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PERSPECTIVES

Determination of Kohn–Sham effective potentials from electron densities using the differential virial theorem

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We present an accurate method for constructing the Kohn–Sham effective potential corresponding to a given electron density in one-dimensional and spherically symmetric systems. The method is based on the differential virial theorem—an exact relation between the effective potential, the electron density, and the kinetic energy density. A distinctive feature of the proposed technique is that it employs a size-consistent bosonic reference potential to ensure the correct asymptotic behavior of the resulting Kohn–Sham potential. We describe a practical implementation of our method and use it to obtain high-quality exchange-correlation and correlation potentials of the neon and argon atoms from *ab initio* densities generated in large Slater- and Gaussian-type basis sets. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4763481]

I. INTRODUCTION

In the Kohn–Sham density-functional theory,[1] one often needs to construct an effective potential $v_s(\mathbf{r})$, such that the ground-state density of a system of noninteracting electrons confined by that potential is equal to a given density $\rho(\mathbf{r})$. The resulting potential $v_s(\mathbf{r})$ is used for assessing density-functional approximations for the exchange-correlation energy,[2–4] as a benchmark for developing model Kohn–Sham potentials,[5] and in embedded density-functional theory.[6–8] While computing the density $\rho(\mathbf{r})$ from a given $v_s(\mathbf{r})$ is a trivial task accomplished by solving the Kohn–Sham equations, the inverse problem of obtaining $v_s(\mathbf{r})$ from $\rho(\mathbf{r})$ is hard. Many diverse density-to-potential mapping algorithms have been proposed and implemented in the last three decades,[9–30] but none of them is as general and robust as desired. This situation stimulates search for new approaches.

In this work, we develop a new density-to-potential technique that is based on the so-called differential virial theorem—an exact relation between the Kohn–Sham potential $v_s(\mathbf{r})$, the density $\rho(\mathbf{r})$, and derivatives of the noninteracting kinetic energy density.[31–36] The possibility of recovering Kohn–Sham potentials from electrons densities using the differential virial theorem was pointed out by March and co-workers,[37–40] but no practical implementations have been reported, with the exception of a system-specific study by Nagy and March.[38] Because this is a pilot project, our consideration is limited to (effectively) one-dimensional systems such as harmonically confined noninteracting electrons and spherical atoms.

II. DIFFERENTIAL VIRIAL THEOREM

We begin with a self-contained derivation of the differential virial theorem for noninteracting electrons in one and three dimensions. Our approach is similar to that of Baltin,[36] but we obtain the final result in a new, simpler form.

A. Three-dimensional systems

Consider a system of N noninteracting electrons moving in an external potential $v_s(\mathbf{r})$. The ground-state wavefunction of this system is a Slater determinant constructed with the N lowest-eigenvalue spin orbitals whose spatial parts $\phi_i(\mathbf{r})$ are solutions to the one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{1}$$

where ϵ_i are the orbital eigenvalues. Here and below, the index i in $\phi_i(\mathbf{r})$ refers to the spin-orbital associated with $\phi_i(\mathbf{r})$. This is done so that all our equations can be converted to the spin-polarized form by adding a spin subscript. To simplify things further, we assume that all orbitals $\phi_i(\mathbf{r})$ are *real*, as is the case in most practical calculations. With these conventions, the ground-state density of our N-electron system is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \phi_i^2(\mathbf{r}). \tag{2}$$

Let us also introduce two forms of the kinetic energy density: the positive-definite

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i(\mathbf{r})|^2, \tag{3}$$

and the Laplacian-dependent

$$\tau_L(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^{N} \phi_i(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}). \tag{4}$$

The quantities $\tau(\mathbf{r})$ and $\tau_L(\mathbf{r})$ are related to each other by

$$\tau_L(\mathbf{r}) = \tau(\mathbf{r}) - \frac{1}{4}\nabla^2 \rho(\mathbf{r}). \tag{5}$$

The derivation consists of manipulations with the Kohn–Sham equations designed to eliminate the orbital energies. We

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start by multiplying Eq. (1) by ϕ_i and summing over i from 1 to N. Using Eqs. (2) and (4) we write the result as

$$\tau_L + v_s \rho = \sum_{i=1}^{N} \epsilon_i \phi_i^2. \tag{6}$$

Taking the gradient of both sides we obtain

$$\nabla \tau_L + \rho \nabla v_s + v_s \nabla \rho = 2 \sum_{i=1}^{N} \epsilon_i \phi_i \nabla \phi_i. \tag{7}$$

Now let us return to Eq. (1), multiply it by $2\nabla\phi_i$, and sum over the occupied orbitals. This gives

$$-\sum_{i=1}^{N} \nabla^2 \phi_i \nabla \phi_i + v_s \nabla \rho = 2 \sum_{i=1}^{N} \epsilon_i \phi_i \nabla \phi_i, \tag{8}$$

where we have used the fact that $\nabla \rho = 2 \sum_{i=1}^{N} \phi_i \nabla \phi_i$. Finally, we subtract Eq. (8) from Eq. (7) and obtain

$$\nabla \tau_L + \sum_{i=1}^{N} \nabla^2 \phi_i \nabla \phi_i + \rho \nabla v_s = 0. \tag{9}$$

This is the differential virial theorem in three dimensions. Note that we cast it here in a maximally transparent orbital-dependent form, whereas all other expressions found in the literature[32, 33, 35, 36] involve derivatives of the kinetic energy density tensor. Another form of this theorem is obtained by replacing τ_L with τ according to Eq. (5), with the result

$$-\frac{1}{4} \nabla \nabla^2 \rho + \nabla \tau + \sum_{i=1}^{N} \nabla^2 \phi_i \nabla \phi_i + \rho \nabla v_s = 0. \tag{10}$$

Equations (9) and (10) relate the potential v_s to the density, kinetic energy density and the orbital-dependent vector quantity $\sum_{i=1}^{N} \nabla^2 \phi_i \nabla \phi_i$.

