Slow long-range decay of bound Hartree-Fock orbitals and enhancement of the exchange interaction and tunneling

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Exchange interaction strongly influences the long-range behaviour of localised electron orbitals. It violates the oscillation theorem (creates extra nodes) and produces a power-law decay instead of the usual exponential decrease at large distances. For inner orbitals inside molecules decay is \( r^{-v} \), for macroscopic systems \( \cos (k_f r) r^{-v} \), where \( k_f \) is the Fermi momentum and \( v = 3 \) for 1D, 3.5 for 2D and 4 for 3D crystal. Slow decay increases the exchange interaction between localised spins and the under-barrier tunneling amplitude. The under-barrier transmission coefficients in solids (e.g. for point contacts) become temperature-dependent.

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I. INTRODUCTION

The Hartree-Fock equation for an electron orbital \( \Psi(r) \) in an atom, molecule or solid has the following form:

\[
- \frac{\hbar^2}{2m} \frac{d^2}{dr^2} \Psi(r) + (U(r) - E) \Psi(r) = K(r) \tag{1}
\]

where

\[
K(r) = \sum_{q} \Psi_q(r) \int \Psi_q(r') \frac{e^2}{|r - r'|} \Psi(r') dr' \tag{2}
\]

Here the summation runs over all electron orbitals \( \Psi_q(r) \) with the same spin projection as \( \Psi(r) \). Now consider, for example, an inner electron atomic orbital 1s. The solution of the Schrödinger equation in potential \( U(r) \) has a very small range \( a_B/Z \) where \( Z \) is the nuclear charge. Outside this range the orbital decreases exponentially as \( \exp(-r/a_B) \). In the Hartree-Fock equation \( \Psi_1(r) = \psi_1(r) \) such rapid decay is impossible. Indeed, if \( \Psi_1(r) \sim \exp(-r/Z/a_B) \) the left-hand-side of eq. \( \Psi_1 \) would be exponentially small while the right-hand-side is still large since \( K(r) \) in eq. \( \Psi_1 \) contains higher orbitals \( \Psi_q(r) \) which have larger range. The behaviour of the inner Hartree-Fock orbitals inside atoms have been studied analytically (in the semiclassical approximation) and numerically (in the semiclassical approximation) and numerically in Ref. \( \Psi_1 \). The dependence on the radius \( r \) can be found from the multipole expansion of \( 1/(r - r') \) in \( K(r) \); the slowest decay normally comes from the dipole term \( \sim r'/(r^2) \) and/or last occupied orbital \( \Psi_q(r) \), \( K \sim \Psi_q(r)/r^2 \). The extra nodes appear since the orbitals \( \Psi_q(r) \) oscillate. For example, the 1s orbital in Cs atom has 3 nodes \( \Psi_1 \) (without the exchange term a ground state has no nodes). The existence of extra nodes in solutions of Hartree-Fock equations was also mentioned in the book \( \Psi_1 \). Outside the atom all orbitals decay with exponential factor for an external electron \( \Psi_1 \).

Inside solids there are electrons in the conducting band which occupy the whole crystal. It has been pointed out in Ref. \( \Psi_1 \) that this leads to a long oscillating tail of bound electron orbitals. The effect of the exchange interaction \( K(r) \) has been estimated in the free band electron approximation \( \Psi_q(r) = \exp(iq \cdot r) \). An orbital of a bound electron decreases at large distances as

\[
\Psi(r) \sim \cos (k_f r)/r^4 \tag{3}
\]

where \( k_f \) is the Fermi momentum.

The derivation of this expression assumes the presence of a partly filled conducting electron band. However, in atoms and molecules of any length the exchange enhancement of the inner orbital tail may be mediated by a complete electron shell. The question is: can the exchange enhancement in solids be mediated by a nonconducting electron band? A special interest in this problem may be motivated by spintronics and solid state quantum computers based on spin qubits. The long-range tail of the wave function could, in principle, lead to an enhancement of the exchange spin-spin interaction between the distant localised spins, and enhancement of the under-barrier tunneling amplitude.

A special feature of the “long-tail” mechanism is that the state of the band electrons does not change, i.e. there is no need to have polarization of the conducting band by the localised spin. The mediating band electrons produce the mean exchange field \( K(r) \) in eq. \( \Psi_1 \) only. Therefore, this “long-tail” effect is different from other effects like the RKKI interaction \( \Psi_1 \) and the double exchange spin-spin interaction suggested by Zener \( \Psi_1 \) (see also Refs. \( \Psi_1 \) and description of Anderson and Kondo problems , e.g., in the book \( \Psi_1 \)).

