PHYSICAL REVIEW A VOLUME 57, NUMBER 5 MAY 1998

Analytical asymptotic structure of the correlation-kinetic component of the Kohn-Sham exchange-correlation potential in atoms

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(Received 30 June 1997)

The contribution of Pauli and Coulomb correlations to the asymptotic structure of the Kohn-Sham density-functional theory exchange-correlation potential in the classically forbidden region of atoms is well established. In this paper we derive the analytical asymptotic structure of the correlation-kinetic component of the potential to decay in this region as $8\kappa_0\chi/5r^5$, where $\kappa_0^2/2$ is the ionization potential and χ is an expectation value of the resulting ion. [S1050-2947(98)09905-3]

PACS number(s): 31.15.Ew, 03.65.−w

The Kohn-Sham [1] (KS) density-functional theory [2,3] exchange-correlation energy functional $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ of the density $\rho(\mathbf{r})$ and its functional derivative (potential) $v_{\mathrm{xc}}(\mathbf{r}) = \delta E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r})$ incorporate electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and the correlation contribution to the kinetic energy. The asymptotic structure of the potential $v_{\mathrm{xc}}(\mathbf{r})$ in the classically forbidden region of atoms and ions (and here we restrict ourselves to these systems) is of significance for properties such as the ionization potential, electron affinity, diamagnetic susceptibility, and multipole polarizabilities. The understanding of the contributions of the various correlations to this asymptotic structure also constitutes an important input to the construction [4] of approximate exchange-correlation energy functionals and potentials. Almbladh and von Barth [5] have shown via a quantum-mechanical derivation that for an N-electron atom for which the N- and $(N-1)$-electron ground states are orbitally nondegenerate, the potential

$$v_{\mathrm{xc}}(\mathbf{r}) \underset{r\to\infty}{\sim} -1/r - \alpha/2r^4,$$

where α is the dipole polarizability of the resulting ion. The leading $(-1/r)$ term is due to [6] the exchange component $v_x(\mathbf{r}) = \delta E_x^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r})$, where $E_x^{\mathrm{KS}}[\rho]$ is the KS exchange energy functional, and attributable [5–8] in this asymptotic region to Pauli correlations, i.e., correlations that arise due to the Pauli exclusion principle. [Note that the functional derivative $v_x(\mathbf{r})$ is comprised [9] of two terms, one representative of Pauli correlations and the other a part of the correlation-kinetic component. There is no explicit correlation-kinetic contribution to the exchange energy $E_x^{\mathrm{KS}}[\rho]$]. As a consequence, the correlation component $v_c(\mathbf{r}) = \delta E_c^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r})$, where $E_c^{\mathrm{KS}}[\rho]$ is the KS correlation energy functional, decays as $(-\alpha/2r^4)$. A comparison of this result with that of a classical calculation, in which the asymptotic electron is treated as a charge external to the ion, leads to the conclusion [5] that the $O(1/r^4)$ term is due to Coulomb correlations. An extension [10] of this argument shows that higher-order contributions due to Coulomb correlations will be of $O(1/r^6, 1/r^8)$, etc., and therefore of even order. However, the energy $E_c^{\mathrm{KS}}[\rho]$ and potential $v_c(\mathbf{r})$ incorporate both Coulomb as well as correlation-kinetic contributions. At present there is no *explicit* understanding of how the latter effects contribute to the asymptotic structure of the exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r})$. In this paper we derive *analytically* the *exact* asymptotic structure of the correlation-kinetic component of $v_{\mathrm{xc}}(\mathbf{r})$ in the classically forbidden region, and show it to be of $O(1/r^5)$. The result is again obtained for the case when both the N- and $(N-1)$-electron systems are orbitally nondegenerate, but it is also valid for degenerate atoms and ions in the central field approximation [11]. We perform our calculations within the framework of the rigorous physical interpretation [12–14,7] of KS density-functional theory. The interpretation [12,13] is in terms of fields which *separately* represent the quantum-mechanical electron-interaction and correlation-kinetic contributions. This description thus delineates between the Pauli-Coulomb and correlation-kinetic parts of the KS exchange-correlation energy functional and derivative, and thereby allows for the explicit determination of the correlation-kinetic component.

