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Exchange interaction between conduction electrons and localized $d(f)$ electrons with allowance for the nonorthogonality of their wave functions

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The Hartree–Fock theory is used, subject to allowance for the nonorthogonality of the wave functions of free and bound electrons, to obtain an expression for the dependence of the energy of the exchange interaction between these electrons on the various overlap integrals and on the spin state of the interacting particles. This expression yields, in particular, a formula for the total exchange integral in the weakly nonorthogonal case when the Heisenberg spin Hamiltonian can be used. Attention is drawn to the linear nature of the dependence of this energy on the quasimomentum of the conduction electrons in magnetic semiconductors.

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The exchange interaction between the conduction electrons (holes) and localized d or f electrons governs a variety of physical properties of magnetic semiconductors.[1,2] The same interaction is responsible for a number of phenomena in magnetic metals and nonmagnetic conducting materials containing paramagnetic impurities.[3–5] The interaction is described by introducing into the Hamiltonian of the system an appropriate term which is usually expressed in the familiar Heisenberg form:

$$\mathscr{H}_{\mathrm{Hb}}=\frac{2I}{N}\sum_{j=1}^{N}\hat{\mathbf{s}}_0\hat{\mathbf{S}}_i, \tag{1}$$

where $\hat{\mathbf{s}}_0$ and $\hat{\mathrm{S}}_j$ are the spin operators, and I is the constant of the investigated material.

It is known that this effective Hamiltonian gives rise to the same energy spectrum as a consistent microscopic description allowing for the Pauli principle and using the constant

$$I=\alpha=N\int\varphi_0^*(\mathbf{r})\varphi_j^*(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\varphi_0(\mathbf{r}')\varphi_j(\mathbf{r})\,d\mathbf{r}d\mathbf{r}' \tag{2}$$

only when the wave functions of the interacting particles are orthogonal. If the nonorthogonality is weak (this may be true, for example, in the interaction between electrons localized at different atoms), Eq. (1) gives an approximately correct dependence of the energy on the spin state of the particles but in this case allowance for the nonorthogonality alters drastically the results obtained.[6,7]

It is quite clear that the assumption not only of the orthogonality of the wave functions of free and localized electrons but also of the smallness of the overlap integrals between them is not, generally, justified in describing the interaction of such electrons. The approximate orthogonality of their functions may be true only under certain specific conditions. Some of the situations under which these conditions apply to the interaction of a conduction electron with a paramagnetic impurity are discussed by Vikhnin *et al.*[5] Numerical calculations of the coefficient I, carried out using the Heisenberg Hamiltonian for rare-earth metals allowing for such a weak nonorthogonality, are reported by Watson *et al.*[7]

In some cases the nonorthogonality of the wave functions of free and bound electrons is allowed by considering virtual transitions[7,8] or introducing—in a special manner—effective potentials.[9] However, a rigorous derivation of the dependences of the relevant terms on the spin states of the interacting particles is difficult and it has not yet been carried out.

The purpose of the present paper is to use the first quantum-mechanical principles in deriving an expression for the contribution made to the energy of the system by the conduction and localized d or f electrons as a result of the exchange interaction between them, as a function of the spin state of these particles without invoking the Heisenberg Hamiltonian; moreover, attention will be drawn to the dependence of this energy contribution on the quasimomentum of the conduction elec-

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trons. One can *a priori* hope to be able to carry out such calculations mainly because the problem can be regarded as of the one-particle type in the case of the conduction electrons.

1. The Hamiltonian of a system composed of a conduction electron and N magnetic atoms, carrying z electrons of the d or f type with unpaired spins, can be written in the form

$$\mathscr{H}=\frac{\hat{\mathbf{p}}_0^2}{2m}+V(\mathbf{r}_0)+\sum_{j=1}^{zN} V(\mathbf{r}_0,\mathbf{r}_j)+\mathscr{H}_l. \tag{3}$$

Here, $\hat{\mathbf{p}}_0$, m, and $\mathbf{r}_0$ are, respectively, the momentum operator, mass, and coordinate of the conduction electron; $V(\mathbf{r}_0)$ represents the Coulomb energy of the interaction of this electron with all N nuclei; $V(\mathbf{r}_0, \mathbf{r}_j)$ is the energy of the Coulomb interaction of a free electron with each of the localized electrons; $\mathbf{r}_j$ are the coordinates of the localized electrons; $\mathscr{H}_l$ is the Hamiltonian of the system in the absence of the conduction electrons. We shall take the many-particle antisymmetric wave function of the problem to be the Slater determinant of one-particle spinor wave functions

$$\Psi=[(1+zN)!]^{-1/2}|\psi_i(\mathbf{r}_j,\sigma_j)|, \quad i,j=0,1,\ldots,zN, \tag{4}$$

where i and j are the indices of the columns and rows, respectively; the index "0" refers to the conduction electron, and $1,\ldots, zN$ describe the localized d or f electrons. The problem is to find the energy

$$E=\int\Psi^*\mathscr{H}\Psi\,d\mathbf{r}_0\ldots d\mathbf{r}_{zN}\Big/\int\Psi^*\Psi\,d\mathbf{r}_0\ldots d\mathbf{r}_{zN}. \tag{5}$$

