PHYSICAL REVIEW A **75**, 032517 (2007)

Asymptotic near-nucleus structure of the electron-interaction potential in local effective potential theories

Zhixin Qian
Department of Physics, Peking University, Beijing 100871, China

Viraht Sahni
Department of Physics, Brooklyn College and the Graduate School, City University of New York, Brooklyn, New York 11210, USA

(Received 30 October 2006; published 26 March 2007)

In local effective potential theories of electronic structure, the electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and correlation-kinetic effects, are all incorporated in the local electron-interaction potential $v_{ee}(\mathbf{r})$. In previous work, it has been shown that for spherically symmetric or sphericalized systems, the asymptotic near-nucleus expansion of this potential is $v_{ee}(r)=v_{ee}(0)+\beta r+O(r^2)$, with $v_{ee}(0)$ being finite. By assuming that the Schrödinger and local effective potential theory wave functions are analytic near the nucleus of atoms, we prove the following via quantal density functional theory (QDFT): (i) Correlations due to the Pauli principle and Coulomb correlations do not contribute to the linear structure; (ii) these Pauli and Coulomb correlations contribute quadratically; (iii) the linear structure is *solely* due to correlation-kinetic effects, the contributions of these effects being determined analytically. We also derive by application of adiabatic coupling constant perturbation theory via QDFT (iv) the asymptotic near-nucleus expansion of the Hohenberg-Kohn-Sham theory exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials. These functions also approach the nucleus linearly with the linear term of $v_x(\mathbf{r})$ being *solely* due to the lowest-order correlation kinetic effects, and the linear term of $v_c(\mathbf{r})$ being due *solely* to the higher-order correlation kinetic contributions. The above conclusions are equally valid for systems of arbitrary symmetry, provided spherical averages of the properties are employed.

DOI: 10.1103/PhysRevA.75.032517 PACS number(s): 31.15.Ew, 71.15.Mb, 71.10.−w

I. INTRODUCTION

The basic idea underlying all time-independent *local* effective potential theories of electronic structure such as Hohenberg-Kohn-Sham density functional theory (HKS-DFT) [1] and quantal density functional theory (QDFT) [2], is the mapping from a system of N electrons in some external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r})=-\nabla v(\mathbf{r})$, where $v(\mathbf{r})$ is the external potential, to one of noninteracting Fermions with equivalent density $\rho(\mathbf{r})$. For example, the potential energy of the electrons in the external field of the nucleus of atoms is $v(\mathbf{r})=-Z/r$, where Z is the atomic number. The Schrödinger equation for the electrons is (in a.u.)

$$\hat{H}\Psi=(\hat{T}+\hat{V}+\hat{U})\Psi=E\Psi, \tag{1}$$

where $\hat{T}=-(1/2)\Sigma_i\nabla_i^2$, $\hat{V}=\Sigma_i v(\mathbf{r}_i)$, $\hat{U}=(1/2)\Sigma_{i\neq j}(1/|\mathbf{r}_i-\mathbf{r}_j|)$, Ψ the wave function, and E the energy. The density of the electrons is $\rho(\mathbf{r})=\langle\Psi|\hat{\rho}|\Psi\rangle$, where the Hermitian operator $\hat{\rho}=\Sigma_i\delta(\mathbf{r}_i-\mathbf{r})$. The corresponding Schrödinger equation for the model electrons (S system) is

$$\left[-\frac{1}{2}\nabla^2+v(\mathbf{r})+v_{ee}(\mathbf{r})\right]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}), \quad i=1,\ldots,N. \tag{2}$$

The S system wave function is the Slater determinant $\Phi\{\phi_i\}$, so that $\rho(\mathbf{r})=\langle\Phi|\hat{\rho}|\Phi\rangle=\Sigma_i\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$. The $v_{ee}(\mathbf{r})$ is the local electron-interaction potential in which all the many-body correlations are incorporated. The correlations are those due to the Pauli exclusion principle and Coulomb repulsion, and the correlation-kinetic effects that represent the difference in kinetic energy betweeen the interacting and noninteracting systems. The highest occupied eigenvalue ϵ_m of Eq. (2) is the negative of the removal energy whether it is the ionization potential of atoms and molecules or the work function of metals [2–4].

It is evident that any rigorous knowledge of the exact structure of the potential $v_{ee}(\mathbf{r})$, and an understanding of how the different electron correlations contribute to this structure, is critical to the accurate construction of the model system. In our previous work [5] we had shown that $v_{ee}(r)$ is finite at the nucleus for spherically symmetric system. (For more general case of arbitrary symmetry, see Ref. [6].) We assume that the asymptotic near-nucleus structure of $v_{ee}(\mathbf{r})$ for spherically symmetric systems is of the general form

$$v_{ee}(r)=v_{ee}(0)+\beta r+\gamma r^2. \tag{3}$$

In Eq. (3) and the following, $\mathbf{r}$ is defined as the electronic coordinate relative to one of the nuclei in the system. $v_{ee}(0)$ represents the value at electron-nucleus coalescence. In this paper we prove the following via QDFT: (i) There are no contributions to the linear term due to correlations arising from the Pauli exclusion principle and Coulomb repulsion; (ii) these Pauli and Coulomb correlations contribute to the quadratic term; (iii) the linear term arises *solely* due to correlation-kinetic effects, with the coefficient β being

$$\beta=\frac{4Z}{3\rho(0)}[t(0)-t_s(0)], \tag{4}$$

where $t(\mathbf{r})$ and $t_s(\mathbf{r})$ are the kinetic energy densities of the interacting and noninteracting S systems, respectively; (iv) finally, employing adiabatic coupling constant perturbation theory [7,8], we derive via QDFT the asymptotic near nucleus structure of the HKS-DFT exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials. Although the above results are derived specifically for spherically symmetric systems, they are also valid for arbitrary symmetry provided a spherical average of these properties are taken. (The results of this paper have also been obtained within the framework of HKS-DFT [9].)

