5901	526.245858	–1.002952	0.0407	526.415203	–0.491103	0.0649
cc-pVQZ	526.817051	–30.185184	0.5909	526.517557	–0.648849	0.0295	526.548203	–0.222111	0.0439
cc-pV5Z	526.817410	–30.185018	0.5910	526.852022	–0.263872	0.0339	526.839832	0.081888	0.0510
cc-pV6Z	526.818234	–30.184971	0.5910	525.371226	–0.890411	0.0404	526.994170	0.400168	0.0326
cc-pCVDZ	526.783930	–30.189199	0.5880	519.362324	–5.498655	0.1435	526.454232	–0.386389	0.0454
cc-pCVTZ	526.809131	–30.186274	0.5901	533.394130	6.109779	0.0933	526.383224	–0.627448	0.0324
cc-pCVQZ	526.818135	–30.185181	0.5909	531.897248	4.947426	0.0456	526.796236	–0.013499	0.0163
cc-pCV5Z	526.817374	–30.185016	0.5910	526.701372	–0.107472	0.0085	526.812305	0.000905	0.0094
cc-pCV6Z	526.817495	–30.184954	0.5910	526.719670	–0.089087	0.0093	526.814256	0.002980	0.0103
UGBS	526.817656	–30.184992	0.5910	526.816951	0.004847	0.0060	526.811751	–0.000259	0.0068
Basis-set limit[d]	526.817513		0.5910						

[a]Numerical grid-based mRKS values from Ref. 51.
[b]All f and g functions were removed except one f with $\alpha = 0.255$.
[c]Estimated exact values from Ref. 52.
[d]Numerical HF values from Ref. 53.

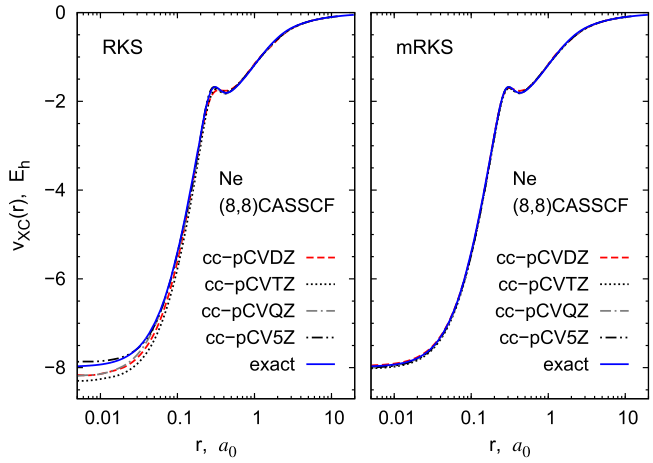


FIG. 1. Exchange-correlation potentials obtained from CASSCF/cc-pCVXZ wave functions of the Ne atom using the RKS and mRKS methods. The exact v_{XC} is from Ref. 52. The mRKS potentials are less sensitive to basis-set incompleteness than RKS. See Table I for the accompanying numerical data.

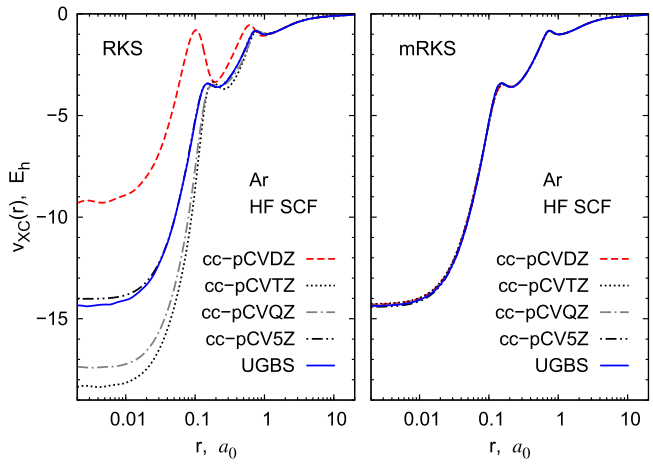


FIG. 2. Exchange-correlation potentials obtained from HF/cc-pCVXZ wave functions of the Ar atom using the RKS and mRKS methods. In this particular case, RKS potentials are accurate only if computed using very large basis sets. See Table I for the accompanying numerical data.

