Electronic structure without exchange?

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The correlation holes for densities of equal and opposite spin around a test electron are determined from the Schrödinger equation with proper boundary conditions. The traditional "exchange" term follows from the boundary condition which respects a spacial exclusion principle for equal spins. The resulting potential compares reasonably well with standard local density potentials and should simplify extensions towards non-local effects.

The Pauli principle excludes multiple occupancy of spin orbitals. When the wave function is a Slater determinant, it gives rise to the concept of exchange, i.e. when two electron indicies in the Coulomb integral are exchanged there will be a perfect annulation of the direct Coulomb term for multiple occupancy [1]. An exchange hole is created around a certain electron, excluding other electrons of the same spin to come too close. When applied to free electron wave functions, this exchange hole has a well-known form, and the resulting exchange potential is in the Hartree-Fock-Slater approximation (HFS) applied to atoms, molecules and solids, which in general are not free electron like. In this way it is possible to reduce the difficult N-body problem to a 1-particle like Schrödinger equation:

\[-\nabla^2\Psi_i(r) + (V_{\text{ext}}(r) + \int \frac{\rho(r')}{|r-r'|} d^3r' + \mu_{\text{xc}}(r))\Psi_i(r) = \epsilon_i\Psi_i(r)\]

where $\Psi_i(r)$ is the wave function for electron state $i$ with energy $\epsilon_i$, and $\rho(r)$ is the electron density. The external potential $V_{\text{ext}}(r)$ is the attractive potential due to all nuclear charges and the exchange-correlation potential is reduced in a local form, $\mu_{\text{xc}}(r)$. The density functional (DF) theory in the local density approximation (LDA) showed that this is correct in variational calculations with the electron density as a variable [1]. The exchange hole still serves as a valid pair correlation function between two electrons of the same spin, but the resulting exchange potential is in the LDA Kohn-Sham (KS) potential 2/3 of that in HFS. Correlation is an additional effect that stems from the fact that all electrons repel each other, so that due to the correlated movement of the electrons there will be a reduced Coulomb term in the in the DF-type Schrödinger equation for a one-particle potential [2]. Similarly as the exchange hole for equal spin, there will be a correlation hole also for opposite spin electron density around an electron, but it is much less profound than the exchange hole especially at high density. Whereas the exchange hole goes to zero at the position of the given electron and totally must contain one electron (meaning that Coulomb repulsion must exclude one electronic charge), the correlation hole integrates up to zero, i.e. it represents just a redistribution of charge around a given electron. Furthermore there is no condition for its amplitude at the site of the first electron. The LDA formalism is applied including the corrections due to correlation and spin-polarization, and it has proven to be very successful in electronic structure calculations [1]. More recent corrections due to weak variations of the density, such as in the generalized gradient approximation (GGA) have improved some results of LDA without making the method more difficult [1].

In this work we propose a different derivation of the DF-type potential for exchange and correlation than what is done in HFS and DF theories. The correlation part between electrons of opposite spin has been presented previously in ref. [1]. Here we adapt the formalism to densities of equal spin, i.e. for the dominating part of the potential which is denoted exchange. The term "exchange" is no longer appropriate, since as we shall see there is only correlation due to Coulomb repulsion between electrons. But there is an important boundary condition which modifies completely the correlation hole for equal or opposite spin. However, the term "exchange" is so common that we in the following continue to use it for the interaction between electrons of equal spin. The goal is to generalize the method for non-constant densities as in real atoms and solids, but in this work we consider free-electron conditions of constant density.

The electron gas parameter $r_s$ determines the average radius around a given electron of density $\rho$, $4\pi/3r_s^3\rho = 1$. An electron at some point will on the average have another electron $\sim r_s$ away from it, so the Coulomb repulsion is of the order $1/r_s$ when using atomic units. The density in a solid is large near to the atoms and $r_s$ is small and rarely larger than 2 a.u., i.e. always smaller than the atomic radius. In the near neighborhood of an electron, which
is fixed at some position \( r = 0 \), other electrons will feel a large repulsive Coulomb potential due to the fixed electron. The amplitude of this potential will even be larger than the mean-field crystal potential that determines the crystal wave function \( \Psi_i(r) \) in eq \[3\]. \( \Psi_i(r) \) will not be a good description for the wave function of other electrons near the one fixed at \( r = 0 \). This is even more so for electrons of equal spin, where a second electron cannot be at the origin. Therefore, in order to determine the exchange and correlation potential one must consider that \( \Psi_i(r) \) is deformed by the Coulomb interaction and the boundary condition for equal spin, around the single electron that we temporarily fix at a local origin. This happens for all surrounding electrons, independent of which shell they belong to, when the Coulomb repulsion exceeds the value of the crystal potential at the local origin. For equal spin, this is even more certain, since the boundary condition for \( r=0 \) apply to all electrons independent of their relative differences in kinetic energy.