To put the present work in context, we note that there had been a long standing controversy about the structure of $v_{ee}(\mathbf{r})$ at and near the nucleus of atoms. The traditional way of determining the *exact* structure of $v_{ee}(\mathbf{r})$ employs methods that assume knowledge of the true density $\rho(\mathbf{r})$. Then one determines, via numerical methods, the $v_{ee}(\mathbf{r})$ that generates the orbitals leading to this density [10]. The densities employed are those obtained from correlated or configuration-interaction type wave functions. While some work [11–13] on the helium atom showed $v_{ee}(\mathbf{r})$ to be finite at the nucleus, work by others [14,15] showed it to be singular there. This singularity is introduced by the inaccuracies in the numerical calculations, for instance, those in the density arising from the limitations of basis sets employed to solve the differential equations for the wave functions or one-particle orbitals [16]. Another key reason [6] for the singularity of $v_{ee}(\mathbf{r})$ at the nucleus is the lack of satisfaction of the electron-nucleus coalescence condition by the approximate wave function from which the density is obtained. For the determination of its structure for few electron molecular systems [17] such as H_2 and LiH, the $v_{ee}(\mathbf{r})$ is assumed to be finite at each nucleus. Additional work on light atoms, showed it to be either finite [18–20] or to diverge at the nucleus [21]. Expressions for $v_{ee}(\mathbf{r})$ at a nucleus have also been derived, but once again they are based on the assumption that [22] it is finite there. In various approximations within HKS-DFT [23–27], the $v_{ee}(\mathbf{r})$ also diverges at the nucleus [21]. With the knowledge that $v_{ee}(\mathbf{r})$ is finite at the nucleus, what remained was to understand whether the structure of $v_{ee}(\mathbf{r})$ approaches the nucleus linearly or quadratically [10–13,28]. It is the answer to this question that we provide in this work.

We begin in Sec. II by giving the key equations of time-independent QDFT. In Sec. III we provide the asymptotic near-nucleus expansion of the interacting and noninteracting system wave functions, and the corresponding expressions for the equivalent densities. The proof that Pauli and Coulomb correlations contribute quadratically and not linearly to the near-nucleus expansion of $v_{ee}(\mathbf{r})$ is given in Sec. IV. In Sec. V we prove that the contribution to the linear term of $v_{ee}(\mathbf{r})$ is solely a consequence of correlation-kinetic effects, and derive an expression for this contribution. Combining the results of the previous two sections, we present in Sec. VI the expression for the near-nucleus structure of $v_{ee}(\mathbf{r})$. Finally, by employing coupling constant perturbation theory within the framework of QDFT, we derive in Sec. VII the near-nucleus structure of the HKS-DFT exchange and correlation potentials. Concluding remarks are made in Sec. VIII.

II. BRIEF INTRODUCTION TO QDFT

In time-independent QDFT [2,29], the potential $v_{ee}(\mathbf{r})$ is the work done to move a model fermion in the force of a conservative field $\mathcal{F}^{\text{eff}}(\mathbf{r})$:

$$v_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{F}^{\text{eff}}(\mathbf{r}') \cdot d\mathbf{l}', \tag{5}$$

where $\mathcal{F}^{\text{eff}}(\mathbf{r})=\mathcal{E}_{ee}(\mathbf{r})+\mathcal{Z}_{t_c}(\mathbf{r})$. Here $\mathcal{E}_{ee}(\mathbf{r})$ is the electron-interaction field representative of the Pauli and Coulomb correlations, and $\mathcal{Z}_{t_c}(\mathbf{r})$ the correlation-kinetic field representative of those effects. For spherically symmetric systems, the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ are each conservative. Thus $v_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r})+W_{t_c}(\mathbf{r})$, where the work done $W_{ee}(\mathbf{r})$, $W_{t_c}(\mathbf{r})$ are separately path-independent. The field $\mathcal{E}_{ee}(\mathbf{r})$ is obtained via Coulomb's law from its quantal source, the pair-correlation density $g(\mathbf{r},\mathbf{r}')$, as

$$\mathcal{E}_{ee}(\mathbf{r}) = \int d\mathbf{r}' g(\mathbf{r},\mathbf{r}')\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}, \tag{6}$$

where $g(\mathbf{r},\mathbf{r}')=\langle\Psi|\Sigma_{i\neq j}\delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j-\mathbf{r}')|\Psi\rangle/\rho(\mathbf{r})$. The pair-correlation density $g(\mathbf{r},\mathbf{r}')$ may also be written as $g(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')+\rho_{xc}(\mathbf{r},\mathbf{r}')$, where $\rho_{xc}(\mathbf{r},\mathbf{r}')$, its nonlocal component is the Fermi-Coulomb hole charge distribution. The pair-correlation density $g_s(\mathbf{r},\mathbf{r}')$ of the S system may also be expressed in terms of its local and nonlocal components: $g_s(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_x(\mathbf{r},\mathbf{r}')$, where the Fermi hole charge $\rho_x(\mathbf{r},\mathbf{r}')=-|\gamma_s(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r})$, with $\gamma_s(\mathbf{r},\mathbf{r}')=\Sigma_{i\sigma}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')$ the Dirac density matrix. Defining the Coulomb hole charge $\rho_c(\mathbf{r},\mathbf{r}')=g(\mathbf{r},\mathbf{r}')-g_s(\mathbf{r},\mathbf{r}')$, the field $\mathcal{E}_{ee}(\mathbf{r})$ may then be written in terms of its components as

$$\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_H(\mathbf{r}) + \mathcal{E}_x(\mathbf{r}) + \mathcal{E}_c(\mathbf{r}), \tag{7}$$

where the quantal sources of the Hartree $\mathcal{E}_H(\mathbf{r})$, Pauli $\mathcal{E}_x(\mathbf{r})$, and Coulomb $\mathcal{E}_c(\mathbf{r})$ fields are the density $\rho(\mathbf{r})$, Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$, and Coulomb hole $\rho_c(\mathbf{r},\mathbf{r}')$, respectively. It follows that $W_{ee}(\mathbf{r})=W_H(\mathbf{r})+W_x(\mathbf{r})+W_c(\mathbf{r})$, where the Hartree $W_H(\mathbf{r})$, Pauli $W_x(\mathbf{r})$, and Coulomb $W_c(\mathbf{r})$ potentials are the work done in the respective fields. The field $\mathcal{Z}_{t_c}(\mathbf{r})$ is defined as

$$\mathcal{Z}_{t_c}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}[\mathbf{z}_s(\mathbf{r}) - \mathbf{z}(\mathbf{r})], \tag{8}$$

where $\mathbf{z}(\mathbf{r})$ is defined in terms of the single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$ as

$$z_i(\mathbf{r}) = 2\sum_j \partial t_{ij}(\mathbf{r})/\partial r_j, \tag{9}$$

with

$$t_{ij}(\mathbf{r}) = \frac{1}{4}[\partial^2/\partial r_i\partial r_j' + \partial^2/\partial r_j\partial r_i']\gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}, \tag{10}$$

the kinetic energy density tensor. The single particle density matrix is defined as

$$\gamma(\mathbf{r},\mathbf{r}') = N\sum_s \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{r}s,\mathbf{x}_2,\dots,\mathbf{x}_N) \times \Psi(\mathbf{r}'s,\mathbf{x}_2,\dots,\mathbf{x}_N). \tag{11}$$

The $\mathbf{z}_s(\mathbf{r})$ is similarly defined in terms of the Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$.

