

Exact exchange-correlation potential and approximate exchange potential in terms of density matrices

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An exact expression in terms of density matrices (DMs) is derived for $\delta F[n]/\delta n(\mathbf{r})$, the functional derivative of the Hohenberg-Kohn functional. The derivation starts from the differential form of the virial theorem, obtained here for an electron system with arbitrary interactions, and leads to an expression taking the form of an integral over a path that can be chosen arbitrarily. After applying this approach to the equivalent system of noninteracting electrons (Slater-Kohn-Sham scheme) and combining the corresponding result with the previous one, an exact expression for the exchange-correlation potential $v_{xc}(\mathbf{r})$ is obtained which is analogous in character to that for $\delta F[n]/\delta n(\mathbf{r})$, but involving, besides the interacting-system DMs, also the noninteracting DMs. Equating the former DMs to the latter ones, we reduce the result for the exact $v_{xc}(\mathbf{r})$ to that for an approximate exchange-only potential $v_x(\mathbf{r})$. This leads naturally to the Harbola-Sahni exchange-only potential.

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I. INTRODUCTION

Starting with the Thomas-Fermi theory [1-3], extended later by Dirac [4], in which the ground-state energy E of a heavy atom of atomic number Z can be written quite explicitly in terms of the electron density $n(\mathbf{r})$ and the nuclear potential energy $v(\mathbf{r}) = -Z/r$ (we use atomic units throughout), much attention has been devoted to the functional

$$\tilde{E}[n] = F[n] + \int d^3r n(\mathbf{r})v(\mathbf{r}), \quad (1.1)$$

following the formal existence theorem of Hohenberg and Kohn [5]. In Eq. (1.1), $v(\mathbf{r})$ denotes the external potential acting on an electron (e.g., due to all nuclei of the system). Exact knowledge of $F[n]$ is clearly equivalent to the complete solution of the many-body problem, which still seems a long way off. But if we accept such (formal) knowledge, then the ground-state density itself is to be determined from the minimization of $\tilde{E}[n]$ with respect to the electron density $n(\mathbf{r})$ normalized to the total number N of electrons in the system under discussion, which yields

$$\mu = \frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}). \quad (1.2)$$

Though, as already stressed, $F[n]$ is not presently known, many approximations have been proposed: see, for example, the book by Parr and Yang [6]. However, the exact expression for $\delta F[n]/\delta n(\mathbf{r})$ (or, at least, a good approximation to it) rather than $F[n]$ itself is necessary to solve Eq. (1.2).

Usually, in order to provide a high accuracy for the dominant contribution to $F[n]$ — the kinetic energy —

the Slater-Kohn-Sham (SKS) scheme is applied [7,8]. In essence then, $F[n]$ is decomposed as

$$F[n] = T_s[n] + E_{es}[n] + E_{xc}[n], \quad (1.3)$$

where $T_s[n]$ is the kinetic-energy functional of a noninteracting-electron system, while $E_{es}[n]$ is the classical electrostatic energy of the electronic cloud of density $n(\mathbf{r})$. What remains on the right-hand side of Eq. (1.3) is the so-called exchange-correlation energy functional $E_{xc}[n]$. In this case, the single Eq. (1.2) is replaced by a system of N single-particle Schrödinger equations: the SKS equations

$$\left\{-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right\}\phi_j(\mathbf{r}, s) = \varepsilon_j\phi_j(\mathbf{r}, s), \quad j = 1, \dots, N, \quad (1.4)$$

in which the effective one-body potential is

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{es}(\mathbf{r}) + v_{xc}(\mathbf{r}). \quad (1.5)$$

Here, the electrostatic potential is given by

$$v_{es}(\mathbf{r}; [n]) = \frac{\delta E_{es}[n]}{\delta n(\mathbf{r})} = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (1.6)$$

and the exchange-correlation potential by

$$v_{xc}(\mathbf{r}; [n]) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (1.7)$$

Therefore, in this approach, one requires, ideally, exact expressions for, or in practice good approximations to, E_{xc} and v_{xc} (see, for instance, Parr and Yang [6]; Harbola and Sahni [9]). It is noteworthy in this context that a number of exact relations concerning E_{xc} and v_{xc}

have been established [10–12]. These can be very useful for testing approximations, and constructing refinements where necessary, for these quantities E_{xc} and v_{xc} .

In the present paper, which is also a contribution in the field of the investigations referred to immediately above, the following aims are realized:

(i) An exact expression for $\delta F[n]/\delta n(\mathbf{r})$ is obtained in terms of first- and second-order density matrices, by employing the differential virial theorem for interacting electrons (the derivation being given in Appendix A).

(ii) $v_{xc}(\mathbf{r})$ is then obtained in exact form by applying the result (i) above together with the analogous result for the equivalent noninteracting system (SKS scheme).

The results (i) and (ii) are somewhat formal, but they will become useful in practice if some controlled approximations for the necessary density matrices can be inserted. We shall also employ the results (i) and (ii) to obtain an approximation for the exchange-only potential, replacing density matrices of the interacting system by the corresponding matrices of the equivalent noninteracting system in the exact relation for the exchange-correlation potential. This substitution not only simplifies the theory significantly, but also removes difficulties with matrices of higher than first order, since all other matrices can then be expressed in terms of the first-order density matrix. In this way an approximation to $v_x(\mathbf{r})$ is obtained from (ii).

The outline of the present paper is then as follows. In Sec. II, immediately below, the aims (i) and (ii) are realized and followed by approximations. In Sec. III some properties of the approximate $v_x(\mathbf{r})$ and Harbola-Sahni conjecture on $v_{xc}(\mathbf{r})$ are studied, while Sec. IV constitutes a summary, together with proposals for possible future studies. In Appendix A the derivation of the differential virial theorem is given.

