

Exchange interaction and correlations radically change behavior of a quantum particle in a classically forbidden region

V. V. Flambaum

School of Physics, The University of New South Wales, Sydney NSW 2052, Australia

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Exchange interaction strongly influences the long-range behavior of localized electron orbitals and quantum tunneling amplitudes. It produces a power-law decay instead of the usual exponential decrease at large distances. For inner orbitals inside molecules decay is r^{-2} , for macroscopic systems $\cos(k_F r)r^{-\nu}$, where k_F is the Fermi momentum and $\nu=3$ for one-dimensional, $\nu=3.5$ for two-dimensional, and $\nu=4$ for three-dimensional crystals. Correlation corrections do not change these conclusions. Slow decay increases the exchange interaction between localized spins and the underbarrier tunneling amplitude. The underbarrier transmission coefficients in solids (e.g., for point contacts) become temperature dependent.

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I. INTRODUCTION

One of the first famous results of quantum mechanics was that a particle may tunnel through a potential barrier. The tunneling amplitude is exponentially small in the classical limit. As we will see below this result may be incorrect if we take into account the exchange interaction. The exchange interaction is described by the nonlocal (integration) operator, and the well-known theorems proven for the Schrödinger equation with a local potential $U(\mathbf{r})$ are violated if we add the exchange term (or any other nonlocal operator). A similar effect is produced by the correlation corrections. In this paper we consider the influence of the exchange interaction and correlations on an electron orbital in an atom, molecule, or solid. The tunneling amplitude is still small in the classical limit; however, the decay of the orbitals in the classically forbidden area is much slower ($r^{-\nu}$) and depends on the dimensionality of the system.

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

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

$$K(\mathbf{r}) = \sum_q \Psi_q(\mathbf{r}) \int \Psi_q(\mathbf{r}')^\dagger \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \Psi(\mathbf{r}') d\mathbf{r}'. \quad (2)$$

Here the summation runs over all electron orbitals $\Psi_q(\mathbf{r})$ with the same spin projection as $\Psi(\mathbf{r})$. Now consider, for example, an inner electron atomic orbital $1s$. The solution of the Schrödinger equation in potential $U(\mathbf{r})$ has a very small range a_B/Z , where Z is the nuclear charge. Outside this range the orbital decreases exponentially as $\exp(-rZ/a_b)$. In the Hartree-Fock equation. (1) such rapid decay is impossible if an atom has more than two electrons. Indeed, if $\Psi(\mathbf{r}) \sim \exp(-rZ/a_b)$ the left-hand side of Eq. (1) would be exponentially small while the right-hand side is still large since $K(\mathbf{r})$ in Eq. (2) contains higher orbitals $\Psi_q(\mathbf{r})$ which have larger range. The behavior of the inner Hartree-Fock orbitals inside atoms has been studied analytically (in the semiclassical approximation) and numerically in Ref. [1] (see also Sec. II A). The dependence on the radius r can be found

from the multipole expansion of $|1/(\mathbf{r}-\mathbf{r}')|$ in $K(\mathbf{r})$; the slowest decay normally comes from the dipole term ($\sim r'/r^2$) and/or last occupied orbital $\Psi_q(\mathbf{r})$, $K \sim \Psi_q(\mathbf{r})/r^2$. The extra nodes appear since the orbitals $\Psi_q(\mathbf{r})$ oscillate. For example, the $1s$ orbital in a Cs atom has three nodes [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 Ref. [2]. Outside the atom all orbitals decay with an exponential factor for an external electron [3].

Inside solids there are electrons in the conduction band which occupy the whole crystal. It has been pointed out in Ref. [1] that the exchange interaction between a localized bound electron and the conduction-band electrons leads to a power tail of the bound-electron orbital. The effect of the exchange interaction $K(\mathbf{r})$ has been estimated in the free-band electron approximation $\Psi_q(\mathbf{r}) = \exp(i\mathbf{q} \cdot \mathbf{r})$. An orbital of a bound electron decreases at large distances as [1]

$$\Psi(\mathbf{r}) \sim \cos(k_F r)/r^4, \quad (3)$$

where k_F is the Fermi momentum. Note that this solution does not contradict the Bloch's theorem since we consider a localized bound electron (e.g., on an impurity atom) which does not belong to any electron band in the periodic potential. It is curious that the $1s$ orbital of an atom placed in a crystal has an infinite number of oscillations.