In the Kohn–Sham density-functional theory, the potential $v_s(\mathbf{r})$ has a special significance: it is the external potential for a fictitious noninteracting system whose ground-state density coincides with the ground-state density of the interacting system of interest. The potential $v_s(\mathbf{r})$ is partitioned as

$$v_s(\mathbf{r}) = v_{\text{nucl}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}), \tag{11}$$

where $v_{\text{nucl}}(\mathbf{r})$ is the field of the nuclei, $v_{\text{H}}(\mathbf{r})$ is the electrostatic (Hartree) potential of $\rho(\mathbf{r})$, and $v_{\text{XC}}(\mathbf{r})$ is the exchange-correlation potential. Since $v(\mathbf{r})$ and $v_{\text{H}}(\mathbf{r})$ are known exactly, one can easily obtain $v_{\text{XC}}(\mathbf{r})$ from $v_s(\mathbf{r})$ and *vice versa*. Thus, the problem of determining $v_{\text{XC}}(\mathbf{r})$ from a given density reduces to determining $v_s(\mathbf{r})$.

B. Spherically symmetric systems

Systems with spherical symmetry (e.g., atoms with completely filled electronic subshells) are effectively one-dimensional because their Kohn–Sham potentials and densities depend only on the distance to the nucleus, r. To adapt the differential virial theorem to such systems, we transform the Kohn–Sham equations to spherical polar coordinates, sep-

arate the variables, and introduce *radial* Kohn–Sham orbitals defined by

$$\phi_i(r) = \sqrt{4\pi}\, r\, R_i(r), \tag{12}$$

where $R_i(r)$ is the conventional radial factor of the three-dimensional orbital $\phi_i(\mathbf{r})$. Such a definition is necessary to preserve the formal analogy between spherical atoms and one-dimensional systems.

In terms of radial orbitals of Eq. (12), the Kohn–Sham equations assume the form

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_i(l_i + 1)}{2r^2} + v_s(r) \right] \phi_i(r) = \epsilon_i \phi_i(r), \tag{13}$$

where l_i is the angular momentum quantum number of the ith orbital. Let us also define the *radial* density

$$\rho(r) = \sum_{i=1}^{N} \phi_i^2(r), \tag{14}$$

such that $\int_0^\infty \rho(r)\, dr = N$, and the radial contribution to the kinetic energy density

$$\tau_L(r) = -\frac{1}{2} \sum_{i=1}^{N} \phi_i(r) \phi_i''(r), \tag{15}$$

where primes denote derivatives with respect to r. We will also need the quantity

$$\tau(r) = \frac{1}{2} \sum_{i=1}^{N} [\phi_i'(r)]^2 = \tau_L(r) + \frac{1}{4} \rho''(r). \tag{16}$$

Observe that the total electronic kinetic energy of the atom is given by

$$T_s = \int_0^\infty \left[\tau(r) + \sum_{i=1}^{N} \frac{l_i(l_i + 1)\, \phi_i^2(r)}{2r^2} \right] dr, \tag{17}$$

where τ may be replaced by τ_L.

Now for the derivation. As in Sec. II A, we multiply Eq. (13) by ϕ_i, sum over i, and differentiate with respect to r to obtain

$$\tau_L' - \sum_{i=1}^{N} \frac{l_i(l_i + 1)}{r^3} \phi_i^2 + \sum_{i=1}^{N} \frac{l_i(l_i + 1)}{r^2} \phi_i' \phi_i$$
$$+ \rho v_s' + v_s \rho' = 2 \sum_{i=1}^{N} \epsilon_i \phi_i' \phi_i. \tag{18}$$

Next we multiply Eq. (13) by $2\phi_i'$ and sum over i,

$$-\tau' + \sum_{i=1}^{N} \frac{l_i(l_i + 1)}{r^2} \phi_i' \phi_i + v_s \rho' = 2 \sum_{i=1}^{N} \epsilon_i \phi_i' \phi_i. \tag{19}$$

Finally, we subtract Eq. (19) from Eq. (18) and use Eq. (16) to write the result as

$$-\frac{1}{4} \rho'''(r) + 2\tau'(r) + \rho(r) v_s'(r) = \sum_{i=1}^{N} \frac{l_i(l_i + 1)\, \phi_i^2(r)}{r^3}.$$
$$\tag{20}$$

This is the differential virial theorem for noninteracting electrons moving in a centrally symmetric potential $v_s(r)$. In a somewhat different form, it was first obtained by Nagy and March[38] (see also Ref. [41]).