III. NEAR-NUCLEUS BEHAVIOR OF THE WAVE FUNCTIONS AND THE DENSITY

We first present the near-nucleus behavior of the wave functions for the interacting system and the noninteracting S system, and of the density. As is customary, and the case in prior work [30,31], we assume that the wave function near the nucleus is smooth. In other words, that the electronic wave function of a bound state for an atom or molecule is analytic except at the nuclear cusps. This assumption requires the stringent condition that the Hamiltonian be analytic except where two or more particles coincide, a condition that may not be mathematically rigorous. However, in mathematical physics, the assumption of smoothness of the wave function is standard practice, and we proceed by making it. Hence we write the ground state many-body wave function as

$$\Psi(\mathbf{r},\mathbf{X}) = \Psi(0,\mathbf{X}) + a(\mathbf{X})r + b(\mathbf{X})r^2 + \cdots + \sum_{m=-1}^{1} [a_{1m}(\mathbf{X})r + b_{1m}(\mathbf{X})r^2]Y_{1m}(\hat{r}) + \cdots + \sum_{m=-2}^{2} b_{2m}(\mathbf{X})r^2 Y_{2m}(\hat{r}) + \cdots, \tag{12}$$

for small r, where $\hat{r}=\mathbf{r}/r$, and $Y_{lm}(\hat{r})$ are the usual spherical harmonics. We use $\mathbf{X}$ for the coordinates $s,\mathbf{r}_2 s_2,\ldots,\mathbf{r}_N s_N$. The coefficients in the wave function satisfy the following relations:

$$a(\mathbf{X}) + Z\Psi(0,\mathbf{X}) = 0,$$

$$2b_{1m}(\mathbf{X}) + Z a_{1m}(\mathbf{X}) = 0. \tag{13}$$

The above relations originate from the cusp of the wave function at the nucleus, and were derived previously in Refs. [30,31]. The expansion of the wave function is obtained by making use of the asymptotic expansion for small r

$$\frac{1}{|\mathbf{r}-\mathbf{r}_i|} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1}\frac{r^l}{r_i^{l+1}} Y^*_{lm}(\hat{r}_i) Y_{lm}(\hat{r}), \tag{14}$$

for $i=2,\ldots,N$. The Schrödinger equation (1) may then be rewritten as

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + r\sum_{m=-1}^{1} Y_{1m}(\hat{r}) g_m(\mathbf{X})\right]\Psi(\mathbf{r},\mathbf{X}) + H^{N-1}_{Z-1}(\mathbf{X})\Psi(\mathbf{r},\mathbf{X}) = E\Psi(\mathbf{r},\mathbf{X}), \tag{15}$$

where

$$g_m(\mathbf{X}) = \frac{4\pi}{3}\sum_{i=2}^{N} \frac{1}{r_i^2} Y^*_{1m}(\hat{r}_i), \tag{16}$$

and $H^{N-1}_{Z-1}(\mathbf{X})$ is the Hamiltonian for $N-1$ electrons in an external potential of $-(Z-1)/r$. The first relation in Eq. (13) follows readily by equating the coefficients of r^{-1} terms, and the second one by equating the coefficients of $r^0 Y_{1m}(\hat{r})$ terms.

The density is defined as

$$\rho(\mathbf{r}) = N\int d\mathbf{X}|\Psi(\mathbf{r},\mathbf{X})|^2, \tag{17}$$

where $\int d\mathbf{X}$ denotes $\Sigma_s \int d\mathbf{x}_1 \ldots d\mathbf{x}_N$. Bear in mind that we are considering spherically symmetric or sphericalized systems. Employing Eq. (12) in conjunction with Eq. (13) and the relation

$$\int Y^*_{1m}(\hat{r}) Y_{1'm'}(\hat{r}) d\hat{r} = \delta_{ll'}\delta_{mm'}, \tag{18}$$

we obtain the density as

$$\rho(r) = N\int d\mathbf{X}\left(|\Psi(0,\mathbf{X})|^2(1-Zr)^2 + 2r^2\,\mathrm{Re}[\Psi^*(0,\mathbf{X})b(\mathbf{X})] + r^2\sum_{m=-1}^{1}\frac{1}{4\pi}|a_{1m}(\mathbf{X})|^2\right) + O(r^3). \tag{19}$$

Evidently

$$\rho(0) = N\int d\mathbf{X}|\Psi(0,\mathbf{X})|^2. \tag{20}$$

One then can see that the density behaves as

$$\rho(r) = (1-Zr)^2\rho(0) + r^2 2N\int d\mathbf{X}\,\mathrm{Re}[\Psi^*(0,\mathbf{X})b(\mathbf{X})] + r^2 N\int d\mathbf{X}\sum_{m=-1}^{1}\frac{1}{4\pi}|a_{1m}(\mathbf{X})|^2 + O(r^3). \tag{21}$$

Once again, with the assumption of smoothness, the orbital of the S system may be written as

$$\phi_{nlm}(\mathbf{r}) = r^l[A_{nl} + B_{nl}r + C_{nl}r^2 + D_{nl}r^3 + \cdots]Y_{lm}(\hat{r}). \tag{22}$$