is more discriminating than Δ_ρ: even visually imperceptible defects of $v_{XC}(\mathbf{r})$ can result in large ΔE_{vir} values, as we showed previously for approximate exchange-only potentials.[8,9,49,50] Note that in Refs. 8 and 9 we studied KS potentials extracted from HF wave functions as approximations to exact-exchange potentials, for which $T_c = 0$, so we defined $\Delta E_{vir} = W - E_X^{HF}$ and evaluated E_X^{HF} using the KS (not HF) orbitals. This is why the HF/UGBS values of ΔE_{vir} in this work are different from those reported in Refs. 8 and 9.

Table I summarizes results of RKS and mRKS calculations for HF, CASSCF, and FCI wave functions of a few atoms. The two methods produce potentials with very similar T_s values, small ΔE_{vir}, and $\Delta_\rho \sim 10^{-3}$ a.u. when a large basis set (e.g., UGBS) is used. This is in accord with our argument that the RKS and mRKS procedures would be equivalent in the basis-set limit. A separate grid-based implementation[51] of the mRKS procedure for the HF wave function of Be gives $\Delta E_{vir} = 6.4\times10^{-12}\ E_h$ and $\Delta_\rho = 2.4\times10^{-12}$ a.u., which explicitly shows that the method is KS-compliant in the basis-set limit.

Figs. 1 and 2 highlight a common feature of all RKS and mRKS potentials: they are smooth and have no spurious oscillations that plague optimized effective potential methods[13,54–57] and KS inversion techniques that fit potentials to Gaussian-basis-set densities.[19,24,34,58,59] This is because Eqs. (11) and (19) contain only terms that are well-behaved in any reasonable basis set. Note also that for a number of potentials shown in Figs. 1 and 2, $|\Delta E_{vir}^{mRKS}| \ll |\Delta E_{vir}^{RKS}|$ even though $\Delta_\rho^{mRKS} > \Delta_\rho^{RKS}$. In such cases, the mRKS potential is visually closer to the basis-set limit, which suggests that the virial energy discrepancy test is more sensitive than the density error test.

Overall, the mRKS method performs extremely well for basis sets of any size, whereas the RKS procedure is reliable only for large basis sets. For instance, in the case of (8,8)CASSCF/cc-pVXZ wave functions of the Ne atom, the RKS procedure fails to converge for the cc-pVTZ and cc-pV5Z basis sets, and even though it converges for the other cc-pVXZ basis sets, the results show no clear trend with respect to basis set variations. By contrast, mRKS potentials obtained from the same wave functions produce consistent T_s values, and $|\Delta E_{vir}|$ generally decreases with increasing basis-set size. Similar observations apply to potentials generated for other atoms.

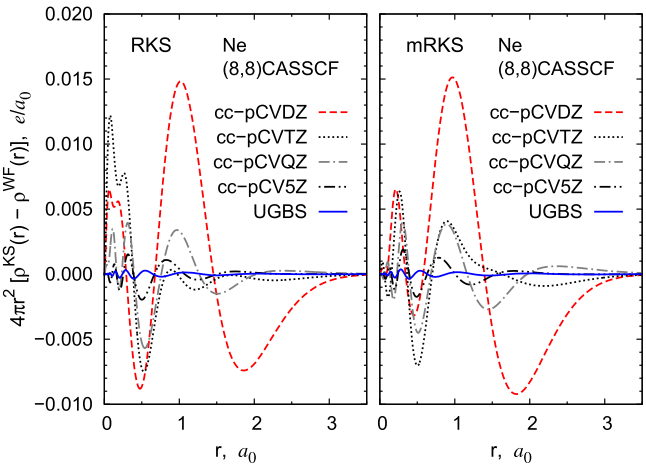


FIG. 3. Discrepancies between the radial KS and *ab initio* densities for the exchange-correlation potentials of Fig. 1.