C. One-dimensional systems

For a genuine one-dimensional system, the Kohn–Sham equations are

$$\left[-\frac{1}{2}\frac{d^2}{dx^2} + v_s(x) \right] \phi_i(x) = \epsilon_i \phi_i(x). \qquad (21)$$

The corresponding differential virial relation can be obtained either from Eq. (10) by reducing the dimensionality or from Eq. (20) by dropping the l_i-dependent term. In either case, the result is

$$-\frac{1}{4}\rho'''(x) + 2\tau'(x) + \rho(x)v_s'(x) = 0, \qquad (22)$$

where $\rho(x)$ and $\tau(x)$ are defined by Eqs. (14) and (16). Equation (22) has been also derived in other ways.[34,42–44]

III. METHOD FOR DETERMINING $v_s(r)$ FROM A GIVEN DENSITY

Equations (20) and (22) naturally lend themselves as tools for recovering Kohn–Sham potentials from electron densities. For a spherical atom, the potential $v_s(r)$ is expressed from Eq. (20) as the indefinite integral

$$v_s(r) = \int \frac{\frac{1}{4}\rho'''(r) - 2\tau'(r) + S(r)}{\rho(r)}\, dr, \qquad (23)$$

where $\rho(r)$ is the input density, while the quantities

$$S(r) \equiv \sum_{i=1}^{N} \frac{l_i(l_i + 1)\phi_i^2(r)}{r^3} \qquad (24)$$

and $\tau(r)$ are constructed from the Kohn–Sham orbitals generated by $v_s(r)$. Clearly, Eq. (23) does not allow one to obtain $v_s(r)$ directly from $\rho(r)$ if the corresponding $\tau(r)$ and $S(r)$ are unknown. This suggests an iterative procedure in which we first construct $v_s(r)$ using some initial guess for $\tau(r)$ and $S(r)$, then solve the Kohn–Sham equations with $v_s(r)$ to obtain a new set of orbitals, construct new $\tau(r)$, $S(r)$, and $v_s(r)$ while keeping the density fixed, and repeat the cycle until $v_s(r)$ is consistent with the input density.

The initial guess we choose is $S^{(0)} = 0$ and $\tau^{(0)} = \tau_W$, where $\tau_W = (\rho')^2/8\rho$ is the von Weizsäcker kinetic energy density evaluated with the input density. To obtain the corresponding initial potential $v_s^{(0)}$, we insert τ_W into Eq. (23) with $S = 0$. The result is the indefinite integral

$$v_s^{(0)}(r) = \int \frac{\frac{1}{4}\rho'''(r) - 2\tau_W'(r)}{\rho(r)}\, dr, \qquad (25)$$

which can be evaluated analytically to give

$$v_s^{(0)} = \frac{\frac{1}{4}\rho'' - \tau_W}{\rho} = \frac{(\sqrt{\rho})''}{2\sqrt{\rho}}, \qquad (26)$$

ignoring the integration constant. This initial guess is convenient for several reasons. First, $\tau_W = \tau$ for any one-orbital density; therefore, $v_s^{(0)}$ is exact for any one- or closed-shell two-electron system where $S = 0$. Second, $v_s^{(0)}$ has the same asymptotic behavior as v_s up to the integration constant omitted in Eq. (26). This is because asymptotic regions of the density ($r \to \infty$) are dominated by one orbital (the highest occupied Kohn–Sham orbital), where τ tends to τ_W and hence v_s tends to $v_s^{(0)}$. Third, $v_s^{(0)}$ depends solely on the input density and requires no assumptions about the final potential v_s. Note that if ρ were the ground-state density of a system of noninteracting bosons, then $v_s^{(0)}$ would be the true external potential (up to a constant). To emphasize this fact, we call $v_s^{(0)}$ the *bosonic potential*. The quantity $v_s^{(0)}$ is also known as the one-electron potential[45] and is closely related to the so-called Pauli potential.[46,47]

In principle, successive approximations to v_s can be obtained using Eq. (23). However, this is not practical because the integral of Eq. (23) cannot be evaluated reliably in regions where ρ is small. Instead, we represent successive approximations $v_s^{(n)}$ in the form

$$v_s^{(n)} = v_s^{(0)} + \Delta v_s^{(n)}, \quad n = 1, 2, 3, \dots, \qquad (27)$$

where $v_s^{(0)}$ is the asymptotically correct reference potential of Eq. (26) and $\Delta v_s^{(n)}$ is a correction vanishing at infinity. To find $\Delta v_s^{(n)}$, we subtract Eq. (25) from Eq. (23) and integrate the difference by parts. The result may be written (omitting the superscripted iteration number) as

$$\Delta v_s(r) = Q(r) + \int_r^\infty \frac{\rho'(x)Q(x) + S(x)}{\rho(x)}\, dx, \qquad (28)$$

where

$$Q(r) = 2\frac{\tau_W(r) - \tau(r)}{\rho(r)}. \qquad (29)$$

Notice that the upper integration limit in Eq. (28) is chosen such that $\lim_{r\to\infty} \Delta v_s(r) = 0$, as required. Equation (29) is still unsuitable for computing the ratio $Q(r)$ at large r, where τ, τ_W, and ρ are small. A much better way to evaluate $Q(r)$ is by using the equivalent expression

$$Q(r) = -\frac{1}{\rho^2(r)}\sum_{i<j}^{\text{occ.}}[\phi_i(r)\phi_j'(r) - \phi_j(r)\phi_i'(r)]^2, \qquad (30)$$

which follows from the identity proven below Eq. (6.144) in Ref. [48]. Use of Eq. (30) ensures that $Q(r)$ has the correct sign ($Q \le 0$) and vanishes at infinity.