Similarly the coefficients in the orbital satisfy the cusp relations:

$$B_{n0} + ZA_{n0} = 0,$$

$$2B_{n1} + ZA_{n1} = 0. \tag{23}$$

The density of the S system, which is supposed to be equivalent to that of the interacting system, is related to the orbitals as

$$\rho(\mathbf{r}) = \sum_{nlm}|\phi_{nlm}(\mathbf{r})|^2. \tag{24}$$

In the preceding summation over the one-particle states and the remaining ones in the paper, the spin summation is implicitly included. Substitution from Eq. (22) leads to

$$\rho(r) = \sum_{nlm} r^{2l}[|A_{nl}|^2 + 2\,\mathrm{Re}(A^*_{nl}B_{nl})r + |B_{nl}|^2 r^2 + 2\,\mathrm{Re}(A^*_{nl}C_{nl})r^2]|Y_{lm}(\hat{r})|^2. \tag{25}$$

Now employing Eq. (23), we obtain

$$\rho(r) = \rho(0)(1 - Zr)^2 + r^2 \frac{1}{4\pi}\left[2\sum_n \mathrm{Re}(A^*_{n0}C_{n0}) + 3\sum_n |A_{n1}|^2 \right] + O(r^3). \tag{26}$$

The fact that $\rho(r)$ is a radial function, together with Eq. (18), has also been employed to obtain Eq. (26).

IV. ELECTRON-INTERACTION FIELD $\mathcal{E}_{ee}(\mathbf{r})$ NEAR THE NUCLEUS

In this section, we show that the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ vanishes at the nucleus. This can be understood on physical grounds. The pair-correlation density, $g(\mathbf{r},\mathbf{r}')$, the quantal source of the field $\mathcal{E}_{ee}(r)$, is in general not spherically symmetric about the electron position at $\mathbf{r}$. However, for an electron at the nucleus, this charge distribution is spherically symmetric. Hence the field due to this charge as obtained by Coulomb's law, must vanish at the nucleus. This result can also be proved mathematically.

For spherically symmetric systems, the field $\mathcal{E}_{ee}(\mathbf{r})$ can only have a radial component, and can only depend upon the radial coordinate, i.e., $\mathcal{E}_{ee}(\mathbf{r}) = \hat{r}\mathcal{E}_{ee,r}(r)$. Thus by employing the identity

$$\hat{r} \cdot \boldsymbol{\nabla} = \partial/\partial r, \tag{27}$$

one has, from Eq. (6),

$$\mathcal{E}_{ee,r}(r) = -\int d\mathbf{r}' g(\mathbf{r},\mathbf{r}') \frac{\partial}{\partial r}\frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{28}$$

According to Eq. (12), obviously $g(\mathbf{r},\mathbf{r}')$ is well behaved (not divergent) at $\mathbf{r}=0$. Therefore,

$$\mathcal{E}_{ee,r}(r)\big|_{r=0} = -\frac{4\pi}{3}\int d\mathbf{r}' g(0,\mathbf{r}')\frac{1}{r'^2}\sum_{m=-1}^{1} Y_{1m}(\hat{r})Y^*_{1m}(\hat{r}') = 0. \tag{29}$$

(For open shell atoms, the central field approximation means taking the spherical average of the field. Thus, in this approximation, the field is again radial and depends only on the radial coordinate.)

Now since $\mathcal{E}_{ee}(\mathbf{r})$ is the negative gradient of the scalar potential function $W_{ee}(\mathbf{r})$, it is evident that there can be no linear term in this function. Thus there is no contribution to the linear term of $v_{ee}(r)$ due to Pauli and Coulomb correlations. These correlations contribute quadratically. As an example, see Ref. [32].

Arguments similar to those above can also be made to prove that the Pauli $\mathcal{E}_x(\mathbf{r})$ and Coulomb $\mathcal{E}_c(\mathbf{r})$ fields defined as

$$\mathcal{E}_{x,c}(\mathbf{r}) = \int d\mathbf{r}' \rho_{x,c}(\mathbf{r},\mathbf{r}')\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}, \tag{30}$$

vanish at the nucleus. [By the notation $\mathcal{E}_{x,c}(\mathbf{r})$ we mean the Pauli $\mathcal{E}_x(\mathbf{r})$ and Coulomb $\mathcal{E}_c(\mathbf{r})$ fields due to the Fermi $\rho_x(\mathbf{r},\mathbf{r}')$ and Coulomb $\rho_c(\mathbf{r},\mathbf{r}')$ holes, respectively.] Once again, for example, for the electron position at the nucleus, the Fermi and Coulomb holes are spherically symmetric about the electron. Hence the corresponding fields must vanish there. Hence these individual correlations contribute to the quadratic structure of $v_{ee}(r)$ via the work $W_x(r)$ and $W_c(r)$ [32].

The classical Hartree field which is defined as

$$\mathcal{E}_H(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}')\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}, \tag{31}$$

corresponding to the Hartree potential, $v_H(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$, also vanishes at the nucleus because the density $\rho(\mathbf{r})$ is spherically symmetric.

In conclusion, the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$, and its Hartree $\mathcal{E}_H(\mathbf{r})$, Pauli $\mathcal{E}_x(\mathbf{r})$, and Coulomb $\mathcal{E}_c(\mathbf{r})$ components all vanish at the nucleus.

V. CORRELATION-KINETIC FIELD $\mathcal{Z}_{t_c}(\mathbf{r})$ NEAR THE NUCLEUS

We shall first present the calculation for the kinetic fields of the interacting system and the S system separately in Sec. V A and Sec. V B. In Sec. V C, we present that for the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$.

The summations over the dummy Cartesian indices are assumed in this section.

A. Kinetic field z(r) of the interacting system

In order to make our presentation simpler, we rewrite Eq. (12) as

$$\Psi(\mathbf{r},\mathbf{X}) = \Psi(0,\mathbf{X})(1 - Zr) + \boldsymbol{\alpha}(\mathbf{X})\cdot\mathbf{r}(1 - Zr/2) + \beta_{ij}(\mathbf{X})r_i r_j, \tag{32}$$

where we have made use of Eq. (13). The relations between $\boldsymbol{\alpha}(\mathbf{X})$ and $a_{1m}(\mathbf{X})$, and $\beta_{ij}(\mathbf{X})$ and $b(\mathbf{X})$, $b_{2m}(\mathbf{X})$ are simply those between the Cartesian tensors and spherical tensors. By substituting Eq. (32) into Eq. (11), we have the structure of the $\gamma(\mathbf{r},\mathbf{r}')$ for small r, r' as

