

Exchange and correlation near the nucleus in density functional theory

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The linear term of the near-nucleus expansion of the spherically averaged exchange-correlation potential $\bar{v}_{xc}(r)$ in density functional theory (DFT) is shown to be nonzero and to arise solely from the correlation-kinetic effects. Analytical expressions for it and for those of the separate exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials are derived. The results were also obtained recently via quantal DFT, but here are obtained via ordinary Hohenberg-Kohn-Sham DFT. It is further pointed out that the linear term in $v_{xc}(\mathbf{r})$ arising mainly from $v_c(\mathbf{r})$ is rather small, and $v_{xc}(\mathbf{r})$ therefore has a nearly quadratic structure near the nucleus. Implications of the results for the construction of the Kohn-Sham system are discussed and examples are given.

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In the implementations of Hohenberg-Kohn-Sham density functional theory (HKS-DFT),¹ the so-called Kohn-Sham (KS) noninteracting system which has electron density $\rho(\mathbf{r})$ equivalent to that of the interacting system is assumed. For the ground state of an (interacting) N -electron system in an external potential $v_{ext}(\mathbf{r})$, the one-particle orbitals $\phi_n(\mathbf{r})$ ($n = 1, \dots, N$) of the corresponding KS system obey the KS equation (in a.u.)

$$[-\nabla^2/2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})]\phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r}), \quad (1)$$

with ϵ_n the eigenvalues. In Eq. (1), $v_H(\mathbf{r})$ is the classical Hartree potential, $v_H(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$, and $v_{xc}(\mathbf{r})$ is the KS exchange-correlation (xc) potential, which is the derivative of the KS exchange-correlation energy functional $E_{xc}[\rho]$ with respect to the density $\rho(\mathbf{r})$, $v_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta \rho(\mathbf{r})$.¹⁻³ $E_{xc}[\rho]$ is usually separated into two parts: the exchange $E_x^{KS}[\rho]$ and correlation $E_c^{KS}[\rho]$ energy functionals. Correspondingly, $v_{xc}(\mathbf{r})$ is split into two components: the KS exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials.¹⁻³

In practice, an approximation has to be made for the unknown $E_{xc}[\rho]$. In this respect, knowledge of the exact properties of $v_{xc}(\mathbf{r})$ is rather valuable to the construction of the KS system. In this Brief Report, it is shown that near a nucleus of an atom, molecule, or a solid,

$$\bar{v}_{xc}(r) = \bar{v}_{xc}(0) + \frac{4}{3}Z[\bar{t}(0) - \bar{t}_s(0)]\frac{r}{\rho(0)} + O(r^2). \quad (2)$$

We use $\bar{f}(r)$ to denote the spherical average of a function $f(\mathbf{r})$. Here, Z is the charge of the nucleus, and $t(\mathbf{r})$ and $t_s(\mathbf{r})$ are the kinetic-energy densities for the interacting system and the KS system, respectively. It is further shown that

$$\bar{v}_{x,c}(r) = \bar{v}_{x,c}(0) + \frac{4}{3}Z\bar{t}_{x,c}(0)\frac{r}{\rho(0)} + O(r^2). \quad (3)$$

[By the notation $\bar{v}_{x,c}(r)$ we mean $\bar{v}_x(r)$ and $\bar{v}_c(r)$, respectively.] Here, $t_x(\mathbf{r})$ is the first-order correction to $t_s(\mathbf{r})$ in the adiabatic coupling constant perturbation scheme (see later discussion and Ref. 4), $t_c(\mathbf{r}) = t_{xc}(\mathbf{r}) - t_x(\mathbf{r})$, and $t_{xc}(\mathbf{r}) = t(\mathbf{r}) - t_s(\mathbf{r})$.