When we first outlined our method at the beginning of this section, we envisioned that the density ρ in Eqs. (28) and (30) would be fixed, whereas $\{\phi_i\}$, τ, and S would be determined by $v_s^{(n)}$. While this prescription works, we found that $v_s^{(n)}$ converges much faster if, in the first few iterations, the correction $\Delta v_s^{(n)}$ is constructed using the density $\rho^{(n)}$ (i.e., the density from the current Kohn–Sham orbitals) rather than the input density.

To evaluate the derivatives and integrals in Eqs. (26) and (28), we use Chebyshev-polynomial representations of all differentiated and integrated quantities. The technology of these calculations is explained in Secs. 5.8 and 5.9 of Ref. [49].

TABLE I. Bosonic potentials for ground-state systems of N noninteracting same-spin fermions harmonically confined in one dimension.

N	$v_s^{(0)}(x) = [\sqrt{\rho(x)}]''/2\sqrt{\rho(x)}$	Asymptotic behavior as $|x| \to \infty$
1	$\dfrac{x^2 - 1}{2}$	$\dfrac{x^2}{2} - \dfrac{1}{2}$
2	$\dfrac{4x^6 - 8x^4 - 7x^2 + 1}{2(2x^2 + 1)^2}$	$\dfrac{x^2}{2} - \dfrac{3}{2} + O\left(\dfrac{1}{x^2}\right)$
3	$\dfrac{16x^{10} - 80x^8 + 56x^6 - 72x^4 + 81x^2 - 9}{2(4x^4 + 3)^2}$	$\dfrac{x^2}{2} - \dfrac{5}{2} + O\left(\dfrac{1}{x^2}\right)$
4	$\dfrac{64x^{14} - 640x^{12} + 1968x^{10} - 3312x^8 + 2988x^6 + 432x^4 - 1215x^2 + 81}{2(8x^6 - 12x^4 + 18x^2 + 9)^2}$	$\dfrac{x^2}{2} - \dfrac{7}{2} + O\left(\dfrac{1}{x^2}\right)$

Reduced to an algorithm, our method is as follows:

1. Represent the input density $\rho(r)$ by an expansion in Chebyshev polynomials. Evaluate $\rho'(r)$ and $\rho''(r)$ and construct the initial guess $v_s^{(0)}$ by Eq. (26). Initialize the iteration counter $n := 0$.
2. Set $n := n + 1$. Using the potential $v_s^{(n-1)}$, solve Eq. (13) in a suitably chosen finite basis set $\{\chi_\mu(r)\}$. (The matrix elements of $v_s^{(n-1)}$ can be evaluated numerically using standard density-functional quadratures.) This gives a set of Kohn–Sham orbitals in the form $\phi_i^{(n)}(r)$ $= \sum_\mu c_{\mu i}^{(n)} \chi_\mu(r)$.
3. Using the orbitals from step 2, generate a Chebyshev-polynomial representation of $(\rho'Q + S)/\rho$ and evaluate the integral in Eq. (28), where ρ may be taken as the input density or constructed from $\{\phi_i^{(n)}\}$. Obtain a new $v_s^{(n)}$ according to Eq. (27).
4. Return to step 2 and iterate until the density $\rho^{(n)}$ generated by $v_s^{(n)}$ matches the input density ρ.

The natural convergence criterion for $v_s^{(n)}$ is the mean absolute error in the density,

$$e_{\text{abs}} = \int |\rho_{\text{final}}(\mathbf{r}) - \rho_{\text{input}}(\mathbf{r})| \, d\mathbf{r}, \qquad (31)$$

where the integration is over the entire domain of ρ. However, when ρ_{input} is specified on a grid and ρ_{final} is generated in a finite basis set, it may be impossible to achieve very small values of e_{abs}. A more suitable convergence criterion for such iterative procedures is the *constancy* of e_{abs} in final iterations. In our implementation, e_{abs} usually stabilized at about 10^{-3}, although much smaller values of e_{abs} are achievable if the finite basis set in step 2 can reproduce the input density exactly (see below).

IV. TEST

Here, we test our method on a one-dimensional system of N noninteracting same-spin fermions of unit mass moving in the harmonic potential $v_s(x) = \frac{1}{2}x^2$. The ground-state density of this system is given by $\rho(x) = \sum_{k=0}^{N-1} \phi_k^2(x)$, where $\phi_k(x)$ are the normalized harmonic oscillator eigenfunctions[50]

$$\phi_k(x) = \frac{(-1)^k}{\pi^{1/4}\sqrt{2^k k!}} e^{x^2/2} \frac{d^k}{dx^k} e^{-x^2}. \qquad (32)$$

Suppose that we are given the exact ground-state density $\rho(x)$ for some N. Our objective is to recover the external potential that generates this density.

To begin, we substitute the exact density into Eq. (26) to obtain the initial potential $v_s^{(0)}$. Table I lists explicit formulas of such potentials for $N \leq 4$. Similar expressions for higher values of N can be readily obtained using any computer algebra system. Observe that, for every N,

$$v_s^{(0)}(x) = \frac{x^2}{2} - \epsilon_N + O\left(\frac{1}{x^2}\right), \quad x \to \infty, \qquad (33)$$

where $\epsilon_N = N - \frac{1}{2}$ is the energy of the highest occupied level of the N-particle system. This shows that the bosonic potential $v_s^{(0)}$ is indeed asymptotically correct up to a constant. Since this constant has no effect on the orbitals and densities, we do not need to worry about it during iterations.