$$\begin{aligned}\gamma(\mathbf{r},\mathbf{r}') = {} & \rho(0)(1 - Zr)(1 - Zr') \\ & + (1 - Zr)(1 - Zr'/2)\mathbf{A}^*\cdot\mathbf{r}' \\ & + (1 - Zr')(1 - Zr/2)\mathbf{A}\cdot\mathbf{r} \\ & + E^*_{ij}(1 - Zr/2)(1 - Zr'/2)r_i r'_j \\ & + [D^*_{ij}(1 - Zr) + F^*_{lij}r_l]r'_i r'_j \\ & + [D_{ij}(1 - Zr') + F_{lij}r'_l]r_i r_j,\end{aligned} \tag{33}$$

where

$$A_i = N\int d\mathbf{X}\, \Psi(0,\mathbf{X})\alpha^*_i(\mathbf{X}), \tag{34}$$

$$E_{ij} = N\int d\mathbf{X}\, \alpha_i(\mathbf{X})\alpha^*_j(\mathbf{X}), \tag{35}$$

$$D_{ij} = N\int d\mathbf{X}\, \Psi(0,\mathbf{X})\beta^*_{ij}(\mathbf{X}), \tag{36}$$

$$F_{ijl} = N \int d\mathbf{X}\, \alpha_i(\mathbf{X}) \beta^*_{jl}(\mathbf{X}). \tag{37}$$

It is necessary to mention that the preceding expression for $\gamma(\mathbf{r},\mathbf{r}')$ is not limited to the spherically symmetric or sphericalized systems, but valid in general. For systems with central-reflection symmetry, Eq. (33) reduces to

$$\gamma(\mathbf{r},\mathbf{r}') = \rho(0)(1 - Zr)(1 - Zr') + E^*_{ij}(1 - Zr/2)(1 - Zr'/2) r_i r'_j + D^*_{ij}(1 - Zr) r'_i r'_j + D_{ij}(1 - Zr') r_i r_j. \tag{38}$$

We note that the second, third, and fourth terms on the right-hand side of the above expression are absent in the literature [31,33]. Also for completeness, we give the following relations:

$$D_{ii} = 3N \int d\mathbf{X} \Psi^*(0,\mathbf{X}) b(\mathbf{X}),$$

$$E_{ii} = 3N \int d\mathbf{X} \frac{1}{4\pi} |a_{1m}(\mathbf{X})|^2. \tag{39}$$

Correspondingly, the expression of Eq. (21) for the density can be rewritten as

$$\rho(r) = \rho(0)(1 - Zr)^2 + \frac{1}{3}(E_{ii} + 2D_{ii}) r^2 + O(r^3). \tag{40}$$

The derivatives in calculating the kinetic energy density tensor via Eq. (10) are tedious but straightforward. After performing them, we arrive at

$$t_{ij}(\mathbf{r}) = \frac{1}{2} \mathrm{Re}\Bigg[Z^2[\rho(0) + \mathbf{A}\cdot\mathbf{r}] \frac{r_i r_j}{r^2} - \frac{Z}{2r}(2 - Zr)(r_i A_j + r_j A_i) + E_{ij}(1 - Zr) - \frac{Z r_l}{2r}[r_i(E_{lj} + 4D_{lj}) + r_j(E_{li} + 4D_{li})] + 2(F_{ijl} + F_{jil}) r_l \Bigg] + O(r_i^2). \tag{41}$$

The corresponding kinetic energy density is

$$t(r) = t_{ii}(r) = \frac{1}{2}[Z^2\rho(0) + E_{ii}] - \frac{2Z}{3} r [D_{ii} + E_{ii}] + O(r^2). \tag{42}$$

The correctness of the expression for $t(r)$ is independently confirmed via its definition as

$$t(\mathbf{r}) = \frac{1}{2} N \int d\mathbf{X}\, \nabla \Psi^*(\mathbf{r},\mathbf{X}) \cdot \nabla \Psi(\mathbf{r},\mathbf{X}). \tag{43}$$

With the result for $t_{ij}(\mathbf{r})$ given in Eq. (41), one can obtain from Eq. (9) the kinetic field $\mathbf{z}(\mathbf{r})$ to be

$$\mathbf{z}(\mathbf{r}) = 2Z^2\rho(0)\frac{\mathbf{r}}{r^2} - \frac{4}{3} Z(3D_{ii} + E_{ii}) \frac{\mathbf{r}}{r} + O(r) \tag{44}$$

or

$$\mathbf{z}(\mathbf{r}) = 2Z^2\rho(0)\frac{\mathbf{r}}{r^2}(1 + 2Zr/3) - \frac{4}{3} Z[2t(0) + 3D_{ii}] \frac{\mathbf{r}}{r} + O(r), \tag{45}$$

where we have made use of the following relation derived from Eq. (42):

$$E_{ii} = 2t(0) - Z^2\rho(0). \tag{46}$$

Equation (46) can also be employed to rewrite the expression for the density in Eq. (40) as

$$\rho(r) = \rho(0)\left\{ 1 - 2Zr + \frac{2}{3\rho(0)}[Z^2\rho(0) + t(0)] r^2 \right\} + \frac{2}{3} r^2 D_{ii} + O(r^3). \tag{47}$$

This expression for the density is employed later.

B. Kinetic field $\mathbf{z}_s(\mathbf{r})$ of the S system

The kinetic energy density tensor for the S system is expressed in terms of the orbitals as

$$t_{s,ij}(\mathbf{r}) = \frac{1}{2} \mathrm{Re} \sum_{nlm} \left[\frac{\partial}{\partial r_i} \phi^*_{nlm}(\mathbf{r}) \right] \left[\frac{\partial}{\partial r_j} \phi_{nlm}(\mathbf{r}) \right]. \tag{48}$$

Substituting Eq. (22) into the above expression and making use of Eq. (23), one has

$$t_{s,ij}(\mathbf{r}) = \frac{1}{2} Z^2 \rho(0) r_i r_j / r^2 + \frac{3}{8\pi} \sum_n |A_{n1}|^2 (\delta_{ij} - Zr\delta_{ij} - Z r_i r_j / r) - 2Z \sum_n \frac{1}{4\pi} \mathrm{Re}(A^*_{n0} C_{n0}) r_i r_j / r + O(r_i^2). \tag{49}$$

The kinetic energy density for the S system correspondingly is

$$\begin{aligned} t_s(r) &= t_{s,ii}(\mathbf{r}) \\ &= \frac{1}{2} Z^2 \rho(0) - 2Zr \sum_n \frac{1}{4\pi} \mathrm{Re}\, A^*_{n0} C_{n0} \\ &\quad + \frac{1}{2}(3 - 4Zr) \sum_n \frac{3}{4\pi} |A_{n1}|^2 + O(r^2). \end{aligned} \tag{50}$$

This expression for $t_s(r)$ is independently confirmed via its definition

$$t_s(\mathbf{r}) = \frac{1}{2} \sum_{nlm} \nabla \phi^*_{nlm}(\mathbf{r}) \cdot \nabla \phi_{nlm}(\mathbf{r}). \tag{51}$$

[We note that the leading term $t_s(0)$ obtained from Eq. (50) has been obtained previously [34].]