In the physical description [12], the correlation-kinetic energy $T_c[\rho]$ and potential $W_{t_c}(\mathbf{r})$ both arise from the correlation-kinetic field $\mathbf{Z}_{t_c}(\mathbf{r})$. Thus, the energy is written in virial form in terms of the field as

$$T_c[\rho] = \tfrac{1}{2}\int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}(\mathbf{r}), \tag{1}$$

and the potential is the work done to move an electron from infinity to its position at $\mathbf{r}$ in the force of this field:

$$W_{t_c}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathbf{Z}_{t_c}(\mathbf{r}')\cdot d\mathbf{l}'. \tag{2}$$

Note that for the systems considered, the work done is path-independent. The field $\mathbf{Z}_{t_c}(\mathbf{r})$ is defined as the difference of two fields $\mathbf{z}_s(\mathbf{r})$ and $\mathbf{z}(\mathbf{r})$ for the KS noninteracting and Schrödinger interacting systems, respectively, as

$$\mathbf{Z}_{t_c}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}[\mathbf{z}_s(\mathbf{r}) - \mathbf{z}(\mathbf{r})], \tag{3}$$

where $\mathbf{z}_s(\mathbf{r})$ and $\mathbf{z}(\mathbf{r})$ in turn are defined in terms of the corresponding noninteracting and interacting system kinetic-energy-density tensors $t^s_{\alpha\beta}(\mathbf{r};[\gamma_s])$ and $t_{\alpha\beta}(\mathbf{r};[\gamma])$, respectively. Thus, for example, the component $z_\alpha(\mathbf{r})$ of the field $\mathbf{z}(\mathbf{r})$ is

$$z_\alpha(\mathbf{r}) = 2\sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r};[\gamma]), \tag{4}$$

where

$$t_{\alpha\beta}(\mathbf{r};[\gamma]) = \frac{1}{4}\left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right)\gamma(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}, \tag{5}$$

and $\gamma(\mathbf{r},\mathbf{r}')$ is the spinless single-particle density matrix defined in terms of the N-electron wave function $\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$ (with $\mathbf{x}\equiv\mathbf{r}\sigma$, $\int d\mathbf{x}\equiv\Sigma_\sigma\int d\mathbf{r}$) as

$$\gamma(\mathbf{r},\mathbf{r}') = N\sum_\sigma \int \Psi^*(\mathbf{r}\sigma,\mathbf{x}_2,\ldots,\mathbf{x}_N) \times \Psi(\mathbf{r}'\sigma,\mathbf{x}_2,\ldots,\mathbf{x}_N)d\mathbf{x}_2,\ldots,d\mathbf{x}_N. \tag{6}$$

The KS theory noninteracting tensor $t^s_{\alpha\beta}(\mathbf{r};[\gamma_s])$ is similarly defined in terms of the idempotent Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ as

$$\gamma_s(\mathbf{r},\mathbf{r}') = \sum_i \sum_\sigma \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma), \tag{7}$$

constructed from the KS orbitals $\phi_i(\mathbf{x})$. We note [12] that the work $W_{t_c}(\mathbf{r})$ is not equivalent to the functional derivative $\delta T_c[\rho]/\delta\rho(\mathbf{r})$. [The KS energy $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ may be written [12] as $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]=E_{\mathrm{xc}}[\rho]+T_c[\rho]$, where $E_{\mathrm{xc}}[\rho]$ is the quantum-mechanical exchange-correlation energy. The derivative of $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ is then $v_{\mathrm{xc}}(\mathbf{r})=\delta E_{\mathrm{xc}}[\rho]/\delta\rho(\mathbf{r})+\delta T_c[\rho]/\delta\rho(\mathbf{r})$. This potential may also be expressed as $v_{\mathrm{xc}}(\mathbf{r}) = -\int_\infty^{\mathbf{r}}[\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}')+\mathbf{Z}_{t_c}(\mathbf{r}')]\cdot d\mathbf{l}'$, where [12] $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}) = \int d\mathbf{r}'\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3$ is the field due to the quantum-mechanical Fermi-Coulomb hole charge $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$. The field of the sum $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})+\mathbf{Z}_{t_c}(\mathbf{r})$ is conservative. For the systems considered, $v_{\mathrm{xc}}(\mathbf{r})=W_{\mathrm{xc}}(\mathbf{r})+W_{t_c}(\mathbf{r})$, where $W_{\mathrm{xc}}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}')\cdot d\mathbf{l}'$ is the work done in the field $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$.]

