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# Interpretation of Electron Correlation in Local-Density Approximation for Exchange

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# Brief Reports

## Interpretation of electron correlation in the local-density approximation for exchange

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We provide a new interpretation of how electron correlations are represented within the local-density approximation for exchange by deducing via Harbola-Sahni theory the corresponding pair-correlation density. The expression differs from that in the literature and contains, in addition to the uniform electron-gas result, a term proportional to the gradient of the density. Thus, the nonuniformity of the electronic density is *explicitly* incorporated in the approximation, and constitutes thereby the reason underlying its success.

The local-density approximation (LDA) for exchange and correlation of Hohenberg-Kohn-Sham[1] density-functional theory is possibly the most widely[1] used approximation scheme for the determination of the electronic structure of matter. The reason for this, other than its ease of application, is the high degree of accuracy achieved. However, what has not yet been understood is why the theory of the *uniform* electron gas on which the LDA is based leads to such accurate results for the properties of *nonuniform* electron-density systems. In this paper we show that the LDA in fact goes beyond uniform electron-gas theory in that it *explicitly* incorporates the inhomogeneity of the electronic density in its representation of electron correlations. This then is the reason underlying the success of the approximation.

The physics of electron correlation for a system of electrons in some external potential $v_{ext}(\mathbf{r})$ is described by the structure of the pair-correlation *density* $g(\mathbf{r},\mathbf{r}')$, which is the electronic density at $\mathbf{r}'$ given an electron at $\mathbf{r}$. The correlations between electrons are a consequence of the Pauli exclusion principle, Coulomb repulsion, and self-interaction. In recent work, Harbola and Sahni[2] have provided a physical interpretation whereby these electron correlations can be incorporated into a *local* potential. According to their interpretation, the local potential as well as the electron-electron interaction ($e$-$e$) potential energy both arise via Coulomb's law from the same quantum-mechanical source charge distribution, viz., the pair-correlation density. The potential is the work required to move an electron in the force field of the pair-correlation density, and the potential energy is the energy of interaction between the electronic and pair-correlation densities. The mathematical justification for the existence of a local potential representing electron correlations is provided by Hohenberg-Kohn-Sham density-functional theory. Within the framework of Kohn-Sham theory,[1] however, the relationship between the potential and the $e$-$e$ potential energy which is a universal func-

tional of the density is mathematical: the local many-body potential is the functional derivative of the energy.

In this work we deduce via Harbola-Sahni theory[2,3] an expression for the pair-correlation density $g_x^{LDA}(\mathbf{r},\mathbf{r}')$ for *nonuniform* electronic systems within the LDA for exchange ($X$) of Dirac,[1] Gaspar,[1] and Kohn and Sham.[1] The expression obtained differs from the one presently considered in the literature[1] to be the pair-correlation density in this approximation, viz., that derived for the *uniform* electron gas via a Slater determinant of plane waves assumed valid at each point of the nonuniform density. It turns out that the expression for $g_x^{LDA}(\mathbf{r},\mathbf{r}')$ contains, in addition to the uniform electron-gas result, a term proportional to the gradient of the density. Thus, the nonuniformity of the electronic system is *explicitly* incorporated in the LDAX, and the physical representation of electron correlations by the approximation far superior than previously understood to be the case. For the pair-correlation density $g_x^{LDA}(\mathbf{r},\mathbf{r}')$, we show that the local potential representing $e$-$e$ interaction in the LDAX is the work required to bring an electron from infinity to its position at $\mathbf{r}$ in the force field of this density. The $e$-$e$ potential energy in turn is the energy of interaction between the LDAX electronic density and this pair-correlation density. Now, within the LDAX, the Harbola-Sahni and Kohn-Sham theories lead[4,5] to the same many-body potential and energy. However, when the electron correlations as represented by this approximation are viewed from the perspective of Kohn-Sham theory, the inhomogeneity-term contribution to the pair-correlation density does not appear, and we explain why this is the case. Finally, by a study of the self-consistently determined structure of $g_x^{LDA}(\mathbf{r},\mathbf{r}')$ as a function of electron position, we explain the high accuracy of the $e$-$e$ potential energy of atoms as determined within this approximation.