The calculation for the kinetic field $z_{s,i}(\mathbf{r}) = 2(\partial/\partial r_j) t_{s,ij}(\mathbf{r})$ is now straightforward, which yields

$$\mathbf{z}_s(\mathbf{r}) = 2Z^2\rho(0)\frac{\mathbf{r}}{r^2} - 12Z\sum_n \frac{1}{4\pi}\mathrm{Re}(A_{n0}^* C_{n0})\frac{\mathbf{r}}{r} - 4Z\sum_n \frac{3}{4\pi}|A_{n1}|^2\frac{\mathbf{r}}{r} + O(r), \tag{52}$$

or, by the use of Eq. (50),

$$\mathbf{z}_s(\mathbf{r}) = 2Z^2\rho(0)\frac{\mathbf{r}}{r^2}(1 + 2Zr/3) - 4Z\frac{\mathbf{r}}{r}\left[\frac{2}{3}t_s(0) + 3\sum_n \frac{1}{4\pi}\mathrm{Re}(A_{n0}^* C_{n0})\right] + O(r). \tag{53}$$

Also by the use of Eq. (50), the expression of the density for the S system in Eq. (26) can be rewritten as

$$\rho(r) = \rho(0)\left\{1 - 2Zr + \frac{2}{3\rho(0)}[Z^2\rho(0) + t_s(0)]r^2\right\} + 2r^2\sum_n \frac{1}{4\pi}\mathrm{Re}(A_{n0}^* C_{n0}) + O(r^3). \tag{54}$$

This expression for the density is employed below.

C. Correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$

We now substitute Eq. (45) and Eq. (53) into Eq. (8), and arrive at

$$\mathcal{Z}_{t_c}(\mathbf{r}) = \frac{4Z}{\rho(r)}\frac{\mathbf{r}}{r}\left[\frac{2}{3}[t(0) - t_s(0)] + D_{ii} - 3\sum_n \frac{1}{4\pi}\mathrm{Re}(A_{n0}^* C_{n0})\right] + O(r). \tag{55}$$

Now the density of the S system is equal to that of the interacting system. Comparing Eq. (47) and Eq. (54) leads to

$$\frac{1}{2\pi}\sum_n \mathrm{Re}(A_{n0}^* C_{n0}) = \frac{2}{3}[t(0) - t_s(0) + D_{ii}]. \tag{56}$$

Making use of the above relation, one obtains, from Eq. (55),

$$\mathcal{Z}_{t_c}(\mathbf{r}) = \frac{4Z}{3}\frac{1}{\rho(0)}[t_s(0) - t(0)]\frac{\mathbf{r}}{r} + O(r). \tag{57}$$

In contrast to the electron interaction field $\mathcal{E}_{ee}(\mathbf{r})$, the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ is nonzero at the nucleus. For an example, see Ref. [35]. In passing, we mention Ref. [36] for a discussion of an approximate relation of the property $\int d\mathbf{r}[t_s(\mathbf{r}) - t(\mathbf{r})]$ to $\rho(0)$.

VI. BEHAVIOR OF $v_{ee}(r)$ NEAR THE NUCLEUS

Combining the results in Eqs. (29) and (57), one finally has, from Eq. (5),

$$\nabla v_{ee}(r) = \frac{4Z}{3\rho(0)}[t(0) - t_s(0)]\frac{\mathbf{r}}{r} + O(r), \tag{58}$$

which also indicates the result shown in Eqs. (3) and (4). The classical Hartree potential due to the density, $v_H(\mathbf{r})$, is usually separated out from $v_{ee}(\mathbf{r})$ and the remaining part is referred as the HKS-DFT exchange-correlation potential $v_{xc}(\mathbf{r})$. Since it is evident from the structure of the Hartree field $\mathcal{E}_H(\mathbf{r})$ that there is no linear term in the Hartree potential $v_H(r)$, Eqs. (3) and (4) imply that

$$v_{xc}(r) = v_{xc}(0) + \frac{4Z}{3\rho(0)}[t(0) - t_s(0)]r + O(r^2). \tag{59}$$

Our calculations hence show that the linear term of $v_{ee}(r)$ [or equivalently $v_{xc}(r)$] arises *solely* from the correlation-kinetic effects.

VII. BEHAVIOR OF THE HKS EXCHANGE $v_x(\mathbf{r})$ AND CORRELATION $v_c(\mathbf{r})$ POTENTIALS NEAR THE NUCLEUS

In HKS-DFT, the exchange-correlation potential $v_{xc}(\mathbf{r})$ is usually split into an exchange $v_x(\mathbf{r})$ and a correlation $v_c(\mathbf{r})$ component. These potentials have been provided a rigorous interpretation in terms of the Pauli, Coulomb, and correlation-kinetic fields via QDFT [2,8] as follows:

$$v_x(\mathbf{r}) = -\int_\infty^{\mathbf{r}} [\mathcal{E}_x(\mathbf{r}') - \mathbf{Z}_{t_c,1}(\mathbf{r}')]\cdot d\mathbf{l}', \tag{60}$$

$$v_c(\mathbf{r}) = -\int_\infty^{\mathbf{r}} [\mathcal{E}_c(\mathbf{r}') - \mathbf{Z}_{t_c,2}(\mathbf{r}') - \mathbf{Z}_{t_c,3}(\mathbf{r}') - \cdots]\cdot d\mathbf{l}', \tag{61}$$

where $\mathbf{Z}_{t_c,1}(\mathbf{r})$, and $\mathbf{Z}_{t_c,2}(\mathbf{r})$, etc., are the lowest order and higher order components, respectively, of the correlation-kinetic field $\mathbf{Z}_{t_c}(\mathbf{r})$ as obtained via the adiabatic coupling constant perturbation scheme [2,8]. Thus we see that HKS exchange potential $v_x(\mathbf{r})$ is representative not only of Pauli correlation but also of the lowest-order correlation-kinetic effects. The correlation potential $v_c(\mathbf{r})$ is representative of Coulomb correlations and higher-order correlation-kinetic effects.