II. POTENTIALS VIA DIFFERENTIAL VIRIAL THEOREM

A. Density matrices and the kinetic-energy density tensor

We consider an N -electron system characterized by the Hamiltonian

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}, \quad (2.1)$$

with the kinetic energy, electron-electron (e - e) repulsion, and electron-nucleus (e - n) attraction energy operators, respectively, defined as

$$\hat{T} = \sum_{i=1}^N -\frac{1}{2} \nabla_i^2, \quad (2.2)$$

$$\hat{U} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(\mathbf{r}_i, \mathbf{r}_j), \quad u(\mathbf{r}_j, \mathbf{r}_i) = u(\mathbf{r}_i, \mathbf{r}_j), \quad (2.3)$$

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i). \quad (2.4)$$

In application to real atoms and molecules we have

$$u(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|, \quad (2.5)$$

$$v(\mathbf{r}) = \sum_{J=1}^M -Z_J / |\mathbf{r} - \mathbf{R}_J| \quad (2.6)$$

(for a molecule characterized by M nuclei of charge Z_J , placed at fixed positions \mathbf{R}_J). But for all general considerations we do not assume these narrowing specifications (2.5) and (2.6).

Let $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ be a normalized eigenfunction (ground- or excited-state one) of the Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (2.7)$$

where the notation $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ for i th space and spin coordinate is adopted. Then the N th-order density matrix (DM) generated by Ψ is just the following product:

$$\begin{aligned} \gamma_N(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{x}'_1, \dots, \mathbf{x}'_N) \\ = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N), \end{aligned} \quad (2.8)$$

while the p th-order reduced DM (for $p < N$) is defined in terms of γ_N by integrating out the $(N - p)$ coordinates (see, e.g., [6])

$$\gamma_p(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}'_1, \dots, \mathbf{x}'_p) = \binom{N}{p} \int d\mathbf{x}_{p+1} \cdots d\mathbf{x}_N \gamma_N. \quad (2.9)$$

Here $\int d\mathbf{x}_i$ means integration $\int d^3r_i$ and summation over s_i together with the replacement of \mathbf{x}'_i by \mathbf{x}_i in the integrand. The corresponding spinless DM is

$$\begin{aligned} \rho_p(\mathbf{r}_1, \dots, \mathbf{r}_p; \mathbf{r}'_1, \dots, \mathbf{r}'_p) \\ = \sum_{s_1, \dots, s_p} \gamma_p(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}'_1, \dots, \mathbf{x}'_p) \Big|_{s'_i = s_i}, \end{aligned} \quad (2.10)$$

while the diagonal elements of spinless DMs are denoted

$$n_p(\mathbf{r}_1, \dots, \mathbf{r}_p) = \rho_p(\mathbf{r}_1, \dots, \mathbf{r}_p; \mathbf{r}_1, \dots, \mathbf{r}_p) \geq 0. \quad (2.11)$$

The subscript “1” can be omitted. The basic quantity — electron number density — is thus $n(\mathbf{r}) = n_1(\mathbf{r}) = \rho_1(\mathbf{r}; \mathbf{r})$.

We define the kinetic-energy density tensor in terms of the DM ρ as

$$\begin{aligned} t_{\alpha\beta}(\mathbf{r}; [\rho]) \\ = \frac{1}{4} \left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha} \right) \rho(\mathbf{r}'; \mathbf{r}'') \Big|_{\mathbf{r}' = \mathbf{r}'' = \mathbf{r}}. \end{aligned} \quad (2.12)$$

This is a real, symmetric tensor, the trace of which is the non-negative kinetic-energy density (scalar)

$$t(\mathbf{r}) = \sum_{\alpha} t_{\alpha\alpha}(\mathbf{r}) \geq 0, \quad (2.13)$$

leading to the global kinetic energy

$$T = \int d^3r t(\mathbf{r}) = \langle \Psi | \hat{T} | \Psi \rangle. \quad (2.14)$$

B. Exact expression for $\delta F[n]/\delta n(\mathbf{r})$

1. Exact expression for the gradient of the external potential

The differential virial theorem derived in Appendix A, Eq. (A7), can be rewritten as

$$\nabla v(\mathbf{r}) = -\mathbf{f}(\mathbf{r}; [u, n, \rho, n_2]), \quad (2.15)$$

where

$$\begin{aligned} \mathbf{f}(\mathbf{r}; [u, n, \rho, n_2]) &= \left\{ -\frac{1}{4} \nabla \nabla^2 n(\mathbf{r}) + \mathbf{z}(\mathbf{r}; [\rho]) \right. \\ &\quad \left. + 2 \int d^3r' [\nabla u(\mathbf{r}, \mathbf{r}')] n_2(\mathbf{r}, \mathbf{r}') \right\} / n(\mathbf{r}). \end{aligned} \quad (2.16)$$

The vector field \mathbf{z} introduced above, related to the kinetic-energy density tensor via

$$z_{\alpha}(\mathbf{r}; [\rho]) = 2 \sum_{\beta} \frac{\partial}{\partial r_{\beta}} t_{\alpha\beta}(\mathbf{r}; [\rho]), \quad (2.17)$$

is a combination of derivatives of DM $\rho(\mathbf{r}'; \mathbf{r}'')$ [see Eq. (2.12)] evaluated at the diagonal $\mathbf{r}' = \mathbf{r}'' = \mathbf{r}$, so \mathbf{z} can be called a "local" functional of ρ .

Equation (2.15) represents an exact relation between the gradient of the e - n potential $v(\mathbf{r})$, the e - e interaction potential $u(\mathbf{r}, \mathbf{r}')$, and the DMs $n(\mathbf{r})$, $\rho(\mathbf{r}; \mathbf{r}')$, $n_2(\mathbf{r}, \mathbf{r}')$, generated by some eigenfunction Ψ of the Hamiltonian \hat{H} constructed of these potentials; see Eqs. (2.1)–(2.4). It should be noted that no assumption concerning the degeneracy of the system state Ψ is involved in obtaining Eq. (2.15). Also, the actual number of electrons N does not appear explicitly in Eqs. (2.15) and (2.16). The equation obtained from Eq. (2.15) by multiplying both sides by $n(\mathbf{r})$, depends on DMs linearly. Therefore the relation (2.15) remains true if the DM ρ_2 (from which n , ρ , and n_2 are derivable) is replaced by a "mixture" of pure-state matrices $\rho_2^{(i)}$:

$$\rho_2 = \sum_i p_i \rho_2^{(i)}, \quad (2.18)$$

where the probabilities p_i satisfy conditions

$$p_i \geq 0, \quad \sum_i p_i = 1. \quad (2.19)$$

But ρ_2 mentioned above can be obtained by reduction [via Eqs. (2.9) and (2.10)] of the so-called ensemble-state density matrix Γ_N , describing a system in a mixed state, rather than by reduction of γ_N , Eq. (2.8), describing a system in the pure state (see, e.g., Parr and Yang [6]). This Γ_N is defined by

$$\Gamma_N = \sum_i p_i \gamma_N^{(i)}, \quad (2.20)$$

where $\gamma_N^{(i)}$ corresponds to $\Psi^{(i)}$, according to Eq. (2.8).