The results in Eqs. (2) and (3) were also obtained in Ref. 5 via quantal density functional theory (Q-DFT).⁶ This Brief

Report shows that a corresponding analysis using ordinary HKS-DFT yields the same results, thereby providing an alternative conceptual and logical framework. We further point out that, in contrast to the conventional wisdom that the exchange potential $v_x(\mathbf{r})$ usually dominates the correlation potential $v_c(\mathbf{r})$, the linear term in $v_{xc}(\mathbf{r})$ near the nucleus arises mainly from $v_c(\mathbf{r})$. Therefore it is rather small, and consequently, $v_{xc}(\mathbf{r})$ is nearly quadratic near the nucleus. This is then illustrated with helium atom, for which a very accurate density is available. In the meantime, various local-density approximations (LDAs) are shown to overestimate the linear term of $v_x(\mathbf{r})$ and underestimate that of $v_c(\mathbf{r})$ to a large degree. Finally, in light of the present results, it is revealed that the static exchange-correlation charge density in the electrostatic interpretation of the KS xc potential⁷ diverges at the nucleus. Several results regarding near-nucleus limiting behavior of the density and the kinetic-energy density are also obtained in this Brief Report.

We start with deriving the following cusp relation for the density and the kinetic-energy density at the nucleus for the interacting system,

$$5Z\bar{\rho}''(0) + \bar{\rho}'''(0) = \frac{8}{3}Z[4Z^2\rho(0) + \bar{t}(0)], \quad (4)$$

and the corresponding one for the KS system,

$$5Z\bar{\rho}''(0) + \bar{\rho}'''(0) = \frac{8}{3}Z\left\{4Z^2\rho(0) + \bar{t}_s(0) + \frac{3}{4Z}\rho(0)[\bar{v}'_H(0) + \bar{v}'_{xc}(0)]\right\}, \quad (5)$$

where the primes denote derivatives with respect to r . Following Ref. 5, by assuming that the ground-state many-body wave function for the interacting N -electron system is smooth near the nucleus, we expand it as

$$\begin{aligned} \Psi(\mathbf{r}, \mathbf{X}) &= \Psi(0, \mathbf{X}) + a(\mathbf{X})r + b(\mathbf{X})r^2 + c(\mathbf{X})r^3 + \dots \\ &+ \sum_{m=-1}^1 [a_{1m}(\mathbf{X})r + b_{1m}(\mathbf{X})r^2]Y_{1m}(\hat{r}) + \dots \\ &+ \sum_{m=-2}^2 b_{2m}(\mathbf{X})r^2 Y_{2m}(\hat{r}) + \dots, \end{aligned} \quad (6)$$

for small r , where $\hat{r}=\mathbf{r}/r$, and \mathbf{X} denotes s, r_2s_2, \dots, r_Ns_N . By substituting the wave function into the many-body Schrödinger equation and equating the coefficients of various powers of r , we obtain the following relations:

$$\begin{aligned} a(\mathbf{X}) + Z\Psi(0, \mathbf{X}) &= 0, \\ 2b_{1m}(\mathbf{X}) + Za_{1m}(\mathbf{X}) &= 0, \end{aligned} \quad (7)$$

$$4Zb(\mathbf{X}) - Z^3\Psi(0, \mathbf{X}) + 6c(\mathbf{X}) = 0.$$

These relations originate from the electron-nucleus cusp of the wave function and were derived previously in Ref. 8. With them, one can see that the density behaves as

$$\begin{aligned} \bar{\rho}(r) &= \left[(1 - Zr)^2 + \frac{Z^3 r^3}{3} \right] \rho(0) \\ &+ 2 \left(r^2 - \frac{5Zr^3}{3} \right) N \int d\mathbf{X} \operatorname{Re}[\Psi^*(0, \mathbf{X})b(\mathbf{X})] \\ &+ (r^2 - Zr^3)N \int d\mathbf{X} \sum_{m=-1}^1 \frac{|a_{1m}(\mathbf{X})|^2}{4\pi} + O(r^4). \end{aligned} \quad (8)$$

The kinetic-energy density,

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

behaves as

$$\begin{aligned} \bar{t}(r) &= \bar{t}(0) - \frac{2}{3}Zr[2\bar{t}(0) - Z^2\rho(0)] \\ &- 2ZrN \int d\mathbf{X} \operatorname{Re}[\Psi^*(0, \mathbf{X})b(\mathbf{X})] + O(r^2), \end{aligned} \quad (9)$$

where

$$\bar{t}(0) = \frac{1}{2}Z^2\rho(0) + N \int d\mathbf{X} \sum_{m=-1}^1 \frac{3}{8\pi} |a_{1m}(\mathbf{X})|^2. \quad (10)$$

We note that the second term on the right-hand side (rhs) of the preceding expression for $\bar{t}(0)$ is absent in the literature.² Combining Eqs. (8) and (10) yields Eq. (4).