First, for electrons of opposite spin and total density \( \rho/2 \) (no spin-polarization) the redistributed charge density can be determined from a Schrödinger equation of type

\[
-\nabla^2 \phi(r) + \left( g/r + \int \frac{\rho(r')}{|r-r'|} d^3 r' + \mu_{xc}(r) \right) \phi(r) = \epsilon \phi(r) \tag{2}
\]

with the boundary condition that the density \( \phi(r)^2 \) should tend to \( \rho/2 \) at the limit of the correlation hole (at \( r = r_s \) or so) \[5\]. In eq. \[3\], \( g \) is the effective interaction strength and the following two potential terms are due to the possible Coulomb exchange-correlation interaction among more than one electron within the correlation hole. (It is not necessary to limit the problem to two electrons, one at \( r = 0 \) and the other around it). Further in eq. \[4\] the effective mass is 1/2. The lowest energy \( \epsilon \) is for \( \phi(r) \) being an s-state, i.e. \( \ell = 0 \).

Secondly, for electrons of the same spin as the one at the center, one can solve a similar type of equation. However, we need to recall the Pauli principle a second time: Two electrons of the same spin cannot be in the same state, and in particular at a given instant they cannot be at the same place. This puts a boundary condition on the wave function \( \varphi(r) \) for electrons of the same spin; \( \varphi(0)=0 \), and it implies solutions of \( \ell \geq 1 \). Furthermore, the electron at the center is unique and cannot be contained in the surrounding cloud,

\[
\int (\varphi(r)^2 - \rho/2) d^3 r = 1 \tag{3}
\]

Since correlation is allowed even between electrons of the same spin, it is possible that \( \varphi(r)^2 \) could be larger than \( \rho/2 \) for some points far from 0, but at the limit of the exchange hole \( \varphi(r)^2 \) should tend \( \rho/2 \) as in case of correlation only. In principle, this requires a continous matching of both the amplitude and the derivative, but in this work only one continuity condition is applied. The equation for \( \varphi \) becomes:

\[
-\nabla^2 \varphi(r) + \left( g/r + \ell(\ell + 1)/r^2 + \int \frac{\rho(r')}{|r-r'|} d^3 r' + \mu_{xc}(r) \right) \varphi(r) = \epsilon \varphi(r) \tag{4}
\]

with \( \ell=1 \) for the lowest energy. The influence of the coupling strength \( g \) is strong on \( \phi(r) \), but only minor on \( \varphi(r) \). The DF value for the xc-energy is

\[
\varepsilon = 0.5 \int \int (\varphi_g(r) - \rho/2)/rd^3 rdg \tag{5}
\]

and

\[
\varepsilon = 0.5 \int \int (\phi_g(r) - \rho/2)/rd^3 rdg \tag{6}
\]

for equal and opposite spin, respectively. The integration over the coupling strength is from 0 to 1, and the potential is found from \[4\]

\[
\mu = \frac{d}{d\rho}(\rho \varepsilon) \tag{7}
\]
These equations are solved for different densities, but some technical points are to be noted. The boundary condition for \( \varphi(r_c) \) is that the derivative at \( r_c \) is zero, where \( 4\pi/3r_c^3\rho = 4 \). This makes approximately \( \varphi^2(r_c) = \rho/2 \). Smaller \( r_c \) gives a very similar \( \mu \)-potential, but the discontinuity at the hole boundary is evident. The same \( r_c \) is used for the correlation between opposite spins with the boundary condition \( \phi^2(r_c) = \rho/2 \). \( \phi(r) \) has one maximum (larger than \( \rho \)) before \( r = r_c \), while \( \varphi(r) \) is an ever increasing function. The results for the coupling strength \( g=1/2 \) are very close to those with the integrated values from 0 to 1. Finally, we ignore the coupling between the two spin densities since it turns out to have a quite small effect on the result (even ignoring terms 3 and 4 in eqs. 2 and 4 give almost the same result).

The high density solution for equal spin \( \varphi(r) \) with \( g=0 \), gives a potential value which is about 12 % larger than the KS-value. The reason for this is probably connected with the imposed cut-off radius. The Slater function \( j_\ell \), which defines the hole in KS-theory, has Friedel-like oscillations outside its first node. A simple exercise will motivate that the present scheme should give the KS-value for interaction \( g=0 \), if the solutions for large \( r \) are retained. For very large \( r \) it is simpler to handle solutions going to zero than solutions which are approaching the electron density. Therefore we search the solutions \( j(r) \) for a fictive positive charge that cancels exactly one electron, and which equals the electron density at \( r=0 \). Instead of eq. 2 we have