To summarize the above, the exact relation (2.15) holds not only for pure-state density matrices, but also for ensemble-state matrices.

2. Path-integral form of the external potential $v(\mathbf{r})$

Equation (2.15) may be viewed as a differential equation for the potential $v(\mathbf{r})$. Because $\mathbf{f}(\mathbf{r}) = -\nabla v(\mathbf{r})$, the force field $\mathbf{f}(\mathbf{r})$ is conservative. Therefore, it follows that the potential at point \mathbf{r}_0 , say, is the work done in bringing an electron from infinity to \mathbf{r}_0 against the force field $\mathbf{f}(\mathbf{r})$:

$$v(\mathbf{r}_0) = - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \mathbf{f}(\mathbf{r}). \quad (2.21)$$

Since $\mathbf{f}(\mathbf{r})$ is conservative, the value of the line integral in Eq. (2.21) does not depend on the path of integration chosen. Note that Eq. (2.21) has been written such that $v(\infty) = 0$: a standard choice of gauge for the potential.

Finally, using the Euler-Lagrange equation (1.2) of the density-functional theory, we can reinterpret Eq. (2.21) as

$$\frac{\delta F[n]}{\delta n(\mathbf{r}_0)} = \mu + \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \mathbf{f}(\mathbf{r}; [u, n, \rho, n_2]). \quad (2.22)$$

The presence of an arbitrary constant μ is connected with the fact that the functional derivative on the left-hand side of Eq. (2.22) is defined only for variations conserving the total number of electrons.

Equation (2.22) together with Eq. (2.16) represents an exact expression for $\delta F/\delta n$ in terms of the e - e interaction potential $u(\mathbf{r}, \mathbf{r}')$ and three objects n , ρ , n_2 derivable from the DM ρ_2 . All remarks on the possible origin of ρ_2 or its construction, made in the preceding section, apply also to the relation (2.22).

C. Exact expression for $v_{xc}(\mathbf{r})$

In this section, in order to have the exchange-correlation potential uniquely defined, we assume that: (i) The original N -interacting electron system is in its ground state. (ii) The electron density of this state possesses the property that it is noninteracting v -representable (see, e.g., Ref. [6]). (iii) The ground state of the equivalent SKS scheme [a system of N noninteracting electrons moving in the external potential $v_s(\mathbf{r})$, Eq.

(1.5)], is nondegenerate and has the same density $n(\mathbf{r})$ as the system in (i). Then the wave function of equivalent system in (iii), $\Phi_s(\mathbf{x}_1, \dots, \mathbf{x}_N)$, is a Slater determinant constructed of the N lowest-energy orbitals $\phi_i(\mathbf{x})$, the eigenfunctions of the SKS Eq. (1.4). The DMs and their diagonal elements, generated from Φ_s , will be distinguished (from DMs generated by Ψ) by a superscript “ s ”; e.g., n_2^s, ρ^s , etc.

We can apply the result (2.15) to case (iii) and obtain obviously

$$\nabla v_s(\mathbf{r}) = -\mathbf{f}_s(\mathbf{r}; [n, \rho^s]), \quad (2.23)$$

where

$$\mathbf{f}_s(\mathbf{r}; [n, \rho^s]) = \{-\frac{1}{4}\nabla\nabla^2 n(\mathbf{r}) + \mathbf{z}(\mathbf{r}; [\rho^s])\}/n(\mathbf{r}). \quad (2.24)$$

Now, keeping in mind the decomposition (1.5) of v_s , we

$$\mathbf{f}_{xc}(\mathbf{r}; [u, n, \rho^s, \rho, n_2]) = \left\{ \mathbf{z}(\mathbf{r}; [\rho^s]) - \mathbf{z}(\mathbf{r}; [\rho]) + \int d^3r' [\nabla u(\mathbf{r}, \mathbf{r}')] [n(\mathbf{r})n(\mathbf{r}') - 2n_2(\mathbf{r}, \mathbf{r}')] \right\} / n(\mathbf{r}) \quad (2.28)$$

[see Eq. (2.17) for the definition of \mathbf{z}]. The force field $\mathbf{f}_{xc}(\mathbf{r})$ is conservative because it stems from the potential $v_{xc}(\mathbf{r})$, i.e., $\mathbf{f}_{xc}(\mathbf{r}) = -\nabla v_{xc}(\mathbf{r})$. Therefore, in complete analogy with Eq. (2.21) we have

$$v_{xc}(\mathbf{r}_0) = - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \mathbf{f}_{xc}(\mathbf{r}; [u, n, \rho^s, \rho, n_2]), \quad (2.29)$$

where again the above line integral is independent of the particular path chosen for integration.

Equation (2.29) represents an exact expression for $v_{xc}(\mathbf{r})$ in terms of objects written explicitly as arguments of \mathbf{f}_{xc} . Contrary to the results (2.21) and (2.22), the expression for v_{xc} , Eq. (2.29), is not valid for ensemble-state DMs (because the equation for $n\nabla v_{xc}$ is not linear in DMs).