Similarly, we write $\phi_n(\mathbf{r})$ of the KS system as

$$\phi_n(\mathbf{r}) = \sum_{lm} r^l [A_{nlm} + B_{nlm}r + C_{nlm}r^2 + D_{nlm}r^3 + \dots] Y_{lm}(\hat{r}). \quad (11)$$

Substituting Eq. (11) into Eq. (1) with $v_{ext}(\mathbf{r}) = -Z/r$, one can obtain

$$\begin{aligned} B_{n00} + ZA_{n00} &= 0, \\ 2B_{n1m} + ZA_{n1m} &= 0, \\ 4ZC_{n00} - [Z^3 + \bar{v}'_H(0) + \bar{v}'_{xc}(0)]A_{n00} + 6D_{n00} &= 0. \end{aligned} \quad (12)$$

Evidently these relations similarly originate from the electron-nucleus cusp of the KS orbitals. Substituting Eq. (11) into the expression for the density of the KS system,

$\rho(\mathbf{r}) = \sum_{n=1}^N |\phi_n(\mathbf{r})|^2$, together with the relations in Eq. (12), one has

$$\begin{aligned} \bar{\rho}(r) &= \rho(0) \left\{ (1 - Zr)^2 + \frac{1}{3}[Z^3 + \bar{v}'_H(0) + \bar{v}'_{xc}(0)]r^3 \right\} \\ &+ \frac{1}{2\pi} \sum_{n=1}^N \operatorname{Re}(A_{n00}^* C_{n00}) \left(r^2 - \frac{5}{3}Zr^3 \right) \\ &+ \frac{1}{4\pi} (r^2 - Zr^3) \sum_{n=1}^N \sum_{m=-1}^1 |A_{n1m}|^2 + O(r^4). \end{aligned} \quad (13)$$

Similarly, the kinetic-energy density for the KS system, $t_s(\mathbf{r}) = \frac{1}{2} \sum_{n=1}^N \nabla \phi_n^*(\mathbf{r}) \cdot \nabla \phi_n(\mathbf{r})$, behaves as

$$\begin{aligned} \bar{t}_s(r) &= \bar{t}_s(0) - \frac{2}{3}Zr[2\bar{t}_s(0) - Z^2\rho(0)] \\ &- 2Zr \sum_{n=1}^N \frac{1}{4\pi} \operatorname{Re}[A_{n00}^* C_{n00}] + O(r^2), \end{aligned} \quad (14)$$

where

$$\bar{t}_s(0) = \frac{1}{2}Z^2\rho(0) + \frac{3}{8\pi} \sum_{n=1}^N \sum_{m=-1}^1 |A_{n1m}|^2. \quad (15)$$

Combining Eqs. (13) and (15) leads to Eq. (5). Once again, we note that the second term on the rhs of Eq. (15) for $\bar{t}_s(0)$ is absent in the literature.² It is exactly this term and the corresponding term in $\bar{t}(0)$ on the rhs of Eq. (10) that make $\bar{t}(0) \neq \bar{t}_s(0)$, a fact which is critical to the nonzero linear term of $\bar{v}_{xc}(r)$. In fact, a comparison of Eqs. (4) and (5) leads to

$$\bar{v}'_H(0) + \bar{v}'_{xc}(0) = 4Z[\bar{t}(0) - \bar{t}_s(0)]/3\rho(0), \quad (16)$$

which equivalently implies Eq. (2), since $\bar{v}'_H(0) = 0$.