At this stage, it also becomes clear that the entire derivation of this paper can be reformulated within adiabatic coupling constant perturbation scheme [7,8]. In such a scheme one has, instead of the result in Eq. (55) for $\mathcal{Z}_{t_c}(\mathbf{r})$,

$$\mathcal{Z}_{t_c}^{\lambda}(\mathbf{r}) = \frac{4Z}{3\rho(0)}[t_s(0) - t^{\lambda}(0)]\frac{\mathbf{r}}{r} + O(r), \tag{62}$$

where λ is the coupling constant. Define $t_x(\mathbf{r})$ as the first order correction to $t_s(\mathbf{r})$ in the adiabatic coupling constant perturbation scheme, and $t_c(\mathbf{r}) = [t(\mathbf{r}) - t_s(\mathbf{r})] - t_x(\mathbf{r})$, we have from Eq. (62)

$$\mathcal{Z}_{t_c,1}(\mathbf{r}) = \frac{4Z}{3\rho(0)}t_x(0)\frac{\mathbf{r}}{r} + O(r), \tag{63}$$

$$\mathcal{Z}_{t_c,2}(\mathbf{r}) + \mathcal{Z}_{t_c,3}(\mathbf{r}) + \cdots = \frac{4Z}{3\rho(0)}t_c(0)\frac{\mathbf{r}}{r} + O(r). \tag{64}$$

Thus the work done in these fields is

$$W_{t_c,1}(r) = W_{t_c,1}(0) + \frac{4Z}{3\rho(0)} t_x(0) r + O(r^2) \tag{65}$$

and

$$\begin{aligned} W_{t_c,2}(r) + W_{t_c,3}(r) + \cdots \\ = W_{t_c,2}(0) + W_{t_c,3}(0) + \cdots + \frac{4Z}{3\rho(0)} t_c(0) r + O(r^2). \end{aligned} \tag{66}$$

Since we have shown in Sec. IV that $\mathcal{E}_x(r)$ and $\mathcal{E}_c(r)$ both vanish at the nucleus, we obtain the expression for $v_x(r)$ and $v_c(r)$ near the nucleus as

$$v_{x,c}(r) = v_{x,c}(0) + \frac{4Z}{3\rho(0)} t_{x,c}(0) r + O(r^2). \tag{67}$$

Thus the $v_x(\mathbf{r})$ approaches the nucleus linearly, the term arising solely due to lowest-order correlation-kinetic effects. The $v_c(\mathbf{r})$ also approaches the nucleus linearly, the contribution to this term arising from higher-order correlation-kinetic effects.

Finally, it is worth mentioning that, as is well known, there is another definition of the kinetic energy density of the interacting and noninteracting systems [37]:

$$\tilde{t}(\mathbf{r}) = -\frac{1}{2} N \int d\mathbf{X}\, \Psi^*(\mathbf{r},\mathbf{X}) \nabla^2 \Psi(\mathbf{r},\mathbf{X}),$$

$$\tilde{t}_s(\mathbf{r}) = -\frac{1}{2} \sum_{nlm} \phi^*_{nlm}(\mathbf{r}) \nabla^2 \phi_{nlm}(\mathbf{r}). \tag{68}$$

Though $\tilde{t}(\mathbf{r})$ and $\tilde{t}_s(\mathbf{r})$ yield respectively the same total kinetic energies for finite systems as $t(\mathbf{r})$ and $t_s(\mathbf{r})$ defined in Eqs. (43) and (51), they differ from $t(\mathbf{r})$ and $t_s(\mathbf{r})$:

$$t(\mathbf{r}) = \tilde{t}(\mathbf{r}) + \frac{1}{4} \nabla^2 \rho(\mathbf{r}),$$

$$t_s(\mathbf{r}) = \tilde{t}_s(\mathbf{r}) + \frac{1}{4} \nabla^2 \rho(\mathbf{r}). \tag{69}$$

The second term on the right-hand side of the preceding relations, which are singular at the nucleus are the same for the interacting and noninteracting systems. Therefore, all the results in this paper hold equivalently in the alternative definition. For instance, one also has, in parallel to Eq. (59),

$$v_{xc}(r) = v_{xc}(0) + \frac{4Z}{3\rho(0)} [\tilde{t}(0) - \tilde{t}_s(0)] r + O(r^2). \tag{70}$$

VIII. CONCLUSIONS

In conclusion we note (i) the electron-interaction potential $v_{ee}(\mathbf{r})$ of the model electrons is finite at the nucleus. Correlations due to the Pauli exclusion principle, Coulomb repulsion, and correlation-kinetic effects *all* contribute to this value. In this paper we have proved the following via QDFT: (ii) that the function $v_{ee}(\mathbf{r})$ approaches the nucleus linearly; (iii) there are no contributions to this linear term due to Pauli and Coulomb correlations; (iv) the Pauli and Coulomb correlations, however, contribute to the quadratic term of this function; (v) the linear term in the structure of $v_{ee}(\mathbf{r})$ is solely due to correlation-kinetic effects. This contribution is determined analytically. We have also obtained by application of adiabatic coupling constant perturbation theory via QDFT (vi) the near nucleus structure of the HKS-DFT exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials. These potentials also approach the nucleus linearly: The linear term of $v_x(\mathbf{r})$ is solely due to the lowest order correlation kinetic effects; the linear term of $v_c(\mathbf{r})$ is solely due to higher-order correlation-kinetic contributions. We further note that the results in this work are valid in general whether the system is an atom, molecule or a solid.