D. Approximate expression for $v_x(\mathbf{r})$

Our further aim is to find, from the exact expression for $v_{xc}(\mathbf{r})$ in Eq. (2.29), an approximate expression for $v_x(\mathbf{r})$ alone. As a guide to this task let us analyze the separation of the exchange energy

$$E_x = \langle \Phi_s | \hat{U} | \Phi_s \rangle - E_{es}[n] \quad (2.30)$$

from the exchange-correlation energy

$$E_{xc} = \langle \Psi | \hat{T} | \Psi \rangle - \langle \Phi_s | \hat{T} | \Phi_s \rangle + \langle \Psi | \hat{U} | \Psi \rangle - E_{es}[n]. \quad (2.31)$$

The above equations represent the standard definitions (see, e.g., Parr and Yang [6]). Therefore, combining Eqs. (2.30) and (2.31) we have

$$E_{xc} = E_x + (T_c + U_c), \quad (2.32)$$

subtract Eq. (2.15) from Eq. (2.23) to obtain

$$\nabla(v_{es}(\mathbf{r}) + v_{xc}(\mathbf{r})) = \mathbf{f}(\mathbf{r}; [u, n, \rho, n_2]) - \mathbf{f}_s(\mathbf{r}; [n, \rho^s]). \quad (2.25)$$

But, using an analogue of Eq. (1.6) in which the Coulombic interaction, Eq. (2.5), is replaced by a general u , we have

$$\nabla v_{es}(\mathbf{r}) = \int d^3r' \nabla u(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'). \quad (2.26)$$

After subtracting Eq. (2.26) from Eq. (2.25) we arrive finally at the result

$$\nabla v_{xc}(\mathbf{r}) = -\mathbf{f}_{xc}(\mathbf{r}; [u, n, \rho^s, \rho, n_2]), \quad (2.27)$$

with

where

$$\begin{aligned} T_c &= \langle \Psi | \hat{T} | \Psi \rangle - \langle \Phi_s | \hat{T} | \Phi_s \rangle \\ &= T - T_s \\ &= \int d^3r \sum_{\alpha} t_{\alpha\alpha}(\mathbf{r}; [\rho - \rho^s]), \end{aligned} \quad (2.33)$$

$$\begin{aligned} U_c &= \langle \Psi | \hat{U} | \Psi \rangle - \langle \Phi_s | \hat{U} | \Phi_s \rangle \\ &= \int d^3r d^3r' u(\mathbf{r}, \mathbf{r}') \{n_2(\mathbf{r}, \mathbf{r}') - n_2^s(\mathbf{r}, \mathbf{r}')\}. \end{aligned} \quad (2.34)$$

We see that, in order to obtain E_x from the expression for E_{xc} , it is enough to neglect the differences between the interacting-system DMs and corresponding SKS-system DMs, i.e., to neglect $(\rho - \rho^s)$ in the expression for T_c , Eq. (2.33), and $(n_2 - n_2^s)$ in the expression for U_c , Eq. (2.34).

Now we adopt the above observation in order to split the exact expression for v_{xc} in Eq. (2.29) into the sum of \tilde{v}_x and \tilde{v}_c ; interpreting these terms as approximate exchange potential and approximate correlation potential, respectively. Thus

$$\begin{aligned} v_{xc}(\mathbf{r}_0) &= \tilde{v}_x(\mathbf{r}_0) + \tilde{v}_c(\mathbf{r}_0) \\ &= - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \tilde{\mathbf{f}}_x(\mathbf{r}) - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \tilde{\mathbf{f}}_c(\mathbf{r}), \end{aligned} \quad (2.35)$$

where the force fields are given by

$$\begin{aligned} \tilde{\mathbf{f}}_x(\mathbf{r}) &= - \int d^3r' [\nabla u(\mathbf{r}, \mathbf{r}')] [2n_2^s(\mathbf{r}, \mathbf{r}') \\ &\quad - n(\mathbf{r})n(\mathbf{r}')] / n(\mathbf{r}) \end{aligned} \quad (2.36)$$

$$\tilde{\mathbf{f}}_c(\mathbf{r}) = - \left\{ \mathbf{z}(\mathbf{r}; [\rho - \rho^s]) + 2 \int d^3 r' [\nabla u(\mathbf{r}, \mathbf{r}')] [n_2(\mathbf{r}, \mathbf{r}') - n_2^s(\mathbf{r}, \mathbf{r}')] \right\} / n(\mathbf{r}). \quad (2.37)$$

While we know that the total force field \mathbf{f}_{xc} is conservative, we lack such knowledge concerning the separate pieces $\tilde{\mathbf{f}}_x$ or $\tilde{\mathbf{f}}_c$ (examples of the nonconservative character of $\tilde{\mathbf{f}}_x$ can be constructed). Therefore some specific path of integration must be chosen to complete the definition (2.35). Seemingly the most natural path is along the radius on which the point \mathbf{r}_0 lies. As the center of the coordinate system, a position of the nucleus is chosen in the case of a single-ion system, the center of symmetry for a symmetrical molecule, and some “inner” point for a molecule or cluster with lower symmetry. Then

$$\tilde{v}_x(\mathbf{r}_0) = \int_{r_0}^{\infty} dr e \cdot \tilde{\mathbf{f}}_x(re), \quad \mathbf{e} = \mathbf{r}_0/r_0. \quad (2.38)$$

The same path must be used for the calculation of \tilde{v}_c in order to leave the sum v_{xc} unchanged.