The derivation of this expression assumes the presence of a partly filled conduction-electron band. However, in atoms and molecules 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 localized spins and enhancement of the underbarrier 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 conduction band by the lo-

calized spin. The mediating band electrons produce the mean exchange field $K(\mathbf{r})$ in Eq. (2) only. Therefore, this “long-tail” effect is different from other effects such as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [4] (including coupling of nuclear magnetic moments by means of the hyperfine interaction with the conduction electrons) and the double-exchange spin-spin interaction suggested by Zener [5] (see also Refs [6,7] and a description of Anderson and Kondo problems, e.g., in book [8]).

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

A. Exchange

Let us first explain how the long tail appears in atoms [1]. The radial equation for a Hartree-Fock electronic orbital $\xi_i(r) = r\phi_i(r)$ is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + (U_{\text{eff}} - E_i) \right] \xi_i(r) = K_i(r), \quad (4)$$

$$U_{\text{eff}} = U + \frac{\hbar^2 l(l+1)}{2mr^2}. \quad (5)$$

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

$$K_i(r) = \sum_{k>0,n} C_{nk} b_{nk} \frac{\xi_n(r)}{r^{k+1}}. \quad (6)$$

Here C_{nk} are the standard angular-momentum-dependent coefficients and $b_{nk} = \int r^k \xi_n(r) \xi_i(r) dr$. 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 behavior of the orbital $\xi_i(r)$. We will use the $1s$ orbital in a Xe atom ($Z=54$) as an example. The last occupied shells are $\dots 5s^2 5p^6$. 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 $1s5p$ has $k=1$, therefore, at $r \sim a_B$ and outside the atom $K_{1s}(r) \approx C_{5p,1} b_{5p,1} \xi_{5p}(r)/r^2$.

The solution of Eq. (4) may be presented as [9]

$$\xi_i(r) = \xi_i^{\text{free}}(r) + \xi_i^{\text{ind}}(r), \quad (7)$$

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

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 ξ_n). In our example the energy of $1s$ is $|E_i| = Z^2 \times 13.6 \text{ eV} = 4 \times 10^4 \text{ eV}$ while the $5p$ energy is $|E_n| \sim 10 \text{ eV}$. Therefore, we can approximately write

$$\xi_i^{\text{ind}}(r) = \frac{K_i(r)}{U_{\text{eff}} - E_i} + \frac{\hbar^2}{2m(U_{\text{eff}} - E_i)} \frac{d^2}{dr^2} \frac{K_i(r)}{U_{\text{eff}} - E_i} + \dots \quad (9)$$

The free solution in this area may be described by the semiclassical (WKB) approximation, $\xi_i^{\text{free}}(r) \sim |p|^{-1/2} \exp(-\int |p| dr / \hbar)$; it has the usual range $a_B/Z = 0.02 a_B$ for $1s$. Comparison with the numerical solution of the Hartree-Fock equation for the $1s$ 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 $r > 10 a_B/Z$. 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 $\xi_{1s}(r) \approx \text{const} \xi_{5p}(r)/r^2$. The exponent in the decay of $\xi_{5p}(r)$ is 50 times smaller than in $\xi_{1s}^{\text{free}}(r)$. Therefore, outside the atom the exchange interaction enhances $\xi_{1s}(r)$ by more than 15 orders of magnitude.

B. Correlations

The effect of the correlations may be described by the nonlocal “correlation potential” $\hat{\Sigma}(r, r', E)$ (integration operator) which modifies electron orbitals (see, e.g., [10]). The correlation potential is defined such that its average value coincides with the correlation correction to the energy,

$$\delta E_i = \langle i | \hat{\Sigma} | i \rangle, \quad (10)$$

$$C(\mathbf{r}_2) \equiv \hat{\Sigma} \Psi_i = \int \hat{\Sigma}(\mathbf{r}_1, \mathbf{r}_2, E_i) \Psi_i(\mathbf{r}_1) d^3 r_1. \quad (11)$$

By solving the Hartree-Fock equation for the electron orbital including the correlation potential $\hat{\Sigma}$, we obtain “Brueckner” orbitals and energies,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} \Psi(\mathbf{r}) + [U(\mathbf{r}) - E] \Psi(\mathbf{r}) = K(\mathbf{r}) + C(\mathbf{r}). \quad (12)$$