The pair-correlation density $g(\mathbf{r},\mathbf{r}')$ is defined as

$$g(\mathbf{r},\mathbf{r}')=\left\langle \Psi \left| \sum_{i,j}{}' \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right| \Psi \right\rangle \bigg/ \left\langle \Psi \left| \sum_i \delta(\mathbf{r}-\mathbf{r}_i) \right| \Psi \right\rangle , \qquad (1)$$

where $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ is the system wave function. The numerator expectation value represents the probability of simultaneously finding electrons at $\mathbf{r}$ and $\mathbf{r}'$, and the denominator expectation is the electronic density $\rho(\mathbf{r})$. Thus, $g(\mathbf{r},\mathbf{r}')$ is the density seen at $\mathbf{r}'$ by an electron at $\mathbf{r}$. When only the correlations due to the Pauli exclusion principle are considered, and the ground-state wave function is a Slater determinant of single-particle orbitals $\phi_i(\mathbf{r})$, the pair-correlation density $g_x(\mathbf{r},\mathbf{r}')$ is obtained as

$$g_x(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_x(\mathbf{r},\mathbf{r}') , \qquad (2)$$

where $\rho_x(\mathbf{r},\mathbf{r}')=|\gamma(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r})$ is the Fermi hole charge density at $\mathbf{r}'$ for an electron at $\mathbf{r}$, and $\gamma(\mathbf{r},\mathbf{r}')=\sum_i\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')$ is the single-particle density matrix with $\gamma(\mathbf{r},\mathbf{r})=\rho(\mathbf{r})$. The pair-correlation density $g_x(\mathbf{r},\mathbf{r}')$ satisfies the constraints $g_x(\mathbf{r},\mathbf{r}')\geq 0$, $g_x(\mathbf{r},\mathbf{r})=\rho(\mathbf{r})/2$, and $\int g_x(\mathbf{r},\mathbf{r}')d\mathbf{r}'=N-1$.

With these definitions let us initially consider the expression $g_x^{(0)}(\mathbf{r},\mathbf{r}')$ for the pair-correlation density in the LDAX as derived in the literature.[1] With a Slater determinant of plane-wave states, the expectation values of Eq. (1) are first obtained, and the resulting expression then assumed valid at each point of the nonuniform density of a system. Thus, we arrive at the expression

$$g_x^{(0)}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_x^{(0)}(\mathbf{r},\mathbf{r}') , \qquad (3)$$

where

$$\rho_x^{(0)}(\mathbf{r},\mathbf{r}')=\tfrac{1}{2}\rho(\mathbf{r})[9j_1^2(x)/x^2] \qquad (4)$$

is the corresponding Fermi hole charge, with $j_1(x)$ the first-order spherical Bessel function, $x=k_FR$, $\mathbf{R}=\mathbf{r}'-\mathbf{r}$, and where $k_F(\mathbf{r})=[3\pi^2\rho(\mathbf{r})]^{1/3}$ is the local value of the Fermi momentum. The density $g_x^{(0)}(\mathbf{r},\mathbf{r}')$ satisfies the constraints of charge neutrality and value at the electron position but not that of positivity for all electron positions. It is asymmetrical about the electron except for an electron position at the nucleus. However, the Fermi hole $\rho_x^{(0)}(\mathbf{r},\mathbf{r}')$ term is spherically symmetric about the electron irrespective of its position. Thus, the contribution of the hole charge $\rho_x^{(0)}(\mathbf{r},\mathbf{r}')$ to the force field at the electron position vanishes, and the force field due to $g_x^{(0)}(\mathbf{r},\mathbf{r}')$, which is $\int d\mathbf{r}' g_x^{(0)}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3$, arises only from the term $\rho(\mathbf{r}')$ of Eq. (3). The resulting potential, which is the work done in the force field of the density $\rho(\mathbf{r}')$, is simply the Hartree potential $v_H(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. Consequently, the single-particle differential equation governing the system is that of the Hartree approximation: $[-\tfrac{1}{2}\nabla^2+v_{\text{ext}}(\mathbf{r})+v_H(\mathbf{r})]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r})$, with $\rho(\mathbf{r})=\sum_i|\phi_i(\mathbf{r})|^2$. Thus, the fact that (via Coulomb's law) $g_x^{(0)}(\mathbf{r},\mathbf{r}')$ gives rise to the Hartree potential shows that it is not the pair-correlation density in the LDAX.