Using the separation of the pair-distribution function n_2^s into its uncorrelated and correlated parts (see, e.g., Parr and Yang [6])

$$n_2^s(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} n(\mathbf{r}_1) n(\mathbf{r}_2) \{1 + h_2^s(\mathbf{r}_1, \mathbf{r}_2)\}, \quad (2.39)$$

and noting that the combination

$$\rho_x(\mathbf{r}_1, \mathbf{r}_2) = h_2^s(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_2) \quad (2.40)$$

is customarily called the exchange hole at \mathbf{r}_2 of an electron at \mathbf{r}_1 , we rewrite Eq. (2.36) as

$$\tilde{\mathbf{f}}_x(\mathbf{r}) = - \int d^3 r' \rho_x(\mathbf{r}, \mathbf{r}') \nabla u(\mathbf{r}, \mathbf{r}'). \quad (2.41)$$

For the case of Coulombic $u(\mathbf{r}, \mathbf{r}')$, Eq. (2.5), Eq. (2.41) leads to

$$\tilde{\mathbf{f}}_x(\mathbf{r}) = \int d^3 r' \rho_x(\mathbf{r}, \mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}. \quad (2.42)$$

We recognize $\tilde{\mathbf{f}}_x(\mathbf{r})$, given by Eq. (2.42), to be identical with the force field $\mathcal{E}_x(\mathbf{r})$ proposed by Harbola and Sahni [9] (in their exchange-only version). This means that our approximation $\tilde{v}_x(\mathbf{r})$ to the exact $v_x(\mathbf{r})$ coincides with the Harbola-Sahni approximation $\tilde{v}_x^{\text{HS}}(\mathbf{r})$. Since these two approximations were derived by using completely different reasonings, their coincidence strongly enhances the expectation that this function is very close to the exact $v_x(\mathbf{r})$.

III. STUDY OF THE APPROXIMATE EXCHANGE POTENTIAL $\tilde{v}_x(\mathbf{r})$ AND VALIDITY OF HARBOLA-SAHNI CONJECTURE ON $v_{xc}(\mathbf{r})$

A. Path dependence of exchange-only potential

While in their pioneering work Harbola and Sahni [9] did not discuss the issue of path dependence, this was analyzed by Ou-Yang and Levy [13]. These authors give an example of $\mathcal{E}_x(\mathbf{r})$ which is not conservative; i.e., for which $\nabla \times \mathcal{E}_x(\mathbf{r}) \neq \mathbf{0}$. In their subsequent paper [14], they demonstrate that $\tilde{v}_x(\mathbf{r})$, given by Eqs. (2.38) and (2.42) [in their notation $h_x^0(\mathbf{r})$], satisfies two necessary conditions for \tilde{v}_x to be identical with v_x , namely

$$E_x = - \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \nabla \tilde{v}_x(\mathbf{r}) \quad (3.1)$$

and

$$\tilde{v}_x(\mathbf{r}; [n_\lambda]) = \lambda \tilde{v}_x(\lambda \mathbf{r}; [n]), \quad (3.2)$$

where the scaled density is defined as $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda \mathbf{r})$. For the proof that $\tilde{v}_x(\mathbf{r})$ satisfies Eq. (3.1) it is essential that the path, chosen for integration, is that adopted in the definition Eq. (2.38); i.e., along a radius. As Ou-Yang and Levy [14] prove in order to have $\tilde{v}_x(\mathbf{r}) \equiv v_x(\mathbf{r})$, besides the two conditions (3.1) and (3.2), a third condition must be satisfied by \tilde{v}_x , namely that $\tilde{v}_x(\mathbf{r})$ be a functional derivative of some functional of n . Unfortunately, this last property has not been shown yet for \tilde{v}_x : therefore there is no general proof that $\tilde{v}_x(\mathbf{r})$ is identical to $v_x(\mathbf{r})$. Evidently, for systems in which the relation

$$\nabla \times \tilde{\mathbf{f}}_x(\mathbf{r}) = \mathbf{0} \quad (3.3)$$

is violated in some region, we can conclude that the potential \tilde{v}_x does not coincide with v_x . But, for systems where Eq. (3.3) is satisfied everywhere, it is not sufficient to claim that the field $\tilde{\mathbf{f}}_x(\mathbf{r})$ is conservative (see discussion in Wang *et al.* [15]). As dictated by symmetry, \tilde{v}_x defined by Eq. (2.35) is path independent for closed-subshell atoms, thus uniquely reducing to the form (2.38). Numerical investigation by Li *et al.* [16] of these systems carried out with the exchange-only Harbola-Sahni potential (i.e., \tilde{v}_x) leads to results which demonstrate the high accuracy of this approximate exchange potential

B. Large- r behavior of exchange-only potential

In order to see the large- r behavior of $\tilde{v}_x(\mathbf{r})$, let us first rewrite the force $\tilde{\mathbf{f}}_x$, Eq. (2.41), as

$$\tilde{\mathbf{f}}_x(\mathbf{r}) = - \nabla \int d^3 r' u(\mathbf{r}, \mathbf{r}') \rho_x(\mathbf{r}, \mathbf{r}') + \int d^3 r' u(\mathbf{r}, \mathbf{r}') \nabla \rho_x(\mathbf{r}, \mathbf{r}'). \quad (3.4)$$

For Coulombic interaction this means a separation into the “Slater” and “non-Slater” contributions:

$$\tilde{\mathbf{f}}_{\mathbf{x}}(\mathbf{r}) = -\nabla v_{\text{SI}}(\mathbf{r}) + \tilde{\mathbf{f}}_{\text{nSI}}(\mathbf{r}), \quad (3.5)$$

with the Slater [7] potential defined as

$$v_{\text{SI}}(\mathbf{r}) = \int d^3 r' \frac{\rho_{\mathbf{x}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.6)$$

and the non-Slater force (in the present approximation) given by

$$\tilde{\mathbf{f}}_{\text{nSI}}(\mathbf{r}) = \int d^3 r' \frac{\nabla \rho_{\mathbf{x}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.7)$$

Thus the total approximate exchange potential can be written as

$$\tilde{v}_{\mathbf{x}}(\mathbf{r}) = v_{\text{SI}}(\mathbf{r}) + \tilde{v}_{\text{nSI}}(\mathbf{r}), \quad (3.8)$$

with

$$\tilde{v}_{\text{nSI}}(\mathbf{r}_0) = \int_{r_0}^{\infty} dr \mathbf{e} \cdot \tilde{\mathbf{f}}_{\text{nSI}}(r\mathbf{e}), \quad \mathbf{e} = \mathbf{r}_0/r_0. \quad (3.9)$$

The above decomposition (3.8) for the Harbola-Sahni exchange potential was performed earlier by Ou-Yang and Levy [14].