Although there has been recent work [15] on the asymptotic structure of the ground-state wave function $\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$ and single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$, from which the asymptotic structure of the tensor $t_{\alpha\beta}(\mathbf{r})$ could, in principle, be determined, we perform our derivation instead in terms of quasiparticle amplitudes. The asymptotic structure of these amplitudes, which are the interacting system counterparts of the single-particle orbitals of the noninteracting system, is exactly known. Thus, following Almbladh and von Barth [5] (and their notation), the reduced density matrix $\gamma(\mathbf{x},\mathbf{x}')$ is written in terms of the quasiparticle amplitudes $f_s(\mathbf{x})$ as

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}'), \tag{8}$$

where s enumerates the complete set $|N-1,s\rangle$ of eigenstates of the $(N-1)$-electron system. In the asymptotic limit when both $r,r'\to\infty$, the density matrix

$$\gamma(\mathbf{x},\mathbf{x}') = f_0(\mathbf{x})f_0^*(\mathbf{x}')\left(1+\frac{1}{r^2r'^2}\sum_{i,j}\hat{r}_i\hat{r}'_j\chi_{ij}\right), \tag{9}$$

where

$$\chi_{ij} = \left\langle N-1\left| d_j \frac{1-P}{[H-E(N-1)]^2} d_i \right| N-1\right\rangle, \tag{10}$$

i,j denote Cartesian coordinates, $\hat{r}_i$ is a component of the unit vector $\hat{\mathbf{r}}$, $\mathbf{d}=\int \mathbf{r}\delta\hat{\rho}(\mathbf{r})d\mathbf{r}$ is the dipole moment operator, $\delta\hat{\rho}(\mathbf{r})=\hat{\rho}(\mathbf{r})-\langle N-1|\hat{\rho}(\mathbf{r})|N-1\rangle$, $\hat{\rho}(\mathbf{r})=\Sigma_i\delta(\mathbf{r}-\mathbf{r}_i)$ is the density operator, and $P=|N-1\rangle\langle N-1|$ the projector onto the $(N-1)$-electron ground state. Note that the coefficient χ_{ij} is an expectation value with respect to the $(N-1)$-electron ground state. Other than that, χ_{ij} does not appear to have a physical interpretation. Since the $(N-1)$-electron system is spherically symmetric, the coefficient χ_{ij} is diagonal, $\chi_{ij}=\delta_{ij}\chi$.

Asymptotically then, the interacting system kinetic-energy-density tensor is

$$\begin{aligned} t_{\alpha\beta}(\mathbf{r};[\gamma]) &= \frac{1}{4}\sum_\sigma\left\{\frac{\partial^2}{\partial r'_\alpha\partial r''_\beta}\left[f_0(\mathbf{x}')f_0^*(\mathbf{x}'')\right.\right.\\ &\quad\left.\times\left(1+\frac{1}{r'^2r''^2}\sum_{i,j}\hat{r}'_i\hat{r}''_j\chi_{ij}\right)\right]\\ &\quad+\frac{\partial^2}{\partial r'_\beta\partial r''_\alpha}\left[f_0(\mathbf{x}')f_0^*(\mathbf{x}'')\right.\\ &\quad\left.\left.\times\left(1+\frac{1}{r'^2r''^2}\sum_{i,j}\hat{r}'_i\hat{r}''_j\chi_{ij}\right)\right]\right\}_{\mathbf{r}'=\mathbf{r}''=\mathbf{r},\sigma'=\sigma''=\sigma}. \end{aligned} \tag{11}$$