There is yet another point to note at this juncture. The $e$-$e$ potential energy which is the energy of interaction between the density and the pair-correlation density is in this case given by the expression $\tfrac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}' \times \rho(\mathbf{r})g_x^{(0)}(\mathbf{r},\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. This expression is the same as

the Kohn-Sham theory expression[1] for the total potential energy in the LDAX. However, the numerical value of the potential energy is not the same as that of the Kohn-Sham LDAX scheme since the orbitals employed to determine this energy are Hartree rather than the Kohn-Sham LDAX orbitals. [This, as noted above, is because the pair-correlation density $g_x^{(0)}(\mathbf{r},\mathbf{r}')$ leads to the Hartree differential equation.] Therefore, the total ground-state energy with $g_x^{(0)}(\mathbf{r},\mathbf{r}')$ as the pair-correlation density will be an upper bound to the Kohn-Sham LDAX result.

In order to obtain the pair-correlation density $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$ in the LDAX, what is required is an expansion of $g_x(\mathbf{r},\mathbf{r}')$ of Eq. (2) in gradients of the density about the uniform electron-gas result. To obtain this expansion one requires the corresponding expansion for the single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$ whose diagonal matrix element is the density $\rho(\mathbf{r})$. In this manner the expansions for both terms of $g_x(\mathbf{r},\mathbf{r}')$ are simultaneously obtained. The expansion for $\gamma(\mathbf{r},\mathbf{r}')$ is known[1] and the pair-correlation density $g_x(\mathbf{r},\mathbf{r}')$ to lowest order in $\nabla$, which is $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$, is given as

$$g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_x^{(0)}(\mathbf{r},\mathbf{r}')+\rho_x^{(1)}(\mathbf{r},\mathbf{r}') , \qquad (5)$$

where

$$\rho_x^{(1)}(\mathbf{r},\mathbf{r}')=\tfrac{9}{4}\rho(\mathbf{r})\left[\frac{j_0(x)j_1(x)}{k_F^3}\widehat{\mathbf{R}}\cdot\nabla k_F^2\right] , \qquad (6)$$

$j_0(x)$ is the zeroth-order spherical Bessel function, and $\widehat{\mathbf{R}}=\mathbf{R}/R$. [Note that the lowest-order correction term in the expansion for the electronic density $\rho(\mathbf{r})$ is of $O(\nabla^2)$.] The pair-correlation density $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$ also satisfies the constraints of charge conservation and value at electron position but not that of positivity. The term $\rho_x^{(1)}(\mathbf{r},\mathbf{r}')$ is not spherically symmetric[5] about the electron position and gives rise[4] to a force field which is $\nabla k_F(\mathbf{r})/\pi$. The local many-body potential due to $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$, which is the work done by an electron in its force field, is then $[v_H(\mathbf{r})-k_F(\mathbf{r})/\pi]$. This expression is readily recognized as the Kohn-Sham theory LDAX potential. Thus, the system differential equation derived from the pair-correlation density $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$ via Coulomb's law and the Kohn-Sham LDAX scheme are the same. Further, the curl of the force field due to $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$ vanishes. This means that the local potential representing electron correlations in the LDAX is path independent. The $e$-$e$ potential energy, which is the interaction energy between the density $\rho(\mathbf{r})$ and the pair-correlation density $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$, is then $\tfrac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\rho(\mathbf{r})g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. However, the term $\rho_x^{(1)}(\mathbf{r},\mathbf{r}')$ does not contribute[5] to this integral so that it reduces to the Kohn-Sham theory expression with $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$ replaced by $g_x^{(0)}(\mathbf{r},\mathbf{r}')$. The important distinction to note is that in this case the potential energy is determined by the LDAX orbitals [which are generated by the density $g_x^{\text{LDA}}(\mathbf{r},\mathbf{r}')$] and not by the Hartree orbitals [that are generated by $g_x^{(0)}(\mathbf{r},\mathbf{r}')$].