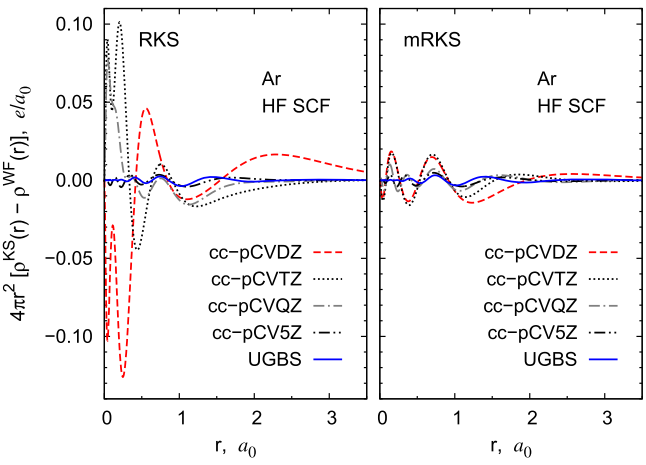


FIG. 4. Discrepancies between the radial KS and *ab initio* densities for the exchange-correlation potentials of Fig. 2.

TABLE II. Selected characteristics of HF and full-valence CASSCF functions of the HCN molecule at the experimental equilibrium geometry ($r_{HC} = 2.013a_0$, $r_{CN} = 2.179a_0$) and of the exchange-correlation potentials generated from those wave functions by the RKS and mRKS methods. Δ_ρ values are in units of electron charge, the rest are in hartrees.

				RKS			mRKS		
Basis set	T	E_{XC}^{WF}	I_{EKT}	T_s	ΔE_{vir}	Δ_ρ	T_s	ΔE_{vir}	Δ_ρ
HCN, HF SCF									
6-31G*	92.550286	−12.041974	0.4906	91.711955	−0.947891	0.0859	92.307987	−0.484915	0.0702
6-311G**	92.742692	−12.046387	0.4950	SCF fails to converge			92.734609	−0.005396	0.0578
cc-pCVDZ	92.648587	−12.046478	0.4925	SCF fails to converge			92.716824	0.105823	0.0501
cc-pCVTZ	92.724093	−12.048439	0.4957	92.759771	0.035200	0.0243	92.756065	0.053961	0.0266
cc-pCVQZ	92.728654	−12.047784	0.4967	92.794723	0.064605	0.0122	92.729610	0.008136	0.0128
cc-pCV5Z	92.729614	−12.047401	0.4970	92.718948	−0.010551	0.0066	92.727317	0.003108	0.0072
aug-cc-pCVDZ	92.618227	−12.034752	0.4972	SCF fails to converge			92.685523	0.103478	0.0493
aug-cc-pCVTZ	92.714623	−12.045619	0.4969	92.734796	0.019105	0.0218	92.743953	0.048228	0.0222
aug-cc-pCVQZ	92.726488	−12.047072	0.4970	92.790808	0.061456	0.0113	92.727416	0.007485	0.0114
aug-cc-pCV5Z	92.729420	−12.047335	0.4970	SCF fails to converge			92.726972	0.002954	0.0062
HCN, (10,9)CASSCF									
6-31G*	92.942118	−12.312273	0.5224	92.232843	−0.701261	0.0525	92.573544	−0.435253	0.0521
6-311G**	93.093351	−12.307472	0.5192	SCF fails to converge			92.974910	0.039466	0.0457
cc-pVDZ	93.010939	−12.305411	0.5168	92.767530	−0.112071	0.0531	92.777863	−0.071566	0.0578
cc-pVTZ	93.062905	−12.306247	0.5208	94.792641	1.309037	0.1795	92.800576	−0.263447	0.0452
cc-pVQZ	93.077491	−12.307166	0.5213	SCF fails to converge			92.962057	−0.006661	0.0347
cc-pV5Z	93.079200	−12.306930	0.5214	93.972821	0.903219	0.0656	92.987779	0.017106	0.0260
cc-pCVDZ	92.988167	−12.305592	0.5179	SCF fails to converge			92.886229	0.059178	0.0419
cc-pCVTZ	93.077684	−12.307350	0.5212	93.027971	0.050491	0.0208	93.010944	0.044703	0.0239
cc-pCVQZ	93.079442	−12.307294	0.5214	93.046686	0.056174	0.0122	92.988799	0.005245	0.0132
cc-pCV5Z	93.080131	−12.307031	0.5214	92.979526	−0.006572	0.0061	92.986814	0.002105	0.0070