\[
-\nabla^2 j(r) + \ell(\ell + 1)/r^2 j(r) = \epsilon j(r)
\]  

when no interaction within the electron cloud is considered. This is the \( V=0 \) central potential problem with the known solutions, the Bessel functions \( j_\ell(\sqrt{\epsilon}r) \). The solution \( j_0 \) fulfills the condition at \( r=0 \), but it is not normalizable over all space. Linear combinations with higher-\( \ell \) functions fulfill the condition at \( r=0 \), but \( (j_0 + j_1) \) is not normalizable either. The low-\( \ell \) combination which fulfills the two conditions is \( (j_0 + j_2) \). The square of this solution is precisely the Slater function, normalized to one electron:

\[
\int_0^\infty (j_0 + j_2)^2 d^3r = 1
\]  

At the first node of \( (j_0 + j_2) \) the normalization is about 0.8, and the potential is about 95 % of its full value, the KS-value. Verification by numerical solutions will be difficult because of the requirement of normalization over all space. But at the same time it would be incorrect to impose a cut-off at the first node, as it will localize the hole too much. Instead we can return to the solutions for the electron density \( (\varphi^2(r) \) instead of the fictive positive density) and extend the solution beyond the first maximum. By letting the interacting density reach the non-interacting density at \( r_c \), and normalizing to unity at a larger radius, one finds that some fraction of the hole is beyond the maximum at \( r_c \), similar to (but still more localized than) the Slater function. This procedure is used with the coupling \( g \), although it is no longer required that \( \varphi^2 \equiv \rho/2 \) at some point, because of the Coulomb repulsion. One can summarize the final results in terms of powers of the density,

\[
\mu = 2.1\rho^{1/3} + 0.07\rho^{1/6}(\text{Ryd})
\]  

where the major part of the second term is the part from different spin. The first part is still a little larger (6 %) than the KS-value for exchange, 1.961\( \rho^{1/3} \) (Ryd). The effective parameter \( (\alpha) \) in front of the \( \rho^{1/3} \)-term is shown in fig 1, together with two commonly used LDA potentials.

In the case of spin polarization, it is possible to solve the equations above for two different densities. Due to the Hartree and \( \mu_{xc} \) terms in eqns. 3 and 4, there is a coupling between the two densities, which diminish the tendency for polarization. However, this interaction will also complicate the search for self-consistent solutions, and approximate results can be obtained rather quickly by omitting the two terms completely. The preliminary results give a slightly larger tendency for polarization than standard spin-polarized versions of LDA.

The resulting potential is close to, but not better than LDA. However, the results are sufficiently promising to continue the search for improved solutions at large \( r \) and for non-locality. Apart from the problem at large \( r \) the formalism contains no free parameters or other ad-hoc assumptions. Further, the present formalism helps to understand one
difference between HF and DF approaches. The exchange in HF acts selectively between orbitals, so the exchange between core and valence appears different from within valence states, for example. In LDA all electrons have the same status independent of the electronic shell, since the density is made up by all electrons, core and valence. (However, in practise HF and LDA results may come out not too different after convergence.) From the way we look at the electron interactions in the present method, it is natural that all electrons should be equal because of the boundary condition at \( r=0 \). Equal spin electrons have zero probability to be at the same place, and this is independent of the energy of their atomic orbital. For opposite spin electrons the probability is not zero but significantly reduced, because the Coulomb repulsion is strong and will separate the electrons, independently of their kinetic energy. Selective shell dependent interactions like a self-interaction correction, is not a natural extension of the present approach. Also methods which assign a strong orbital dependent parameter like a Hubbard parameter to some of the electrons, are difficult to understand, because the electron cannot distinguish between the interaction to a special orbital from the rest of the electron density. However, all this reasoning has to be revised if the interaction length \( (r_c \text{ roughly}) \), becomes large in comparison to the size of an atom. A large part of the core density may exist as a "bump" within the radius \( r_c \), and corrections due to non-locality will be important. Therefore it is essential to correct the LDA as in GGA \[5\] or for even stronger non-constant density corrections, especially for f-electron systems where self-interaction or Hubbard models give different results than LDA.

In conclusion, the most important result is that the hole for equal spins has similar shape as the exchange hole for free electrons. As a cut-off radius is imposed, it will be slightly more localized and give a slightly stronger potential than the exchange hole which has small oscillations far away. The zero amplitude at the origin is the result of a boundary condition, and it is the rigidity of the Schrödinger equation which determines the shape of the exchange hole for equal spins. Further development of the long-range tails of the hole is necessary before applications, and generalization for non-constant density will be of great interest.

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FIG. 1. The prefactor $\alpha$ which determines the density potential according to $\mu_{xc} = \alpha \rho^{1/3}$. The broken and dotted lines are from refs. [4] and [3], respectively.