We next discuss why the inhomogeneity-term contribution to the pair-correlation density does not appear in the

Kohn-Sham formulation of the LDAX. In this formulation one begins by approximating the $e$-$e$ potential-energy functional of the density by the expression for the uniform electron gas, and then assumes the expression to be valid locally at each point of the nonuniform electronic-density system. This potential energy, as noted previously, is the interaction energy between the density $\rho(\mathbf{r})$ and the pair-correlation density $g_x^{(0)}(\mathbf{r},\mathbf{r}')$. The local many-body potential is then determined as the functional derivative of the approximate potential-energy functional and this turns out to be $[v_H(\mathbf{r})-k_F(\mathbf{r})/\pi]$. This is the same result as that derived from $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ by Coulomb's law. The point to note, however, is that having begun with the assumption that the pair-correlation density is $g_x^{(0)}(\mathbf{r},\mathbf{r}')$, from which via the functional derivative the LDAX potential and subsequently the energy are then obtained, there is no mechanism within this self-consistent framework to indicate that the electron correlations represented by the inhomogeneity term $\rho_x^{(1)}(\mathbf{r},\mathbf{r}')$ are being accounted for. The fact that these additional correlations are *intrinsic* to the LDAX can only be understood when the approximation is viewed from the perspective of Coulomb's law. Of course, as is evident, the use of the pair-correlation density $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ in the Kohn-Sham scheme leads to the same expressions for the energy, potential, and eigenvalues as when $g_x^{(0)}(\mathbf{r},\mathbf{r}')$ is employed.

We next present in Fig. 1 the self-consistently determined structure of the pair-correlation density $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ for the neon atom for two representative electron positions. The cross section in the electron-nucleus ($\theta'=0$) plane is plotted, with the nucleus at the origin. For comparison the exact pair-correlation density $g_x(\mathbf{r},\mathbf{r}')$ determined via analytical Hartree-Fock wave functions[6] is also shown. We also plot the Hartree-Fock density $\rho(\mathbf{r})$ to observe the difference between it and the pair-correlation density for that electron position. The two electron positions considered are at $r=0.036$ a.u. in the high-density region, and $r=0.307$ a.u. at the intershell minimum of the radial probability density. The densities at these electron positions differ by two orders of magnitude. In the deep interior [Fig. 1(a)] and up to the radial probability density maximum of the $K$ shell, the $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ has considerable structure. For electron positions beyond this point [Fig. 1(b)] the oscillations in the structure of $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ are not observable on the scale of the figure. The significant point to note is how well $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ approximates the exact result. For electron positions beyond the intershell minimum the two are indistinguishable. This is also the case beyond the first intershell minimum for other atoms. Thus, $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$ differs from the exact pair-correlation density only over the small high-density region about the nucleus. In addition these differences are not substantial. This explains why the LDAX results for the total $e$-$e$ potential energy are so accurate. For completeness we quote in Table I the self-consistently determined[1] LDAX and Hartree-Fock theory[6] total $e$-$e$ potential energies for the noble gas atoms. Note that for neon and heavier atoms the LDAX errors are less than 1%.