Only the properties of $\bar{t}(0)$ and $\bar{t}_s(0)$ have been employed in the preceding derivation, while accuracy to the linear terms in $\bar{t}(r)$ in Eq. (9) and $\bar{t}_s(r)$ in Eq. (14) enables us to obtain an interesting cusp relation,

$$\bar{t}'_{xc}(0) = -\frac{2}{3}Z\bar{t}'_{xc}(0), \quad (17)$$

with the aid of a comparison of the respective coefficients for the r^2 and r^3 terms in Eqs. (8) and (13).

To investigate further the near-nucleus behavior of the KS exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials separately, we employ the adiabatic coupling constant perturbation scheme.⁴ In such a scheme, one has, instead of Eq. (2),

$$\bar{v}_{xc}^\lambda(r) = \bar{v}_{xc}^\lambda(0) + \frac{4}{3}Z[\bar{t}^\lambda(0) - \bar{t}_s^\lambda(0)] \frac{r}{\rho(0)} + O(r^2). \quad (18)$$

On the other hand, it has been shown that⁹

$$v_{xc}^\lambda(\mathbf{r}) = \lambda v_x(\mathbf{r}) + v_c^\lambda(\mathbf{r}), \quad (19)$$

and $v_c^\lambda(\mathbf{r})$ commences in second order of λ . By comparing Eqs. (18) and (19), one arrives at Eq. (3). In the meantime, one has

$$\bar{t}'_{x,c}(0) = -\frac{2}{3}Z\bar{t}_{x,c}(0), \quad (20)$$

in addition to Eq. (17).

It is well known that $t_x(\mathbf{r})$ integrates to zero, i.e., $T_x = \int d\mathbf{r} t_x(\mathbf{r}) = 0$. Notice that $t_x(\mathbf{r})$ is, however, not necessarily zero except for homogeneous systems. Nevertheless, this fact somewhat indicates that the linear term of $\bar{v}_{xc}(r)$ mainly arises from $\bar{v}_c(r)$, according to Eq. (3). In other words, the linear term is rather small, and $v_{xc}(\mathbf{r})$ is nearly quadratic near the nucleus. This argument might be corroborated by the fact that both the following sphericalized approximate exchange potentials approach the nucleus quadratically: (a) the Pauli correlated approximation $W_x(\mathbf{r})$ of Q-DFT,^{6,10} which is the part of the exchange potential arising purely from the Fermi hole,⁵

$$\bar{W}_x(r) = \bar{W}_x(0) + O(r^2); \quad (21)$$

(b) the Krieger-Li-Iafrate approximation¹¹ to the optimized exchange potential (OEP),¹²

$$\bar{v}_x^{KLI}(r) = \bar{v}_x^{KLI}(0) + O(r^2). \quad (22)$$

Equation (21) follows directly from the fact that the Fermi hole for an electron at the nucleus of a sphericalized system is spherically symmetric.⁵ Equation (22) can be analytically derived. (It is worth mentioning that the exact OEP, being the exact exchange-only scheme,¹² approaches the nucleus linearly according to the result of this Brief Report.) Therefore, in contrast to the common wisdom that $v_x(\mathbf{r})$ dominates $v_c(\mathbf{r})$, as is the case in most other regions, $v_c(\mathbf{r})$ plays a much more significant role in the linear term of $v_{xc}(\mathbf{r})$ near the nucleus.

A nearly exact result for the density of the helium atom is available, which makes it an excellent testing ground for various approximate energy functionals. The single occupied KS orbital for the two electrons with opposite spins is simply $\phi(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}/2$. The kinetic-energy density at the nucleus of the KS system can be readily shown, by employing this orbital, to be

$$t_s(0) = \frac{1}{2}Z^2\rho(0). \quad (23)$$

Therefore, according to Eq. (2), one has $v'_{xc}(0) = 2Z[2t(0)/\rho(0) - Z^2]/3$. Further employment of the cusp relation of Eq. (4) yields

$$v'_{xc}(0) = [5Z\rho''(0) + \rho'''(0) - 12Z^3\rho(0)]/2\rho(0), \quad (24)$$

a result obtained previously in Ref. 13. Furthermore, in this case, $v_x(r) = -v_H(r)/2$. Therefore $v_x(r)$ has no contribution to the linear order, and $v_c(r)$ makes the entire contribution to the linear term of $v_{xc}(r)$. Notice that interestingly the second term on the rhs of Eq. (15) for $t_s(0)$ is absent in Eq. (23) in this special case, since both electrons occupy the $1s$ orbital. This is, in fact, also true for three- or four-electron systems such as Li and Be atoms and their isoelectronic sequences since all electrons occupy single-particle states with $l=0$. The corresponding second term on the rhs of Eq. (10) for