In the asymptotic large- r region the exchange hole can be shown to behave as

$$\rho_{\mathbf{x}}(\mathbf{r}, \mathbf{r}') = \rho_{\mathbf{x}}(\infty, \mathbf{r}') \{1 + O(e^{-br})\}, \quad b > 0. \quad (3.10)$$

Therefore the non-Slater components, $\tilde{\mathbf{f}}_{\text{nSI}}(\mathbf{r})$, Eq. (3.7), of the force, and, subsequently, $\tilde{v}_{\text{nSI}}(\mathbf{r})$, Eq. (3.9), of the potential, are exponentially small, while the Slater potential $v_{\text{SI}}(\mathbf{r})$, Eq. (3.6), tends to $-1/r$. This provides the correct behavior of $\tilde{v}_{\mathbf{x}}(\mathbf{r})$, Eq. (3.8) (see, e.g., the figures of $\tilde{v}_{\mathbf{x}}^{\text{HS}}(\mathbf{r})$ in Li *et al.* [16]).

C. Degree of validity of the Harbola-Sahni conjecture on $v_{\text{xc}}(\mathbf{r})$

Under the assumptions stated in Sec. II C, it is known that the exchange-correlation energy can be written (see, e.g., Parr and Yang [6]) as

$$E_{\text{xc}} = \frac{1}{2} \int d^3 r d^3 r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) \bar{\rho}_{\text{xc}}(\mathbf{r}, \mathbf{r}'), \quad (3.11)$$

where

$$\begin{aligned} \bar{\rho}_{\text{xc}}(\mathbf{r}, \mathbf{r}') &= \bar{h}_2(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \\ &= \{2\bar{n}_2(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')\}/n(\mathbf{r}) \end{aligned} \quad (3.12)$$

[compare Eqs. (2.40) and (2.39)]. Here the bar over a quantity denotes the coupling-constant averaged value

$$\bar{n}_2(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda n_2^{(\lambda)}(\mathbf{r}, \mathbf{r}'), \quad (3.13)$$

when the original system ($\lambda = 1$) and the equivalent SKS system ($\lambda = 0$) are related by means of adiabatic

connection [6]. An alternative expression for E_{xc} , already presented in Eqs. (2.31)–(2.34), is

$$E_{\text{xc}} = T - T_s + \frac{1}{2} \int d^3 r d^3 r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}'), \quad (3.14)$$

where ρ_{xc} is defined similarly as $\bar{\rho}_{\text{xc}}$ in Eq. (3.12), but with \bar{n}_2 replaced by $n_2^{(1)} \equiv n_2$.

Using the notation of Eq. (3.11), the Harbola-Sahni [9] conjecture concerning the exchange-correlation potential means that it is given by

$$\tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r}_0) = - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \tilde{\mathbf{f}}_{\text{xc}}^{\text{HS}}(\mathbf{r}), \quad (3.15)$$

where

$$\begin{aligned} \tilde{\mathbf{f}}_{\text{xc}}^{\text{HS}}(\mathbf{r}) &= \mathcal{E}_{\text{xc}}(\mathbf{r}) \\ &= \int d^3 r' \bar{\rho}_{\text{xc}}(\mathbf{r}, \mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \\ &= - \int d^3 r' \bar{\rho}_{\text{xc}}(\mathbf{r}, \mathbf{r}') \nabla \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \end{aligned} \quad (3.16)$$

[compare Eqs. (1), (4), and (5) of Harbola and Sahni [9]].

Below we shall demonstrate that $\tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r})$ is not identical to the exact $v_{\text{xc}}(\mathbf{r})$, by employing *reductio ad absurdum*. Let us assume that $\tilde{v}_{\text{xc}}^{\text{HS}}$ is a legitimate potential. Then Eq. (3.15) implies that the gradient of this potential is given by

$$\nabla \tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r}) = -\tilde{\mathbf{f}}_{\text{xc}}^{\text{HS}}(\mathbf{r}). \quad (3.17)$$

Now calculate the following energy [in analogy with Eq. (3.1)]

$$\begin{aligned} E_{\text{dif}} &= \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \{\nabla \tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r}) - \nabla v_{\text{xc}}(\mathbf{r})\} \\ &= \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \{\mathbf{f}_{\text{xc}}(\mathbf{r}) - \tilde{\mathbf{f}}_{\text{xc}}^{\text{HS}}(\mathbf{r})\}, \end{aligned} \quad (3.18)$$

showing an (eventual) difference between the Harbola-Sahni expression (3.17) and the exact one, Eq. (2.27), for the gradient of the potential. Using Eqs. (2.28) and (3.16) we evaluate E_{dif} to be

$$E_{\text{dif}} = E_{\text{dif}}^T + E_{\text{dif}}^U, \quad (3.19)$$

where

$$\begin{aligned} E_{\text{dif}}^T &= \int d^3 r \mathbf{r} \cdot \{\mathbf{z}(\mathbf{r}, [\rho^s]) - \mathbf{z}(\mathbf{r}; [\rho])\} \\ &= 2 \sum_{\alpha\beta} \int d^3 r r_{\alpha} \frac{\partial}{\partial r_{\beta}} \{t_{s,\alpha\beta}(\mathbf{r}) - t_{\alpha\beta}(\mathbf{r})\} \\ &= 2(T - T_s) \end{aligned} \quad (3.20)$$

[see Eq. (2.17) and compare with Eqs. (2.13) and (2.14)], and

$$\begin{aligned}
E_{\text{dif}}^U &= \int d^3r d^3r' \frac{\mathbf{r} \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} n(\mathbf{r}) \{ \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}') - \bar{\rho}_{\text{xc}}(\mathbf{r}, \mathbf{r}') \} \\
&= \int d^3r d^3r' \frac{\mathbf{r} \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} 2 \{ n_2(\mathbf{r}, \mathbf{r}') - \bar{n}_2(\mathbf{r}, \mathbf{r}') \}.
\end{aligned} \tag{3.21}$$