It is easy to write the correlation potential explicitly. In the second-order perturbation theory in the residual interaction there are four terms. The direct term $\hat{\Sigma}^d(\mathbf{r}_1, \mathbf{r}_2, E_i)$ is given by

$$e^4 \sum_{n,\beta,\gamma} \int d\mathbf{r}_3 d\mathbf{r}_4 \frac{\psi_n^\dagger(\mathbf{r}_4) \psi_\beta(\mathbf{r}_4) \psi_\gamma(\mathbf{r}_2) \psi_\beta^\dagger(\mathbf{r}_3) \psi_\gamma^\dagger(\mathbf{r}_1) \psi_n(\mathbf{r}_3)}{r_{24} r_{13} (E_i + \epsilon_n - \epsilon_\gamma - \epsilon_\beta)}. \quad (13)$$

Note that $\hat{\Sigma}^d$ is a single-electron and energy-dependent operator. At large distance this term becomes the well-known local polarization potential $\sim 1/r^4$ (see, e.g., [10]), so it is not interesting for us. An interesting contribution comes from the exchange-correlation potential $\hat{\Sigma}^{\text{exch}}$

$$e^4 \sum_{n,\beta,\gamma} \int d\mathbf{r}_3 d\mathbf{r}_4 \frac{\psi_n^\dagger(\mathbf{r}_4) \psi_\beta(\mathbf{r}_4) \psi_\gamma(\mathbf{r}_2) \psi_\beta^\dagger(\mathbf{r}_1) \psi_\gamma^\dagger(\mathbf{r}_3) \psi_n(\mathbf{r}_3)}{r_{24} r_{13} (E_i + \epsilon_n - \epsilon_\gamma - \epsilon_\beta)}. \quad (14)$$

In this case we have the situation similar to the exchange interaction. Consider, for example, the correlation correction

to the Xe 1s orbital ($i=1s$) and $n=5p$. The energy of 1s is large and to make an estimate we can neglect $\epsilon_{5p}-\epsilon_\gamma-\epsilon_\beta$ in the denominator the Eq. (13). After the summation over β and γ we obtain the exchange-correlation term $C^{\text{exch}}(\mathbf{r}) \sim 2e^2/(rE_{1s})K(\mathbf{r})$, where $K(\mathbf{r})$ is the usual exchange term. Therefore, at large r the correlation term is suppressed in comparison with the exchange term by the small factor $2e^2/(rE_{1s})$. For the 1s orbital at $r=a_B$ the suppression factor is $4/Z^2$. The correlations are more important for higher orbitals where the suppression factor is $2e^2/(rE_i)$ and $|E_i| \ll |E_{1s}|$.

We may conclude that within the perturbation-theory treatment the correlations do not produce qualitative changes in the properties of the long-range tail. Their effect is similar to that of the exchange; however, the decay is faster (extra $1/r$).

III. ONE-, TWO-, AND THREE-DIMENSIONAL SYSTEMS

If we consider a molecule instead of an atom, the 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 behavior.

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

$$K(\mathbf{r}) = \int g(\mathbf{r}-\mathbf{r}') \left[\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} - \frac{e^2}{r} \right] \Psi_b(\mathbf{r}') d\mathbf{r}', \quad (15)$$

$$g(\mathbf{r}-\mathbf{r}') \equiv \sum_n \Psi_n(\mathbf{r}) \Psi_n(\mathbf{r}')^\dagger. \quad (16)$$

Summation goes over F mobile electron states $\Psi_n(\mathbf{r})$ with the same spin projection. To account for the orthogonality condition $\int \Psi_n(\mathbf{r}')^\dagger \Psi_b(\mathbf{r}') d\mathbf{r}' = 0$ in Eq. (15) we excluded the zero multipolarity term from the Coulomb integrals, replacing $\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$ by $\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} - \frac{e^2}{r}$. In “exact” expression (15) the subtracted term $\frac{e^2}{r}$ disappears after the integration over \mathbf{r}' since $\int \Psi_n(\mathbf{r}')^\dagger \Psi_b(\mathbf{r}') d\mathbf{r}' = 0$.