To solve the Kohn–Sham equations with $v_s^{(n)}$, we used a basis set of m ($m \geq N$) lowest-eigenvalue harmonic oscillator wavefunctions of Eq. (32). These functions become eigenstates of the system at convergence, so the first N of them suffice to reproduce the input N-particle density *exactly*. Therefore, m need not be much greater than N. In fact, we observed that our iterative procedures fail to converge when $m - N > 5$.

Figure 1 shows four intermediate potentials $v_s^{(n)}$ for a system of $N = 10$ particles. For ease of comparison, each depicted potential is shifted vertically to satisfy the exact condition $\epsilon_N = N - \frac{1}{2}$. We see how the initial oscillatory potential $v_s^{(0)}$ becomes visually indistinguishable from the exact v_s after 20 iterations. In this particular example, we were able to improve the potential for a total of $n = 93$ iterations, when the absolute density error dropped to $e_{\text{abs}} = 8.05 \times 10^{-10}$.

V. RESULTS

A. Potentials from Slater-type basis set densities

Consider the accurate ground-state density of the Ne atom published by Bunge and Esquivel.[51] This density was obtained by a configuration-interaction singles and doubles (CISD) calculation in a Slater-type orbital (STO) basis set of the composition $(6s, 7p, 3d, 2f, 1g)$ and is available in the form of a natural orbital expansion. The same density has been used as a test for density-to-potential techniques by a multitude of other workers.[13, 19, 20, 24, 27, 52, 53]
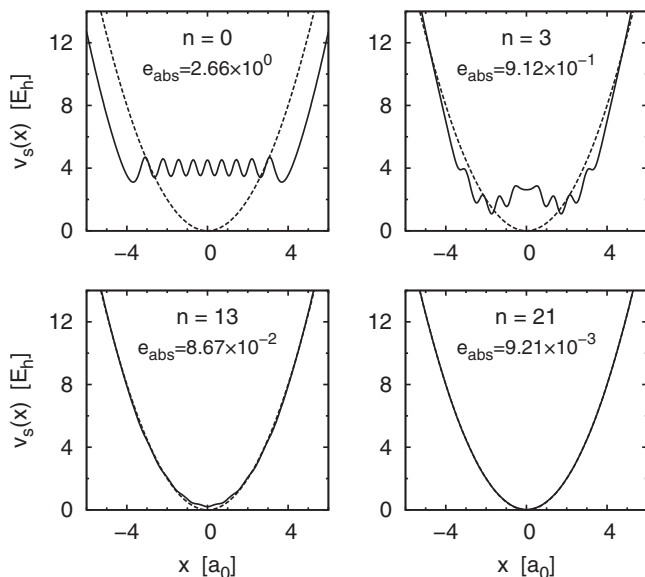
FIG. 1. Recovery of the external potential $v_s(x) = \frac{1}{2}x^2$ for the ground state of $N = 10$ noninteracting electrons occupying the 10 lowest levels of the one-dimensional harmonic oscillator. Each $v_s^{(n)}$, shown by a solid line, is constructed by Eq. (27) and shifted vertically so that the highest occupied energy level coincides with the exact value $\epsilon_{10} = 9/2$. The exact $v_s(x)$ is shown in each panel as a dashed curve.

To determine the Kohn–Sham potential corresponding to a given density, our method requires a finite basis set to represent the Kohn–Sham orbitals. For a spherical neon atom, only s and p functions need to be included. The STO basis set of Bunge and Esquivel, however, contains only six s and seven p functions, which is not enough to reproduce the input CISD density with high accuracy. Therefore, we decided to represent the Kohn–Sham orbitals of the atom using a different (larger) ancillary even-tempered STO basis set. Two such basis sets of the composition $(10s, 11p)$ and $(14s, 15p)$ were constructed using the parameters listed in Table II. Kinetic energy matrix elements in these basis sets were evaluated analytically, whereas matrix elements of $v_s^{(n)}$ were computed numerically using the first Fejér quadrature[54,55] whose nodes coincide with the 2048 Chebyshev interpolation points spanning the range from $r = 10^{-5}a_0$ to $15a_0$.

Figure 2 shows the *exchange-correlation* potentials of the Ne atom recovered from the Bunge–Esquivel density using two ancillary STO basis sets for the orbitals. These potentials

TABLE II. Even-tempered STO basis sets used for expanding the Kohn–Sham orbitals of the Ne atom. The exponents are given by $\zeta_{lk} = \alpha_l \gamma_l^k$, where $k = 1, 2, 3, \ldots$ and l is the angular momentum quantum number.

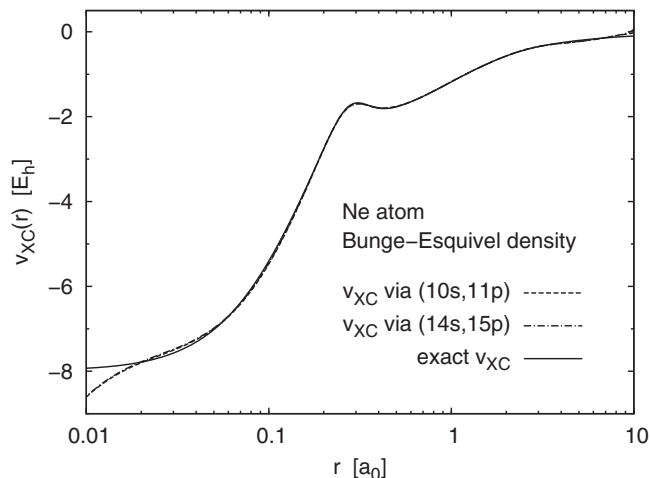| Type	l	α_l	γ_l
		$(10s, 11p)$	
s	0	0.893049	1.487490
p	1	0.600370	1.487490
		$(14s, 15p)$	
s	0	0.633049	1.327949
p	1	0.600370	1.348032