In the case of HF/cc-pCVXZ wave functions of the Ar atom, RKS potentials for basis sets smaller than cc-pCV5Z are too high or too low near the nucleus (Fig. 2) and have virial energy discrepancies of up to 6 E_h (Table I). At the same time, plots of mRKS potentials of the HF/cc-pCVXZ series are barely distinguishable (Fig. 2).

Detailed analysis of discrepancies between $\rho^{KS}(\mathbf{r})$ and $\rho^{WF}(\mathbf{r})$ for the potentials shown in Figs. 1 and 2 furnishes another demonstration that, for large basis sets, the RKS and mRKS procedures are practically equivalent and produce nearly KS-compliant potentials (Figs. 3 and 4). For small and medium basis sets, mRKS densities have much smaller deviations from $\rho^{WF}(\mathbf{r})$ near atomic nuclei than do RKS densities.

RKS and mRKS calculations for HF wave functions of certain systems exhibit a curious basis-set effect: the use of a minimal basis sets results in $\Delta_\rho = 0$ (Table I, HF/STO-3G for Be and Ar). This occurs when there are no virtual HF orbitals or when no virtual orbital has the symmetry of any occupied orbital; then the (m)RKS procedure yields occupied KS orbitals that are unitarily transformed occupied HF orbitals, which implies $\rho^{KS} = \rho^{HF}$. However, in such cases, $\Delta E_{vir} \neq 0$, meaning that the (m)RKS potential is not truly KS-compliant.

The mRKS method also works well for molecules. To demonstrate this, we generated exchange-correlation potentials from HF and full-valence CASSCF wave functions of the HCN molecule using various standard Gaussian basis sets. Here the original RKS method again failed to converge for some basis sets, whereas the mRKS procedure converged without difficulty in all cases (Table II). As in the examples involving atoms, the converged RKS and mRKS potentials for HCN are similar and become practically identical for large basis sets such as cc-pCV5Z. Moreover, mRKS potentials for HCN obtained with increasingly large basis sets of the cc-pCVXZ (X = D, T, Q, 5) series are virtually indistinguishable by eye (Fig. 5), which shows that it is not necessary to use large basis sets in the mRKS method to obtain eminently reasonable potentials.

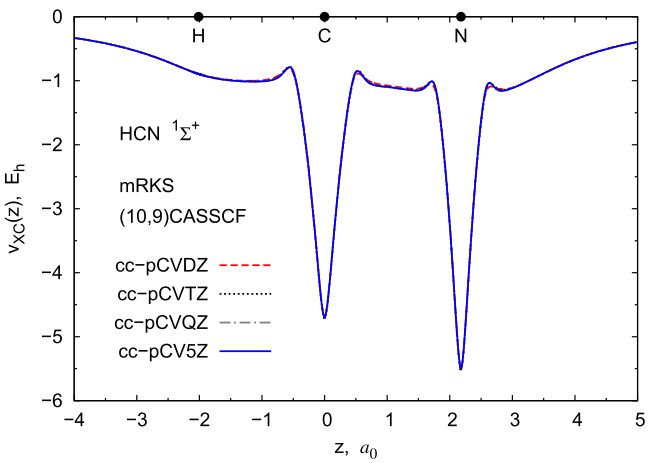


FIG. 5. Exchange-correlation potentials obtained by the mRKS method from full-valence CASSCF wave functions of the HCN molecule. See Table II for the accompanying numerical data.