In previous work [38], it has been shown that in the classically forbidden region of spherically symmetric systems, the contribution to the asymptotic structure of $v_{ee}(\mathbf{r})$ due to Pauli correlations is of $O(1/r)$, that of Coulomb correlations of $O(1/r^4)$, and those of correlation-kinetic effects of $O(1/r^5)$. Thus, together with the present results, the structure of $v_{ee}(\mathbf{r})$ in the asymptotic near nucleus and classically forbidden regions of such systems is now known analytically. [For the analytic asymptotic structure of $v_{ee}(\mathbf{r})$ in the classically forbidden region at the semi-infinite metal-vacuum interface, and the contribution of each type of correlation to this structure, we refer the reader to Refs. [2,39].]

Finally, the result derived also has bearing on the construction of approximate HKS-DFT electron-interaction energy functionals of the density. In numerical codes employing such approximate functionals, the structure of the corresponding $v_{ee}(\mathbf{r})$ is obtained as the functional derivative. The derivative, being dependent on the density, exhibits a sharp cusp [40] at the nucleus just as does the density. However, calculations [13,32] based on accurate wave functions show the slope of the function $v_{ee}(\mathbf{r})$ at and near the nucleus to be extremely small. Thus these approximate energy functionals ought now be modified so that their functional derivative has the correct near nucleus asymptotic structure.

We conclude by noting that the results of the paper can also be derived via the HKS-DFT [9]. However, the advantage of working within the framework of QDFT is that the near nucleus structure of $v_{ee}(\mathbf{r})$ can be understood as a function of the separate electron correlations that contribute to it.

ACKNOWLEDGMENTS

Z.Q. acknowledges support from the Chinese National Science Foundation under Grant No. 10474001. The work of V.S. was supported in part by the Research Foundation of CUNY.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] V. Sahni, *Quantal Density Functional Theory* (Springer-Verlag, Berlin, Heidelberg, 2004).

[3] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[4] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[5] Z. Qian and V. Sahni, Int. J. Quantum Chem. **79**, 205 (2000).

[6] X. Y. Pan and V. Sahni, Phys. Rev. A **67**, 012501 (2003).

[7] J. Harris and R. O. Jones, J. Phys. F: Met. Phys. **4**, 1170 (1974); D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975); O. Gunnarsson and B. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[8] M. Levy and N. H. March, Phys. Rev. A **55**, 1885 (1997); Z. Qian and V. Sahni, Int. J. Quantum Chem. **80**, 555 (2000).

[9] Z. Qian (unpublished).

[10] See, for example, K. Peirs, D. Van Neck, and M. Waroquier, Phys. Rev. A **67**, 012505 (2003), and references therein.

[11] D. W. Smith, S. Jagannathan, and G. S. Handler, Int. J. Quantum Chem., Quantum Chem. Symp. **13**, 103 (1979).

[12] E. R. Davidson, Int. J. Quantum Chem. **37**, 811 (1990).

[13] C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).

[14] C.-O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).

[15] A. C. Pedroza, Phys. Rev. A **33**, 804 (1986).

[16] For example, see S. Larsson and V. H. Smith, Jr., Phys. Rev. **178**, 137 (1969); C. Bunge, At. Data Nucl. Data Tables **18**, 293 1976; E. Yurtsever and J. Hinze, J. Chem. Phys. **69**, 3431 (1978); J. Wang, H. L. Schmider, and V. H. Smith, Jr., Phys. Rev. A **62**, 016501 (2000).

[17] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, Phys. Rev. A **52**, 1870 (1995).

[18] Q. Zhao, and R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994).

[19] R. C. Morrison and Q. Zhao, Phys. Rev. A **51**, 1980 (1995).

[20] C. Filippi, X. Gonze, and C. J. Umrigar, in *Recent Developments and Applications of Density Functional Theory*, edited by J. Seminario (Elsevier, Amsterdam, 1996).

[21] J. Chen, R. O. Esquivel, and M. J. Stott, Philos. Mag. B **69**, 1001 (1994).

[22] S. Liu, R. G. Parr, and A. Nagy, Phys. Rev. A **52**, 2645 (1995).

[23] R. Singh, L. Massa, and V. Sahni, Phys. Rev. A **60**, 4135 (1999).

[24] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

[25] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[26] J. P. Perdew, in *Electronic Structure of Solids' 91*, edited by P. Ziesche and H. Eschrig (Academic Verlag, Berlin, 1991).

[27] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[28] A. Nagy and K. D. Sen, J. Chem. Phys. **115**, 6300 (2001).

[29] A. Holas and N. H. March, Phys. Rev. A **51**, 2040 (1995); V. Sahni, Phys. Rev. A **55**, 1846 (1997).

[30] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957); E. Steiner, J. Chem. Phys. **39**, 2365 (1963); R. T. Pack and W. B. Brown, J. Chem. Phys. **45**, 556 (1966); V. A. Rassolov and D. M. Chipman, J. Chem. Phys. **104**, 9908 (1996); M. Hoffmann-Ostenhof and R. Seiler, Phys. Rev. A **23**, 21 (1981); B. R. Johnson, Phys. Rev. A **24**, 2339 (1981); X. Y. Pan and V. Sahni, J. Chem. Phys. **119**, 7083 (2003).

[31] W. A. Bingel, Z. Naturforsch. A **18a**, 1249 (1963).

[32] M. Slamet and V. Sahni, Phys. Rev. A **51**, 2815 (1995).

[33] R. F. W. Bader and P. M. Beddall, J. Chem. Phys. **56**, 3320 (1972).

[34] Zs. Janosfalvi, K. D. Sen, and A. Nagy, Phys. Lett. A **344**, 1 (2005).

[35] V. Sahni, Top. Curr. Chem. **182**, 1 (1996).

[36] S. B. Liu, R. C. Morrison, and R. G. Parr, J. Chem. Phys. **125**, 174109 (2006).

[37] L. Cohen, J. Chem. Phys. **70**, 788 (1979); **80**, 4277 (1984); P. W. Ayers, R. G. Parr, and A. Nagy, Int. J. Quantum Chem. **90**, 309 (2002).

[38] Z. Qian and V. Sahni, Phys. Rev. A **57**, 4041 (1998); Int. J. Quantum Chem. **70**, 671 (1998). See also C.-O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985); L. J. Sham, Phys. Rev. B **32**, 3876 (1985).

[39] Z. Qian and V. Sahni, Int. J. Quantum Chem. **104**, 929 (2005).

[40] See inset of Fig. 8.4 of Ref. [2].