To investigate this problem in the present paper we perform calculation of the tail using the Bloch waves and tight-binding band electron wave functions.

II. ATOM

Let us first explain how the long tail appears in atoms \( \Psi_1 \). The radial equation for a Hartree-Fock electronic orbital \( \xi_i(r) = \tau \psi_i(r) \) is

\[
[- \frac{\hbar^2}{2m} \frac{d^2}{dr^2} + (U_{eff} - E_i)]\xi_i(r) = K_i(r) \tag{4}
\]
\[ U_{\text{eff}} = U + \frac{\hbar^2 l(l+1)}{2m r^2}. \] (5)

The radial exchange term can be obtained using the multipole expansion of \(1/|\mathbf{r} - \mathbf{r}'| \). Outside the radius of an inner orbital \( \xi \) (e.g. in the area \( r > a_B/Z \) for 1s)

\[ K_i(r) = \sum_{k, n} C_{nk} b_{nk} \frac{\xi_n(r)}{r^{k+1}}. \] (6)

Here \( C_{nk} \) are the standard angular momentum dependent coefficients and \( b_{nk} = \int r^k \xi_n(r) \xi(r) dr \). For the multipolarity \( k = 0 \) the integral \( b_{nk} = 0 \) due to the orthogonality of radial wave functions with the same angular momentum.

Now we can discuss the large distance behaviour of the orbital \( \xi_i(r) \). We will use 1s orbital in Xe atom (\( Z = 54 \)) as an example. The last occupied shells are \( 5s^25p^6 \). The orbital 5s does not contribute to \( K_i(r) \) since in this case the multipolarity of the exchange integral is \( k = 0 \) and the orthogonality condition makes \( b_{nk} = 0 \). The exchange integral 1s5p is \( k = 1 \), therefore, \( r \sim a_B \) and outside the atom \( K_i(\mathbf{r}) \approx C_{5p,1} b_{5p,1} \xi_5(r)/r^2 \).

The solution of Eq. (4) may be presented as

\[ \xi_i(r) = \xi_{i,\text{free}}(r) + \xi_{i,\text{ind}}(r) \] (7)

\[ \xi_{i,\text{ind}}(r) = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + (U_{\text{eff}} - E_i)\right]^{-1} K_i(r) \] (8)

Outside the radius of the inner orbital \( (r > a_B/Z \) for 1s) the energy \( E_i \) is much larger than other terms in the denominator of Eq. (8) which are of the order of \( E_n \) (since the operator in the denominator acts on \( \xi_n \)). In our example the energy of 1s is \( |E_i| = Z^2 \times 13.6 \text{ eV} \approx 4 \times 10^4 \) eV while the 5p energy is \( |E_n| \approx 10 \) eV. Therefore, we can approximately write

\[ \xi_{i,\text{ind}}(r) \approx \frac{K_i(r)}{U_{\text{eff}} - E_i} + \frac{\hbar^2}{2m(U_{\text{eff}} - E_i)} \frac{d^2}{dr^2} K_i(r) + \cdots \] (9)

The free solution in this area may be described by the semiclassical (WKB) approximation, \( \xi_{i,\text{free}}(r) \sim |p|^{-1/2} \exp(-\int |p|dr/h) \); it has the usual range \( a_B/Z = 0.02a_B \) for 1s. Comparison with the numerical solution of the Hartree-Fock equation for 1s orbital has shown that within \( \sim 1\% \) accuracy it is enough to keep the first two terms in the expansion Eq. (9) beyond the classical turning point, and only one term at \( r > 10a_B/Z \). Similar results have been obtained for the Dirac-Hartree-Fock orbitals which include the spin-orbit interaction and other single-particle relativistic corrections [1]. Thus we see that at large distances \( \xi_{1s}(r) \approx \text{const} \xi_{5p}(r)/r^2 \).

### III. 1D, 2D AND 3D SYSTEMS

If we consider a molecule instead of atom, inner electron orbital will behave the same way, \( \xi_{\text{inner}}(r) \approx \text{const} \xi_{\text{valence}}(r)/r^2 \). In macroscopic systems there is a large number of electrons occupying the valence band and the contribution of different valence electrons interfere in the exchange term in Eq. (2). This interference changes the long range behaviour.