FIG. 2. Exchange-correlation potentials of the Ne atom determined from the accurate density of Ref. 51 using the STO basis sets of Table II to represent the Kohn–Sham orbitals. The computed potentials are shifted so that their HOMO eigenvalues satisfy Eq. (35) with $\epsilon_{HOMO}^{exact} = 0.7945\ E_h$.[57] The exact v_{XC} is from Ref. 56.

were extracted from v_s by the equation

$$v_{XC}(r) = v_s(r) + \frac{Z}{r} - v_H(r), \qquad (34)$$

where $Z = 10$ is the charge of the Ne nucleus. To facilitate comparison, we shifted both potentials vertically to satisfy the exact highest occupied molecular orbital (HOMO) condition[58]

$$\epsilon_{HOMO} = \epsilon_{HOMO}^{exact} \equiv -I, \qquad (35)$$

where I is the exact nonrelativistic ionization energy of the system. The $(10s, 11p)$ and $(14s, 15p)$ curves ($e_{abs} = 1.88 \times 10^{-3}$ and 5.95×10^{-4}, respectively) are virtually indistinguishable from each other and almost coincide with the exact $v_{XC}(r)$ between 0.05 and $3a_0$.

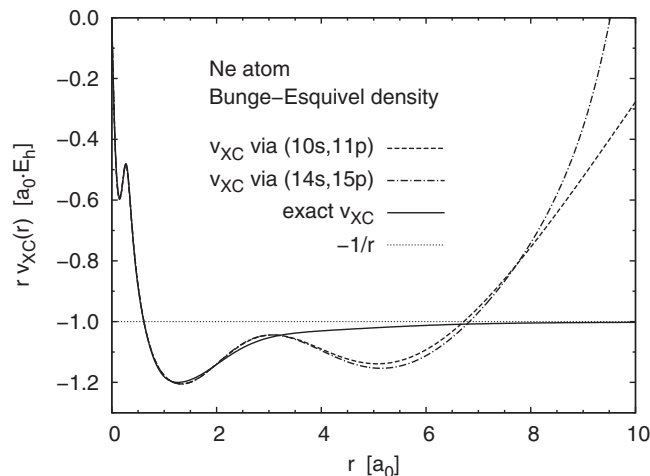Figure 3 reveals that the exchange-correlation potential corresponding to the Bunge–Esquivel Ne atom density does

FIG. 3. Same as in Fig. 2, except that all potentials are plotted in the form $r v_{XC}(r)$ to emphasize the differences in their asymptotic behavior.

TABLE III. The total kinetic energy and orbital eigenvalue differences from the Kohn–Sham potentials corresponding to the Bunge–Esquivel density of the Ne atom.

Method	T_s (E_h)	$\Delta\epsilon = \epsilon_{\mathrm{HOMO}} - \epsilon_i$ (E_h)	
		$1s \rightarrow 2p$	$2s \rightarrow 2p$
This work			
via STO(10s, 11p)	128.641	30.054	0.857
via STO(14s, 15p)	128.617	30.039	0.857
Literature			
Reference 19	128.625	30.023	0.855
Reference 52	128.639	30.023	0.856
References 24 and 27	128.609		
Reference 13		30.03	0.86

not have the correct asymptotic behavior

$$\lim_{r \to \infty} r v_{\mathrm{XC}}(r) = -1. \qquad (36)$$

The product $r v_{\mathrm{XC}}(r)$ has a spurious second minimum around $r = 5a_0$ and diverges at $r > 6a_0$ instead of approaching -1. These features are real and due to subtle errors in the input density at large r. For example, the Bunge–Esquivel density decays slightly faster than the exact Ne atom density, which means that the potential corresponding to the Bunge–Esquivel density has to be more strongly confining than $-1/r$ as $r \to \infty$. The same features were also observed by van Leeuwen and Baerends[20] who constructed the exchange-correlation potential of Ne from the same input density using a grid-point-based procedure.

In Table III, we report the values of T_s and Kohn–Sham eigenvalue differences obtained by our method from the Bunge–Esquivel density; they are compared to similar values obtained from the same density by other workers. The agreement is good in all cases.

B. Potentials from Gaussian basis set densities

For the purpose of generating Kohn–Sham potentials, densities expressed in Gauss-type-orbital (GTO) basis sets are qualitatively different from STO densities. Several workers reported[24,59,60] that potentials recovered from GTO densities exhibit large oscillations not found in exact potentials. These oscillations are real in that they reflect the actual behavior of the Laplacian of a typical GTO density.[24] One can avoid these oscillations by using large basis sets (see, however, Ref. 61). Keeping this in mind, let us examine exchange-correlation potentials corresponding to accurate GTO densities of the Ne and Ar atoms.