Using symmetry of n_2 and \bar{n}_2 we transform Eq. (3.21) to obtain

$$\begin{aligned}
E_{\text{dif}}^U &= \int d^3r d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \{ n_2(\mathbf{r}, \mathbf{r}') - \bar{n}_2(\mathbf{r}, \mathbf{r}') \} \\
&= \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \{ \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}') - \bar{\rho}_{\text{xc}}(\mathbf{r}, \mathbf{r}') \} \\
&= [E_{\text{xc}} - (T - T_s)] - E_{\text{xc}},
\end{aligned} \tag{3.22}$$

where Eqs. (3.14) and (3.11) were used in the last step. So we get finally from Eq. (3.19)

$$E_{\text{dif}} = T - T_s. \tag{3.23}$$

But, as it is known (Levy and Perdew [10]),

$$T_c = T - T_s > 0. \tag{3.24}$$

Thus we have arrived at a contradiction and therefore $\tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r}) \neq v_{\text{xc}}(\mathbf{r})$. The values of the correlation kinetic energy T_c , Eq. (3.24), are known to be rather small compared with E_{xc} (see, e.g., Zhao *et al.* [17]); so, on average, $\tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r})$ may be quite close to $v_{\text{xc}}(\mathbf{r})$. But one has also to bear in mind that there is no proof that the definition of $\tilde{v}_{\text{xc}}^{\text{HS}}(\mathbf{r})$ in Eq. (3.15) is path independent. Therefore some particular path must be chosen to make this definition complete. It seems to us that the path used in Eq. (2.38) is the best choice, because it proved to be essential for satisfying the requirement Eq. (3.1) by $\tilde{v}_{\text{x}} = \tilde{v}_{\text{x}}^{\text{HS}}$.

IV. SUMMARY AND DISCUSSION

The major result of the present study is the path integral formula (2.29) together with Eq. (2.28) for the exchange-correlation potential $v_{\text{xc}}(\mathbf{r})$ in terms of quantities directly derivable from the second-order density matrix of the interacting system, of the first-order density matrix of the noninteracting (SKS) system, and of the electron-electron interaction potential.

The simplest possible practical result to obtain from the exact formula (2.29) can be summarized in terms of the following steps:

(a) Replace any interacting density matrix entering the theory by the independent-particle SKS equivalent.

(b) Write the second-order density matrix in terms of the SKS first-order density matrix according to the rules given, e.g., in Parr and Yang [6] for DMs generated from determinantal wave function.

Assumption (a) above is equivalent to the neglect of correlation and hence leads to approximation to the exchange-only potential $\tilde{v}_{\text{x}}(\mathbf{r})$ [given in Eqs. (2.38) and (2.41)]. For Coulombic e - e interaction this potential is then found to coincide with the Harbola-Sahni (HS) exchange-only potential. Existing numerical calculations on the latter potential are very encouraging and appear to approximate very accurately (except in the region between atomic shells) the correct exchange potential of the closed-shell atoms. For such atoms, the HS approximation has no path arbitrariness, but for other systems like molecules and clusters, path dependence of their formula will need careful study.

To conclude, we wish to stress a direction which looks promising for future work. It is important to have a careful approximation to the interacting second-order density matrix entering the theory, in the presence of electron correlations (ultimately, as a functional of electron density). In this general context, the pioneering work of Gutzwiller [18] should be referred to. With his correlated wave function, and by judicious approximation, he was able to construct low-order density matrices transcending these from a single Slater determinant.

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APPENDIX: DIFFERENTIAL VIRIAL THEOREM

This local relation between the density, potentials, and the kinetic-energy density tensor can be obtained by a procedure similar to that we employed earlier [19] for noninteracting electrons. The starting point is the Schrödinger equation (2.7). Because $\hat{\mathcal{H}}$ is real, this equation is satisfied separately by the real and imaginary part of the wave function $\Psi = \Psi^{\text{Re}} + i\Psi^{\text{Im}}$, i.e.,

$$E = \frac{\hat{\mathcal{H}}\Psi^{\text{Re}}}{\Psi^{\text{Re}}} = \frac{\hat{\mathcal{H}}\Psi^{\text{Im}}}{\Psi^{\text{Im}}}. \tag{A1}$$

Using the definitions (2.1)–(2.4) we first transform (A1) into

$$\hat{\mathcal{V}} + \hat{\mathcal{U}} - E = -\frac{\hat{\mathcal{T}}\Psi^{\text{Re}}}{\Psi^{\text{Re}}} = -\frac{\hat{\mathcal{T}}\Psi^{\text{Im}}}{\Psi^{\text{Im}}}, \tag{A2}$$

and next, by differentiating both sides of the left part of Eq. (A2) with respect to $r_{1\alpha}$, we obtain

$$v_{/1\alpha}(\mathbf{r}_1) + \sum_{j=2}^N u_{/1\alpha}(\mathbf{r}_1, \mathbf{r}_j) = \frac{1}{2}(\Psi^{\text{Re}})^{-1} \sum_{i=1}^N \sum_{\beta} \Psi_{/1\alpha/i\beta/i\beta}^{\text{Re}} - \frac{1}{2}(\Psi^{\text{Re}})^{-2} \Psi_{/1\alpha}^{\text{Re}} \sum_{i=1}^N \sum_{\beta} \Psi_{/i\beta/i\beta}^{\text{Re}}. \tag{A3}$$

Here the notation for partial derivatives $f_{/i\alpha} = \partial f / \partial r_{i\alpha}$ is adopted. After multiplying both sides of Eq. (A3) by $(\Psi^{\text{Re}})^2$ we arrive at the result

$$\begin{aligned} \left\{ v(\mathbf{r}_1) + \sum_{j=2}^N u(\mathbf{r}_1, \mathbf{r}_j) \right\}_{/1\alpha} (\Psi^{\text{Re}})^2 &= \sum_{i=1}^N \sum_{\beta} \left\{ \frac{1}{2} \Psi^{\text{Re}} \Psi_{/1\alpha/i\beta/i\beta}^{\text{Re}} - \frac{1}{2} \Psi_{/1\alpha}^{\text{Re}} \Psi_{/i\beta/i\beta}^{\text{Re}} \right\} \\ &= \sum_{i=1}^N \sum_{\beta} \left\{ \frac{1}{4} (\Psi^{\text{Re}} \Psi^{\text{Re}})_{/1\alpha/i\beta/i\beta} - (\Psi_{/1\alpha}^{\text{Re}} \Psi_{/i\beta}^{\text{Re}})_{/i\beta} \right\}. \end{aligned} \quad (\text{A4})$$