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

$$\Psi_n(\mathbf{r}) = L^{-1/2} e^{ik_n x} v_k(\mathbf{r}), \quad (17)$$

where $v_k(\mathbf{r})$ is a periodic function in the x direction and $L = Na$ is the length of the chain. To perform the summation in Eq. (16) analytically we neglect dependence on k in $v_k(\mathbf{r})$. Taking the standard set of the wave vectors $k_n = 2\pi n/L$, $n = 0, \pm 1, \dots, \pm q$, where $F = 2q + 1$, we obtain

$$g(\mathbf{r}-\mathbf{r}') = v(\mathbf{r})v(\mathbf{r}') \frac{\sin[k_f(x-x')]}{x-x'}, \quad (18)$$

where $k_f = f\pi/a$ and $f = F/N$ is the band filling factor. Now we can find the exchange term Eq. (15). The leading term in

the multipole expansion ($r' \ll r$) of $\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} - \frac{e^2}{r} \approx \frac{e^2(\mathbf{r}\cdot\mathbf{r}')}{r^3}$ leads to the dipole approximation for $K(\mathbf{r})$ at large distance,

$$K(\mathbf{r}) = \frac{e^2 v(\mathbf{r})}{\pi r^3} \left[\sin(k_f x) \int x' \cos(k_f x') v(\mathbf{r}') \Psi_b(\mathbf{r}') d\mathbf{r}' - \cos(k_f x) \int x' \sin(k_f x') v(\mathbf{r}') \Psi_b(\mathbf{r}') d\mathbf{r}' \right]. \quad (19)$$

It is easy to extend the problem to two-dimensional (2D) and three-dimensional (3D) cases. In the 2D case we obtain

$$g(\mathbf{r}-\mathbf{r}') = v(\mathbf{r})v(\mathbf{r}') \frac{J_1(k_f R)}{2\pi R} \sim \frac{\sin(k_f R - \pi/4)}{R^{3/2}}, \quad (20)$$

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

$$g(\mathbf{r}-\mathbf{r}') = \frac{v(\mathbf{r})v(\mathbf{r}')}{2\pi^2 R^2} \left[-\cos(k_f R) + \frac{\sin(k_f R)}{k_f R} \right]. \quad (21)$$

Substituting these results into Eq. (15) we obtain in the dipole approximation that the exchange interaction term decays as

$$K(r) \sim \cos(k_f r) r^{-\nu}, \quad (22)$$

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

The long-range tail in Eq. (22) is due to the exchange interaction between bound electrons and conducting electrons which travel freely inside the crystal and may be found at any distance from the bound electron. As we have seen in Sec. II, the perturbation-theory treatment of the correlations does not change our conclusions. This is the normal-metal case where the correlations are relatively weak. In this case the long-range tail of a bound-electron orbital is the real physical phenomenon which should be taken into account, for example, in calculating tunneling amplitudes or exchange interaction between distant localized spins.

Note that expressions (19) and (22) do not vanish if the conduction-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. One may compare this crystal complete band case with a molecule where valence electrons present on all atoms even in the absence of the conductivity. Therefore, one may have, in principle, an enhanced tunneling amplitude or enhanced exchange interaction between distant spins (power suppression $r^{-\nu}$ instead of exponential suppression) even in nonconducting materials. However, if there are strong electron-electron correlations (due to the strong repulsion between valence electrons located at the same site), they transform the Bloch-Hartree-Fock (conductor) state into the Mott insulator state where there are no free electrons and no long tail.

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. 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 elec-

tron wave functions. In the tight-binding approximation a wave function of a mobile electron is

$$\Psi_n(\mathbf{r}) = N^{-1/2} \sum_l e^{ik_n l a} \Psi_1(\mathbf{r} - l\mathbf{a}), \quad (23)$$

where $\Psi_1(\mathbf{r} - l\mathbf{a})$ is the one-site wave function. The substitution of Ψ_n from Eq. (23) into Eq. (16) and summation over n gives the following results:

$$g(\mathbf{r} - \mathbf{r}') = \sum_{l,m} B(F, l - m) \Psi_1(\mathbf{r} - l\mathbf{a}) \Psi_1(\mathbf{r}' - m\mathbf{a})^\dagger, \quad (24)$$

$$B(F, l) = \frac{\exp(i2\pi l F/N) - 1}{N[\exp(i2\pi l/N) - 1]} \approx \frac{\exp(i\pi f l)}{\pi l} \sin(\pi f l), \quad (25)$$

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 $g(\mathbf{r} - \mathbf{r}')$ from Eq. (24) into Eq. (15) 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. (23), is equal to the antisymmetrized product of the localized electron wave functions $\Psi_1(\mathbf{r} - l\mathbf{a})$. The exchange interaction with the localized 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 $r = la$. 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 underbarrier 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 [11,12].

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