The input densities used in this section were generated by the all-electron second-order Møller–Plesset perturbation theory (MP2) and coupled-cluster singles and doubles (CCSD) methods. To minimize spurious oscillations in the resulting potentials, we need large GTO basis sets. To construct such a basis set for the Ne atom, we started with a set of 26s and 19p primitive GTOs of the universal Gaussian basis set[62] (UGBS) with exponents listed, respectively, on lines 2 through 27 and 1 through 19 in Table II of Ref. 62. These s and p functions were combined with the d, f, and g functions of the Ne cc-
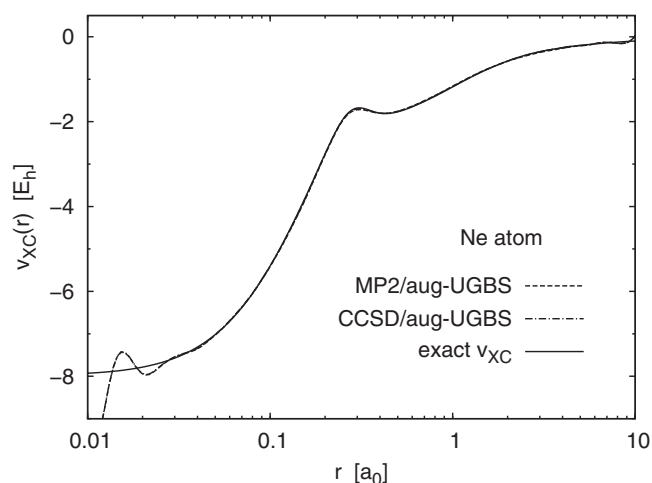

FIG. 4. Exchange-correlation potentials of the Ne atom determined from the MP2/aug-UGBS and CCSD/aug-UGBS densities. The MP2 and CCSD curves are shifted to satisfy the exact HOMO condition ($\epsilon_{\mathrm{HOMO}}^{\mathrm{exact}} = 0.7945$ E_h) and are visually indistinguishable. The exact v_{XC} is from Ref. 56.

pwCVQZ basis set of Peterson and Dunning[63] and one diffuse d function of the Ne aug-cc-pwCVQZ basis. The resulting basis set has the composition (26s, 19p, 6d, 3f, 1g). For argon, we took 29s and 22p primitive GTOs of the UGBS with exponents listed, respectively, on lines 2 through 30 and 1 through 22 in Table II of Ref. 62 and augmented them with the d, f, and g functions of the Ar cc-pwCVQZ basis set and one diffuse d function of the Ar aug-cc-pwCVQZ basis. The resulting basis set has the composition (29s, 22p, 7d, 4f, 2g). We call each of these basis sets the augmented UGBS (aug-UGBS). As before, we used 2048-node Chebyshev grids from $r = 5 \times 10^{-5}a_0$ to $r = 15a_0$.

Figure 4 shows the exchange-correlation potentials of the Ne atom determined from the MP2 ($e_{\mathrm{abs}} = 6.14 \times 10^{-4}$) and CCSD ($e_{\mathrm{abs}} = 6.26 \times 10^{-4}$) GTO densities. These potentials are almost the same as the potentials generated from the STO densities (Fig. 2); they also coincide with the exact exchange-correlation potentials from Ref. 56 everywhere except in the very vicinity of the nucleus and in the asymptotic region. The exchange-correlation potentials of the Ar atom determined from the MP2 ($e_{\mathrm{abs}} = 1.47 \times 10^{-3}$) and CCSD ($e_{\mathrm{abs}} = 1.49 \times 10^{-3}$) densities are shown in Fig. 5. Note that the exact potentials of the Ar atom are not available for comparison.

Our procedure can be also used to construct *correlation* potentials, $v_{\mathrm{C}} = v_{\mathrm{XC}} - v_{\mathrm{X}}$, where v_{X} is the exact exchange potential corresponding to the same density as v_{XC}. Because the exact v_{X} is not readily available, we approximate it by $\tilde{v}_{\mathrm{X}} = v_s^{\mathrm{HF}} + Z/r - v_{\mathrm{H}}$, where v_s^{HF} is the Kohn–Sham effective potential recovered from the Hartree–Fock density generated in the same basis set as the correlated density. The shapes of $\tilde{v}_{\mathrm{X}}$ and the true v_{X} are known to be very similar.[23,64]

The correlation potentials of the Ne and Ar atoms determined in this manner are shown in Figs. 6 and 7. The potential recovered from the CCSD density is especially close to the benchmark potential of Ref. 56, more so than the Ne atom correlation potentials reported in the literature.[65–68] For the Ar atom, the second maxima of our correlation
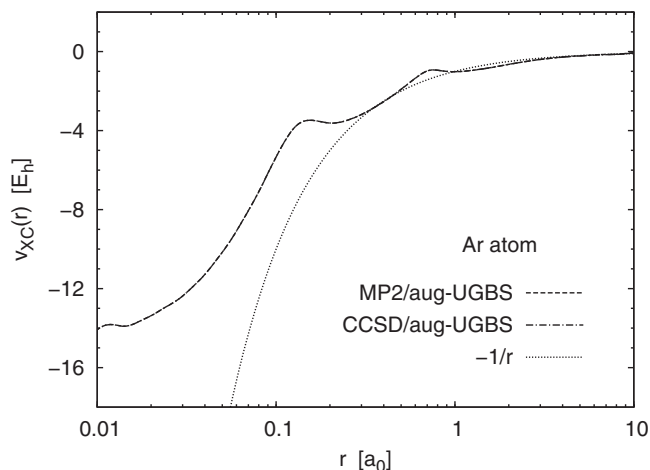
FIG. 5. Exchange-correlation potentials of the Ar atom determined from the MP2/aug-UGBS and CCSD/aug-UGBS densities. The MP2 and CCSD curves are shifted to satisfy the exact HOMO condition ($\epsilon_{HOMO}^{exact} = 0.582\ E_h$) and are visually indistinguishable.