An equation, analogous to Eq. (A4), with Ψ^{Re} replaced by Ψ^{Im} , can also be obtained from Eq. (A2). After adding two such equations we find

$$\left\{ v(\mathbf{r}_1) + \sum_{j=2}^N u(\mathbf{r}_1, \mathbf{r}_j) \right\}_{/1\alpha} |\Psi|^2 = \sum_{i=1}^N \sum_{\beta} \left\{ \frac{1}{4} (|\Psi|^2)_{/1\alpha/i\beta/i\beta} - (\Psi_{/1\alpha}^{\text{Re}} \Psi_{/i\beta}^{\text{Re}} + \Psi_{/1\alpha}^{\text{Im}} \Psi_{/i\beta}^{\text{Im}})_{/i\beta} \right\}. \quad (\text{A5})$$

Next, we multiply both sides by N , sum over s_1 , and integrate over $d\mathbf{x}_2 \cdots d\mathbf{x}_N$ to obtain

$$\begin{aligned} v_{/1\alpha}(\mathbf{r}_1) n(\mathbf{r}_1) + \sum_{j=2}^N N \sum_{s_1} \int d\mathbf{x}_2 \cdots d\mathbf{x}_N u_{/1\alpha}(\mathbf{r}_1, \mathbf{r}_j) |\Psi|^2 \\ = \frac{1}{4} \nabla_1^2 n_{/1\alpha}(\mathbf{r}_1) - 2 \sum_{\beta} \left\{ N \sum_{s_1} \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \frac{1}{2} (\Psi_{/1\alpha}^{\text{Re}} \Psi_{/1\beta}^{\text{Re}} + \Psi_{/1\alpha}^{\text{Im}} \Psi_{/1\beta}^{\text{Im}}) \right\}_{/1\beta} \\ + \sum_{j=2}^N \sum_{\beta} N \sum_{s_1} \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \left\{ \frac{1}{4} (|\Psi|^2)_{/1\alpha/j\beta} - (\Psi_{/1\alpha}^{\text{Re}} \Psi_{/j\beta}^{\text{Re}} + \Psi_{/1\alpha}^{\text{Im}} \Psi_{/j\beta}^{\text{Im}}) \right\}_{/j\beta}. \end{aligned} \quad (\text{A6})$$

The last integral on the right-hand side of Eq. (A6) vanishes after integration over $dr_{j\beta}$ (because, being a solution of the Schrödinger equation, the wave function Ψ and its derivatives vanish for $|\mathbf{r}_j| \rightarrow \infty$). The expression in the curly brackets in the other integral can be recognized as the kinetic-energy density tensor $t_{\alpha\beta}(\mathbf{r}_1)$ defined in Eq. (2.12). The term involving $u_{/1\alpha}$ can be rewritten [using the symmetry of Ψ and the definition of n_2 , Eqs. (2.8)–(2.11)] as

$$\begin{aligned} N(N-1) \sum_{s_1} \int d\mathbf{x}_2 \cdots d\mathbf{x}_N u_{/1\alpha}(\mathbf{r}_1, \mathbf{r}_2) |\Psi|^2 \\ = 2 \int d^3 r_2 u_{/1\alpha}(\mathbf{r}_1, \mathbf{r}_2) n_2(\mathbf{r}_1, \mathbf{r}_2). \end{aligned}$$

Finally, Eq. (A6) is reduced to the equation

$$\begin{aligned} v_{/\alpha}(\mathbf{r}) n(\mathbf{r}) + 2 \int d^3 r' u_{/\alpha}(\mathbf{r}, \mathbf{r}') n_2(\mathbf{r}, \mathbf{r}') \\ = \frac{1}{4} \nabla^2 n_{/\alpha}(\mathbf{r}) - 2 \sum_{\beta} t_{\alpha\beta/\beta}(\mathbf{r}), \end{aligned} \quad (\text{A7})$$

which will be termed the differential virial theorem. This is an exact, local (at space point \mathbf{r}) relation involving the external potential $v(\mathbf{r})$, the e - e interaction potential $u(\mathbf{r}, \mathbf{r}')$, the diagonal elements of the first- and second-

order DMs, $n(\mathbf{r})$ and $n_2(\mathbf{r}, \mathbf{r}')$, and the first-order DM $\rho(\mathbf{r}_1; \mathbf{r}_2)$ “close to diagonal” — see the definition (2.12) of $t_{\alpha\beta}$. When Eq. (A7) is written for the system with Coulomb potentials [i.e., definitions (2.5) and (2.6) are used] and differentiations of these potentials are performed, the equation obtained turns out to be equivalent to the balance equation between the momentum flux and the force density for the electron system, obtained by Ziesche *et al.* [20] in a quite different way.

The reason for calling Eq. (A7) the differential virial theorem is connected with the fact that the (global) virial theorem can be derived from it by applying the operation $\int d^3 r \sum_{\alpha} r_{\alpha}$ to both sides of Eq. (A7), so it gives

$$\begin{aligned} 2T &= \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \nabla v(\mathbf{r}) \\ &+ 2 \int d^3 r d^3 r' n_2(\mathbf{r}, \mathbf{r}') \mathbf{r} \cdot \nabla u(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (\text{A8})$$

[Eqs. (2.13) and (2.14) have been used]. Equation (A8) represents the virial theorem in its most general form (see, e.g., in Levy and Perdew [10]). In the case of Coulombic $u(\mathbf{r}, \mathbf{r}')$, Eq. (2.5), the second integral in Eq. (A8) can be evaluated, using the symmetry of n_2 , to be $-E_{ee}$. So, in this case, Eq. (A8) gives

$$2T + E_{ee} = \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \nabla v(\mathbf{r}), \quad (\text{A9})$$

the familiar virial theorem for a Coulombically interacting system.

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