Performing the partial derivatives, we obtain after considerable algebra

$$\begin{aligned} t_{\alpha\beta}(\mathbf{r};[\gamma]) &= \frac{1}{2}\frac{r_\alpha r_\beta}{r^2}\sum_\sigma\left\{\left(\frac{\partial f_0(\mathbf{x})}{\partial r}\right)\left(\frac{\partial f_0^*(\mathbf{x})}{\partial r}\right)\left(1+\frac{\chi}{r^4}\right)\right.\\ &\quad\left.-\frac{2\chi}{r^5}\frac{\partial}{\partial r}[f_0(\mathbf{x})f_0^*(\mathbf{x})]+\frac{3\chi}{r^6}f_0(\mathbf{x})f_0^*(\mathbf{x})\right\}\\ &\quad+\frac{\chi}{2r^6}\delta_{\alpha\beta}\sum_\sigma f_0(\mathbf{x})f_0^*(\mathbf{x}). \end{aligned} \tag{12}$$

In deriving Eq. (12) we have used the fact that the asymptotic structure of $f_0(\mathbf{x})$ depends only on r [see Eq. (17) below].

For the KS noninteracting system, the asymptotic structure of both the density $\rho(\mathbf{r})$ and idempotent density-matrix $\gamma_s(\mathbf{x},\mathbf{x}')$ are governed [6] by the highest occupied KS orbital $\phi_N(\mathbf{x})$. As the densities of the interacting and noninteracting systems are the same, the asymptotic structure of $\phi_N(\mathbf{x})$ is

$$\phi_N(\mathbf{x}) = f_0(\mathbf{x})\left(1+\frac{\chi}{2r^4}\right). \tag{13}$$

Thus, the noninteracting system kinetic-energy-density tensor is

$$t^s_{\alpha\beta}(\mathbf{r};[\gamma_s]) = \frac{1}{4}\sum_{\sigma}\left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta}+\frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right) \times \phi_N(\mathbf{x}')\phi^*_N(\mathbf{x}'')\big|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r},\sigma'=\sigma''=\sigma}, \tag{14}$$

which on substitution of Eq. (13) reduces to

$$t^s_{\alpha\beta}(\mathbf{r};[\gamma_s]) = \frac{1}{2}\frac{r_\alpha r_\beta}{r^2}\sum_\sigma \left\{\left(\frac{\partial f_0(\mathbf{x})}{\partial r}\right)\left(\frac{\partial f_0^*(\mathbf{x})}{\partial r}\right) \times\left(1+\frac{\chi}{r^4}+\frac{\chi^2}{4r^8}\right)-\frac{2\chi}{r^5} \times\left(1+\frac{\chi}{2r^4}\right)\frac{\partial}{\partial r}[f_0(\mathbf{x})f_0^*(\mathbf{x})] + \frac{4\chi^2}{r^{10}}f_0(\mathbf{x})f_0^*(\mathbf{x})\right\}. \tag{15}$$

Thus on neglecting terms of $O(1/r^8)$ and higher order, we have

$$t^s_{\alpha\beta}(\mathbf{r};[\gamma_s]) - t_{\alpha\beta}(\mathbf{r};[\gamma]) = -\tfrac{1}{2}\chi\sum_\sigma\left(\frac{3r_\alpha r_\beta}{r^8}+\frac{\delta_{\alpha\beta}}{r^6}\right)f_0(\mathbf{x})f_0^*(\mathbf{x}). \tag{16}$$

Observe the similarity of the interacting and noninteracting system tensors. An important difference, however, is the term with the δ function in the expression for $t_{\alpha\beta}(\mathbf{r};[\gamma])$, which is absent in $t^s_{\alpha\beta}(\mathbf{r};[\gamma_s])$. This term contributes to the kinetic-energy-density $t(\mathbf{r}) = \Sigma_\alpha t_{\alpha\alpha}(\mathbf{r})$, and thus to the difference in kinetic energy of the two systems. Asymptotically, this difference $[t_s(\mathbf{r})-t(\mathbf{r})]$ is precisely $(-3\chi/r^6)\Sigma_\sigma f_0(\mathbf{x})f_0^*(\mathbf{x})$.