FIG. 7. Correlation potentials of the Ar atom determined from the MP2/aug-UGBS and CCSD/aug-UGBS densities. The undetermined vertical shift is chosen by inspection.

potentials (at $r \approx 0.35a_0$) are about half as large as the corresponding maxima in Refs. 67 and 68. This may be because the basis sets used in those references did not include core correlation functions. When we repeated our calculations using the aug-UGBS with the core correlation functions *removed*, the magnitude of the second peak of v_C almost doubled.

To test the quality of the curves shown in Figs. 6 and 7, we used the virial relation for correlation potentials,[69]

$$E_C + T_C = -\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_C(\mathbf{r})\,d\mathbf{r}, \qquad (37)$$

where E_C is the correlation energy, and T_C is the correlation contribution to the kinetic energy. The values of $E_C + T_C$ for the exact v_C and the correlation potentials recovered from the MP2 and CCSD densities of the Ne atom were found to be -0.0653, -0.0577, and $-0.0463 E_h$, respectively. The values of $E_C + T_C$ for the MP2 and CCSD potentials of the Ar
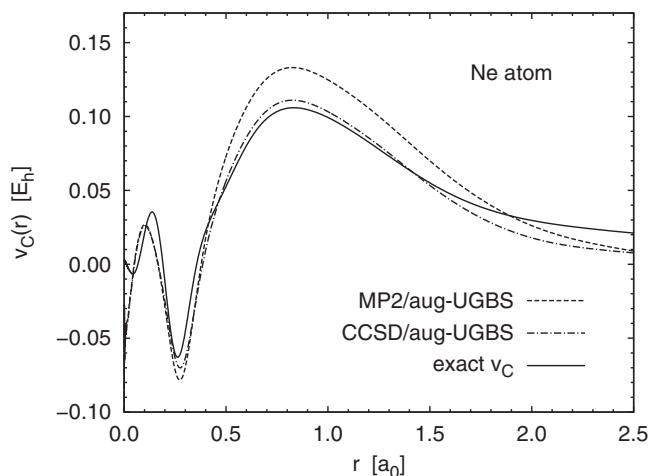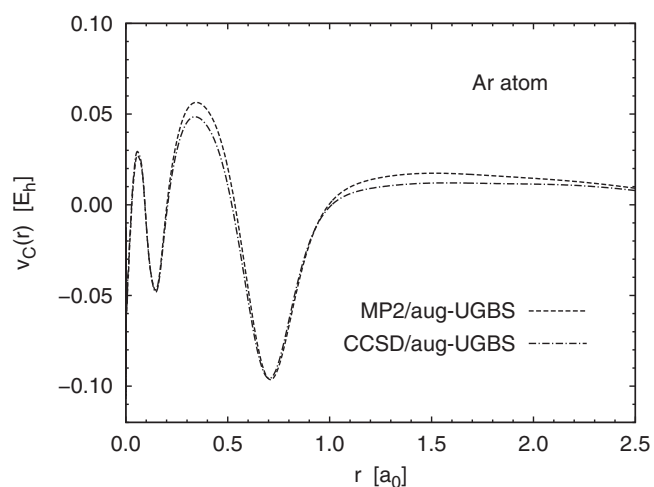
atom are -0.0804 and $-0.0798\ E_h$, respectively. In assessing these results, one should keep in mind that (i) virial integrals can be very sensitive to shape variations of Kohn–Sham potentials,[70,71] and (ii) markedly different potentials can have very similar virials.[71,72]

Another interesting observation is that, in contrast to the exchange-correlation potentials of Figs. 4 and 5, the correlation potentials of Figs. 6 and 7 exhibit no spurious features near the nucleus (even when plotted on a logarithmic scale). This is because the shape and magnitude of spurious oscillations of v_{XC} and $\tilde{v}_X$ turn out to be identical and thus cancel out when we compute the difference $v_C = v_{XC} - \tilde{v}_X$.

VI. CONCLUDING REMARKS

We showed that the differential virial theorem can be used for accurate determination of Kohn–Sham potentials from electron densities. An essential feature of our method is the use of the bosonic reference potential $v_s^{(0)}$ of Eq. (26) that is asymptotically correct (up to a constant) for any finite system and exact for all one-orbital systems. The bosonic potential is also size-consistent in contrast to the Fermi–Amaldi potential commonly used as a reference in other density-to-potential algorithms.[19,26] Generalization of our method to three-dimensional (3D) systems would require solving Eq. (10) on a 3D grid. This is certainly more laborious, but feasible.

In agreement with earlier reports,[24] we find that in order to obtain a smooth exchange-correlation potential from a GTO density, the GTO basis set must be very large. Even potentials recovered from accurate STO densities may have residual defects near the nuclei and at large r. We also find that when two exchange-correlation potentials are generated from two different densities computed in the *same* GTO basis set, the spurious features in both potentials are almost identical. This implies that these features are inherent to the chosen basis set and suggests a way of eliminating them.

FIG. 6. Correlation potentials of the Ne atom determined from the MP2/aug-UGBS and CCSD/aug-UGBS densities. The exact v_C is from Ref. 56.

ACKNOWLEDGMENTS

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