TABLE I. Comparison of the exact results for $v_{x,c}(0)$ and $v'_{x,c}(0)$ and those calculated with LDAs for the helium atom. (a), (b), and (c) respectively refer to Vosko-Wilk-Nusair, Perdew-Wang, and Wigner parametrizations (Ref. 16) for the correlation energy functionals. Atomic units are used.

	$v_x(0)$	$v_c(0)$	$v'_x(0)$	$v'_c(0)$
Exact	-1.69	-0.062	0	3.8
LDA	-1.51	-0.092 (a) -0.082 (b) -0.055 (c)	2.02	0.036 (a) 0.035 (b) 0.0025 (c)

$t(0)$ is, however, nonzero, which makes the entire contribution to $v'_{xc}(0)$.

All the commonly used generalized gradient approximation (GGA) functionals suffer from spurious divergence for $v_{xc}(\mathbf{r})$ at the nucleus.^{13,14} This is also true for the later proposed GGA in Ref. 15. The divergence originates from terms in $v_{xc}(\mathbf{r})$ containing factor $\nabla^2\rho(\mathbf{r})$, which has a behavior of $O(1/r)$ at the nucleus. The LDA, on the other hand, yields reasonable result for $v_x(0)$ and $v_c(0)$ as shown in Table I for the helium atom. But, as shown in Table I, the LDA for the exchange component largely overestimates $v'_x(0)$, and the three LDAs proposed for the correlation component all hugely underestimate $v'_c(0)$, contrary to the fact revealed in this Brief Report that the correlation component plays a dominant role in the linear term of $v_{xc}(\mathbf{r})$ near the nucleus.

Finally, we take the electrostatic interpretation of the KS xc potential⁷ as another example to illustrate the possible implications of our investigation for the construction of the KS system. In this interpretation, the concept of static exchange-correlation charge density $q_{xc}(\mathbf{r})$ is introduced for the KS xc potential,

$$\nabla^2 v_{xc}(\mathbf{r}) = -4\pi q_{xc}(\mathbf{r}). \quad (25)$$

The result shown in Eq. (2) indicates that $q_{xc}(\mathbf{r})$ diverges at the nucleus,

$$\bar{q}_{xc}(r \rightarrow 0) = -\frac{2}{3\pi r} \frac{Z[\bar{t}(0) - \bar{t}_s(0)]}{\rho(0)}. \quad (26)$$

This unphysical feature reveals inherent shortcomings of the electrostatic interpretation of $v_{xc}(\mathbf{r})$. It implies that the part of $v_{xc}(\mathbf{r})$ due to the correlation-kinetic effects cannot be properly interpreted in terms of a static charge density. Furthermore, according to the result in Eq. (3), the shortcomings persist in the analogous interpretation⁷ of the exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ potentials separately, in terms of static exchange $q_x(\mathbf{r})$ and correlation $q_c(\mathbf{r})$ charge densities.

We conclude by mentioning again that the analytical results in Eqs. (2) and (3) can also be derived via the Q-DFT.⁵ In this Brief Report, we have further pointed out that the linear term in the expansion of $v_{xc}(\mathbf{r})$ arises mainly from the correlation component, and consequently, should be quite small. In other words, $v_{xc}(\mathbf{r})$ is nearly quadratic near the

nucleus. Moreover, the results have been illustrated numerically, together with those calculated in LDAs, by use of the accurate density for the helium atom. Implications of the results to the electrostatic interpretation of KS xc potential⁷ have also been discussed.

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