With the asymptotic structure of $f_0(\mathbf{x})$ known [5,16] to be

$$f_0(\mathbf{x}) \sim c r^\lambda e^{-\kappa_0 r}(1+A_1 r^{-1}+A_2 r^{-2}+A_3 r^{-3}+\cdots), \tag{17}$$

where $\lambda=(Z_N-N+1)/\kappa_0-1$, Z_N is the total charge of the nuclei, $\kappa_0^2/2=E(N-1)-E(N)$, and the A_i are coefficients, we have from Eqs. (3), (4), and (16) that

$$\rho(\mathbf{r})Z_{t_c,\alpha}(\mathbf{r}) = 2\sum_\beta \frac{\partial}{\partial r_\beta}[t^s_{\alpha\beta}(\mathbf{r};[\gamma_s])-t_{\alpha\beta}(\mathbf{r};[\gamma])]. \tag{18}$$

Since asymptotically $\rho(\mathbf{r})\sim\Sigma_\sigma|f_0(\mathbf{x})|^2$, we then obtain the correlation-kinetic field to decay as

$$\mathbf{Z}_{t_c}(\mathbf{r}) \underset{r\to\infty}{\sim} 8\kappa_0\chi\frac{\mathbf{r}}{r^7} \tag{19}$$

and the corresponding potential to vanish as

$$W_{t_c}(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{8\kappa_0\chi}{5r^5}. \tag{20}$$

Thus, we see that the asymptotic structure of the correlation-kinetic component of the functional derivative $v_{\mathrm{xc}}(\mathbf{r})$ decays as $O(1/r^5)$, and depends upon the ionization potential and an expectation value taken with respect to the $(N-1)$-electron system ground state. Correlation-kinetic effects in atoms are therefore *short-ranged*. Furthermore, the field and potential both vanish as positive functions [17]. Now to prove [5] that the highest occupied KS eigenvalue is minus the ionization potential requires an expansion of $v_{\mathrm{xc}}(\mathbf{r})$ only to $O(1/r^4)$. Thus, correlation-kinetic effects are of less significance than those of Pauli and Coulomb correlations for properties such as the ionization potential, electron affinity, etc., when determined from the highest occupied eigenvalue. Further, since the correlation-kinetic field and that due to the Coulomb hole are the same order of magnitude [13,18] and both are short-ranged, the corresponding correlation-kinetic $T_c[\rho]$ and Coulomb energies are about the same. These understandings, and the fact that in the classically forbidden region of atoms, correlation-kinetic effects are shorter-ranged than those of Coulomb correlations, ought now to be incorporated into approximate energy functionals and potentials.

Finally, for the atomic systems considered, it is stated in the literature [3,15,16,19] that in the limit r, $r'\to\infty$, both the interacting and noninteracting density matrices $\gamma(\mathbf{r},\mathbf{r}')$ and $\gamma_s(\mathbf{r},\mathbf{r}')$, respectively, tend in leading order to $\sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')}$. It is evident from our derivation that to obtain the difference between the interacting and noninteracting system kinetic-energy-density tensors, and hence the kinetic-energy densities and kinetic energies in this limit, the higher-order contributions to this leading term must be taken in account.

In conclusion, we have derived the exact analytical asymptotic structure of the correlation-kinetic $W_{t_c}(\mathbf{r})$ component of the KS exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r})$ to decay as $O(1/r^5)$ in the classically forbidden region of atoms. It thus vanishes more rapidly than the Coulomb correlation component. The structure of the correlation-kinetic potential is, of course, a function of the choice of external potential. Thus, for example, in the case of Hooke's atom [20], for which the external potential is harmonic, the potential $W_{t_c}(\mathbf{r})$ decays [21] asymptotically more slowly than the Coulomb correlation component. This is in contrast to the case of Coulomb external potential considered here.

This work was supported in part by a grant from the Research Foundation of the City University of New York.

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