The equation for a bound electron wave function \( \Psi_\text{b}(\mathbf{r}) \) in a crystal contains the exchange term from Eq. (2) describing the exchange interaction of the bound electron with \( 2F \) mobile electrons:

\[ K(\mathbf{r}) = \int g(\mathbf{r} - \mathbf{r}') \left[ \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{e^2}{r} \right] \Psi_\text{b}(\mathbf{r}') d\mathbf{r}'. \] (10)

\[ g(\mathbf{r} - \mathbf{r}') \equiv \sum_n \Psi_n(\mathbf{r}) \Psi_n(\mathbf{r}')^\dagger. \] (11)

Summation goes over F mobile electron states \( \Psi_\text{m}(r) \) with the same spin projection. To account for the orthogonality condition \( \int \bar{\Psi}_n(\mathbf{r})\Psi_\text{b}(\mathbf{r}) d\mathbf{r}' = 0 \) in Eq. (10) we excluded the zero multipolarity term from the Coulomb integrals, replacing \( \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{e^2}{r} \) by \( \int F(\mathbf{r}) d\mathbf{r}' \). In the "exact" expression (10) the subtracted term \( \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \) disappears after the integration over \( \mathbf{r}' \) since \( \int \bar{\Psi}_n(\mathbf{r})\Psi_\text{b}(\mathbf{r}) d\mathbf{r}' = 0 \).

Let us start discussion of crystals from the simplest problem - a 1D chain of \( N \) atoms separated by distance \( a \). The wave function of a mobile electron can presented as

\[ \Psi_\text{m}(\mathbf{r}) = L^{-1/2} e^{ikx} v_k(\mathbf{r}), \] (12)

where \( v_k(\mathbf{r}) \) is a periodic function in \( x \)-direction and \( L = Na \) is the length of the chain. To perform the summation in Eq. (11) analytically we neglect dependence on \( k \) in \( v_k(\mathbf{r}) \). Taking the standard set of the wave vectors \( k_n = 2\pi n/L, n = 0, \pm 1, \pm 2, \ldots \), where \( F = 2q + 1 \), we obtain

\[ g(\mathbf{r} - \mathbf{r}') = v(\mathbf{r}) v(\mathbf{r}') \frac{\sin [k_f(x - x')]}{x - x'}. \] (13)

where \( k_F = f\pi/a \) and \( f = F/N \) is the band filling factor. Now we can find the exchange term Eq. (10). The leading term in the multipole expansion \( \langle r'^2 \rangle \) leads to the dipole approximation for \( K(\mathbf{r}) \) at large distance:

\[ K(\mathbf{r}) \approx \frac{e^2 v(\mathbf{r})}{\pi r^3} \sin (k_f x) \int x' \cos (k_f x') v(\mathbf{r}') \Psi_\text{b}(\mathbf{r}') d\mathbf{r}' \]

\[ - \cos (k_f x) \int x' \sin (k_f x') v(\mathbf{r}') \Psi_\text{b}(\mathbf{r}') d\mathbf{r}' \] (14)

It is easy to extend the problem to 2D and 3D cases. In 2D case we obtain

\[ g(\mathbf{r} - \mathbf{r}') = v(\mathbf{r}) v(\mathbf{r}') \frac{J_1(k_f |\mathbf{R}|)}{2\pi |\mathbf{R}|} \sim \frac{\sin (k_f |\mathbf{R}| - \pi/4)}{|\mathbf{R}|^{3/2}} \] (15)

where \( \mathbf{R} = \mathbf{r} - \mathbf{r}' \) and \( J_1 \) is the Bessel function. In 3D case

\[ g(\mathbf{r} - \mathbf{r}') = v(\mathbf{r}) v(\mathbf{r}') \frac{1}{2\pi^2 R^2} \left[ - \cos (k_f R) + \frac{\sin (k_f R)}{k_f R} \right]. \] (16)
Substituting these results into Eq (10) we obtain in the dipole approximation that the exchange interaction term decays as

\[ K(r) \sim \cos(k_f r) r^{-\nu} \]  

(17)

where \( k_f \) is the Fermi momentum and \( \nu = 3 \) for 1D, \( \nu = 3.5 \) for 2D and \( \nu = 4 \) for 3D crystal, i.e. \( \nu = (5 + d)/2 \) where \( d = 1, 2, 3 \) is the dimension.