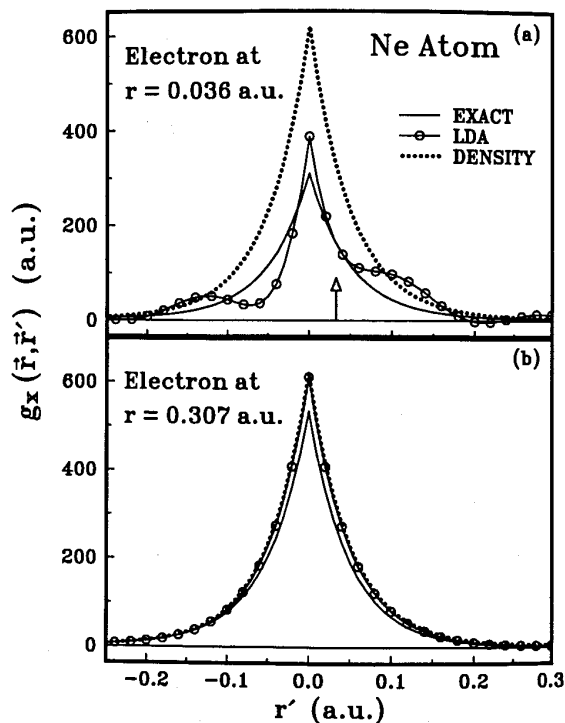In contrast to $g_x^{\mathrm{LDA}}(\mathbf{r},\mathbf{r}')$, the LDAX Fermi hole which



FIG. 1. Pair-correlation density $g_x(\mathbf{r},\mathbf{r}')$ for the neon atom as determined within the local-density approximation for exchange (LDAX) and Hartree-Fock theory (Exact). The cross section in the electron-nucleus ($\theta'=0$) plane is plotted as a function of the distance $r'$ from the nucleus for electron positions at (a) $r=0.036$ a.u. and (b) $r=0.307$ a.u. The Hartree-Fock theory electronic density is also plotted.

is[5] $[\rho_x^{(0)}(\mathbf{r},\mathbf{r}')+\rho_x^{(1)}(\mathbf{r},\mathbf{r}')]$ differs from the exact hole for all electron positions. Furthermore, the difference between these Fermi holes is more significant.[5] As a result the percent errors in the self-consistently determined LDAX exchange energies (see Table I) are an order of magnitude greater. This degree of accuracy of the LDAX exchange energy can also be explained[1,7] by the fact that it is the spherical average of the Fermi hole that contributes to the exchange energy, and in the interior of

TABLE I. The total electron-electron potential energy of noble gas atoms in atomic units as determined self-consistently within the local-density approximation for exchange (LDAX) and in Hartree-Fock (HF) theory together with the LDAX percent error. The numbers in parentheses are the percent errors in the results for the corresponding LDAX exchange energies.

| Atom | LDAX[a] | HF[b] | % Error |
|------|---------|-------|---------|
| He | 1.1212 | 1.0258 | 9.30 (16.86) |
| Be | 4.7783 | 4.4892 | 6.44 (14.59) |
| Ne | 54.539 | 54.039 | 0.93 (9.67) |
| Ar | 203.17 | 201.42 | 0.87 (7.98) |
| Kr | 1081.9 | 1078.5 | 0.32 (5.73) |
| Xe | 2708.4 | 2700.9 | 0.28 (4.83) |
| Rn | 8257.6 | 8244.0 | 0.16 (3.79) |

[a]See Ref. 1.
[b]See Ref. 6.

atoms this average is reasonably accurate.

In conclusion, we have provided via Harbola-Sahni theory an insight into how electron correlations are described within the local-density approximation for exchange (LDAX). The current interpretation of the approximation is that each point of the interacting nonuniform electron gas is homogeneous but with a density corresponding to the local value at that point. However, the new description shows the approximation to be far more physically realistic because it explicitly incorporates the inhomogeneity of the density into its representation of electron correlations. Thus, we now understand the physical reason why the LDAX scheme leads to accurate e-e potential and total ground-state energies. Finally, we note that as a consequence of our interpretation, the criti-

cism of the LDAX which questions the validity of employing expressions derived from a Slater determinant of plane waves in regions where the potential is varying and in the classically forbidden region where the wave function is exponential, is no longer justified. It is evident that the wave function which gives rise to the LDAX pair-correlation density $g_x^{LDA}(\mathbf{r},\mathbf{r}')$ does in fact incorporate to a significant degree the physics apropos to these regions.

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