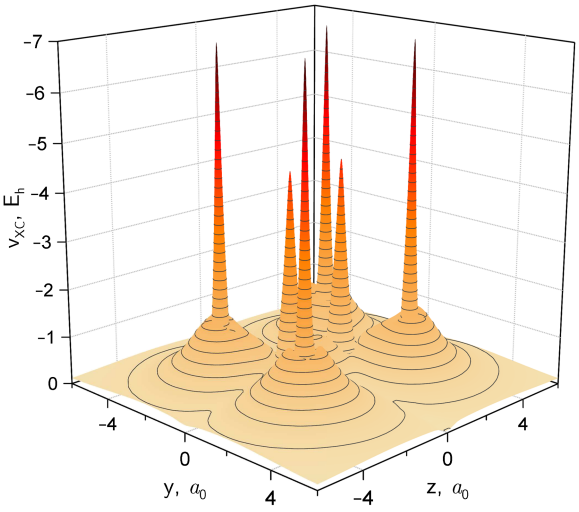


FIG. 6. Exchange-correlation potential of $CF_2{=}CF_2$ obtained by the mRKS method from the HF/6-311G* wave function for the HF/6-311G* geometry. The plot shows v_{XC} in the molecular plane. The z axis is along the C═C bond.

An example of an mRKS exchange-correlation potential for a polyatomic molecule (tetrafluoroethylene) is shown in Fig. 6. RKS-type potentials generated from HF wave functions are known to be excellent approximations to exchange-only optimized effective potentials.[8,9] The message of this figure is that molecular exchange-correlation potentials of high quality can be effortlessly generated by the mRKS method.

IV. CONCLUSION

We have derived Eq. (19) and showed that it works considerably better than its predecessor, Eq. (11), for the purpose of generating exchange-correlation potentials from *ab initio* wave functions in Gaussian basis sets. Equation (11) is in turn more useful than Eq. (2).

The transition from Eq. (2) to Eq. (11) and then to Eq. (19) is based on the relations

$$\tau_L = -\frac{1}{4}\nabla^2\rho + \tau = -\frac{1}{4}\nabla^2\rho + \tau_W + \tau_P \qquad (29)$$

for each of the interacting and noninteracting systems. For $\rho^{\mathrm{KS}} = \rho^{\mathrm{WF}}$, these relations imply that

$$\frac{\tau_L^{\mathrm{WF}}}{\rho^{\mathrm{WF}}} - \frac{\tau_L^{\mathrm{KS}}}{\rho^{\mathrm{KS}}} = \frac{\tau^{\mathrm{WF}}}{\rho^{\mathrm{WF}}} - \frac{\tau^{\mathrm{KS}}}{\rho^{\mathrm{KS}}} = \frac{\tau_P^{\mathrm{WF}}}{\rho^{\mathrm{WF}}} - \frac{\tau_P^{\mathrm{KS}}}{\rho^{\mathrm{KS}}}. \qquad (30)$$

Equation (29) is always true, whereas Eq. (30) holds only when $\rho^{\mathrm{KS}} = \rho^{\mathrm{WF}}$, which in our method happens at convergence in a complete (infinite) basis set and for minimal-basis-set HF wave functions of certain systems. This means that RKS-type iterations by Eqs. (2), (11) and (19) are generally not equivalent and should result in different potentials.

In calculations using standard Gaussian basis sets, Eq. (2) almost never converges, Eq. (11) converges for some but not all basis sets, while Eq. (19) always converges in our experience, at least for systems with a single-reference character. The RKS and mRKS methods are essentially equivalent in a nearly complete basis set, but the mRKS method is much more accurate and robust in commonly used basis sets, making it possible to routinely generate exchange-correlation potentials for atoms and molecules at any level of *ab initio* theory. Therefore, we recommend the mRKS procedure as a permanent replacement for the original RKS method.

The extensive numerical evidence presented in this work shows that mRKS potentials generated using incomplete (finite) basis sets are excellent approximations to the basis-set-limit v_{XC} for a particular type of wave function (HF, CASSCF, FCI, etc.). The mRKS technique can also be used for the construction of exchange-correlation potentials of adiabatic time-dependent density-functional theory.[60–62] Extensions of the mRKS method to spin-polarized post-HF wave functions and to systems that are not pure-state v-representable remain the subject of future work.

ACKNOWLEDGMENTS

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