Note that the expressions (14) (17) do not vanish if the electron band is complete. Instead they have fast oscillations if the electron Fermi momentum \( k_f \) is large. This conclusion looks surprising since a complete band does not contribute to the conductivity. If this conclusion is correct, one may have an enhanced tunneling amplitude or enhanced exchange interaction between distant spins (power suppression \( r^{-\nu} \) instead of exponential suppression) even in non-conducting materials. However, this phenomenon may be an artefact of the Hartree-Fock approximation for the wave function (antisymmetric product of the Bloch waves). We, in fact, have assumed that the electrons in complete band are not localised, i.e. they are still described by the Bloch waves (12) spread over all the crystal. Electron correlations may kill this effect, for example, by creating the Mott insulator where all electrons are localised. On the other hand, it would be incorrect to say that the long-range exchange is impossible in principle. For example, correlation corrections do not prevent valence electrons from being present on all atoms in a molecule where there is no conductivity.

The long-tail effect does not appear in any approach where the exchange interaction is replaced by an effective potential or by a density-dependent potential, e.g. in the density functional approach. Approximate calculations may also lead to other incorrect conclusions. For example, the long-range tail for a complete band case does not appear in the tight-binding approximation for the electron wave functions. In the tight-binding approximation a wave function of mobile electron is

\[ \Psi_n(r) = N^{-1/2} \sum_l e^{i k_n l a} \Psi_1(r-l a), \]  

(18)

where \( \Psi_1(r-l a) \) is the one-site wave function. The substitution of \( \Psi_n \) from Eq. (18) into Eq. (11) and summation over \( n \) gives the following results:

\[ g(r-r') = \sum_{l,m} B(F,l-m) \Psi_1(r-l a) \Psi_1(r' - m a) \]  

(19)

\[ B(F,l) = \frac{\exp(i 2 \pi l F / N) - 1}{N (\exp(i 2 \pi l F / N) - 1)} \approx \frac{\exp(i \pi f l)}{\pi l} \sin(\pi f l), \]  

(20)

where \( l > 0, f = F/N \) is the band filling factor and the last expression is obtained for \( l \ll N \). For \( l = 0 \) we have \( B(F,0) = f \). Substitution of \( g(r-r') \) from Eq. (19) into Eq. (10) shows that if the band is partly filled, the tight-binding approximation leads to the same conclusion \( K(r) \sim \cos(k_f r) r^{-\nu} \). However, for the completely filled band \( f = 1 \) and \( \sin(\pi f l) = 0 \). This means that the long-range exchange term vanishes in the absence of mobile carriers, electrons or holes. The explanation is simple: in the tight-binding approximation the complete band wave function made of the running waves Eq. (10) is equal to the antisymmetrised product of the localised electron wave functions \( \Psi_1(r-l a) \). The exchange interaction with the localised electrons does not produce the long-range tail. To compare with the Bloch wave expression one may say that the tight-binding result for the complete band corresponds to \( K(r) \sim \sin(k_f r) = 0 \) for \( r = l a \). However, the oscillations of \( K(r) \) do not lead to vanishing of its effect on the wave functions - compare with the solution for atomic orbitals in the previous section.

At finite temperature conducting electrons and holes appear. This activates the long-tail mechanism even in the tight-binding approximation and makes the under-barrier transmission coefficient temperature dependent. Here it may be appropriate to recall that a temperature dependence of the transmission coefficient has been observed near the “0.7 (2e^2/h) structure” in the point contact conductance measurements [3, 10].

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[1] V.A. Dzuba, V.V. Flambaum, P.G. Silvestrov. J.Phys.B 15, L575 (1980).
[2] C. Froese Fischer. The Hartree-Fock Method for Atoms (New York: John Wiley).
[3] N.C. Handy, M.T. Marron, H.J. Silverstone, Phys. Rev. 180, 45 (1969); G.S. Handler, D.W. Smith J.Chem.Phys 73, 3996 (1980).
[4] M.A. Ruderman, C. Kittel. Phys. Rev. 96, 99 (1954). T. Kasuya, Progr. Theor. Phys. 16, 45 (1956). K. Yosida, Phys. Rev. 106, 893 (1957).
[5] C. Zener. Phys.Rev. 81, 440 (1951); 82, 403 (1951).
[6] P.W. Anderson, H. Hasegawa. Phys. Rev 100, 675 (1955).
[7] P.-G. de Gennes. Phys.Rev. 118 141 (1960).
[8] P. Phillips. Advanced solid state physics (Westview press, Boulder, 2003).
[9] K.J. Thomas, J.T. Nicholls, M.Y. Simmons, M. Pepper, D.R. Mace, and D.A. Ritchie. Phys. Rev. Lett. 77, 135 (1996).
[10] K.J. Thomas, J.T. Nicholls, N.J. Appleyard, M.Y. Simmons, M. Pepper, D.R. Mace, W.R. Tribe, and D.A. Ritchie. Phys. Rev. B 58, 4846 (1998).