As stressed earlier, the important feature in our case is the nonorthogonality of the wave functions of the conduction electron and of the d (f) electrons; therefore, it is desirable to show this nonorthogonality explicitly, i.e., in terms of the overlap integrals, and not in some effective way via virtual transitions[7,8] or effective potentials.[9] For this reason we shall use the traditional Heitler–London approach, i.e., we shall assume that all the one-particle wave functions are the eigenfunctions of the corresponding one-particle Hamiltonians and are nonorthogonal relative to one another. The denominator of Eq. (5) is the determinant of the overlap integrals L_{ij}[10]:

$$\begin{gathered}L_{ij}=\int\psi_j^*(\mathbf{r})\psi_i(\mathbf{r})\,d\mathbf{r},\\ L_{ii}=1,\quad L_{i0}=L_{0i}^*=l_i/\sqrt{N},\quad L_{i,i+1}=\mathscr{L},\quad i\neq 0.\end{gathered} \tag{6}$$

The following two approximations will be used in calculating the energy (5) on the basis of such wave functions.

1. We shall consider materials for which $\mathscr{L}\ll 1$ and we shall include only the terms $\sim|l_i|^2$; we shall ignore the terms $\sim|l_i|^2 O(\mathscr{L})$, where $O(\mathscr{L})$ is a polynomial containing various powers of $\mathscr{L}$.

2. We shall ignore the influence of the exchange interaction of the conduction and d (f) electrons on the wave function of the latter electrons, i.e.,$^{1)}$

$$\mathscr{H}_l|\psi_i(\mathbf{r}_j,\sigma_j)|=E_l|\psi_i(\mathbf{r}_j\sigma_j)|, \quad i,j\neq 0. \tag{7}$$

In connection with the first of these approximations one must point out that allowance for the finite width of the d-electron (or f-electron) band [terms which are, in our terminology, proportional to $|l_i|^2O(\mathscr{L})$] on the exchange between them and conduction electrons in ferromagnetic semiconductors was made by Balkareĭ and Nikitov.[11] Eremin and Khaliullin[9] considered a contribution made by the terms proportional to $|l_i|^2\mathscr{L}$ to the exchange between the localized d (f) electrons in ferromagnetic metals.

2. We shall use Eqs. (3)–(7), rule on determinants, and invariance of the total Hamiltonian (3) under transposition of the coordinates of the interacting particles to obtain the following expression for the energy of the system in question:

$$\begin{aligned}E=\langle 0|\hat{V}_H|0\rangle-\frac{1}{N}\sum_{j=1}^{zN}\Big\{&\alpha_j-l_j\beta_j+l_j\langle j|\hat{V}_H|0\rangle-l_j^2\langle 0|\hat{V}_H|0\rangle\\ &+\sum_{i\neq j}l_i\langle j,i|V(\mathbf{r},\mathbf{r}')|0,j\rangle\Big\}\Big\{1-\frac{1}{N}\sum_{j=1}^{zN}|l_j|^2\Big\}^{-1}.\end{aligned} \tag{8}$$

Here,

$$\hat{V}_H=\frac{\hat{\mathbf{p}}_0^2}{2m}+V(\mathbf{r}_0)+\sum_{j=1}^{zN}\int|\psi_j(\mathbf{r}')|^2V(\mathbf{r}_0,\mathbf{r}')\,d\mathbf{r}', \tag{9}$$

$$\beta_j=\sqrt{N}\int\psi_j^*(\mathbf{r})\psi_0(\mathbf{r})V(\mathbf{r},\mathbf{r}')|\psi_j(\mathbf{r}')|^2\,d\mathbf{r}\,d\mathbf{r}', \tag{10}$$

α_j and l_j are defined above [see Eqs. (2) and (6)]; the angular brackets are used to denote the matrix elements, for example,

$$\langle j,i|V(\mathbf{r},\mathbf{r}')|0,j\rangle=\frac{1}{\sqrt{N}}\int\psi_j^*(\mathbf{r})\psi_i^*(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\psi_0(\mathbf{r})\psi_j(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'. \tag{11}$$

We note that neglect of the overlap integrals between the wave functions of the d (f) electrons results, for the selected normalization, in

$$\frac{1}{N}\sum_{j=1}^{zN}|l_j|^2<1.$$

For $l_j=0$ the energy formula (8) clearly gives the well-known expression which occurs in the Hartree–Fock theory. The last term of the numerator in Eq. (8) does not contain explicitly the overlap integrals $\mathscr{L}$ of the wave functions of the localized electrons but it is proportional to the first power of these integrals, which readily follows from Eq. (11).

In view of the above comments, we shall ignore this term.$^{2)}$

We now recall that one-particle wave functions are spinors:

$$\psi_j(\mathbf{r},\sigma_j)=\varphi_j(\mathbf{r})\begin{vmatrix}a_{j+} & \psi_+\\ a_{j-} & \psi_-\end{vmatrix}. \tag{12}$$

The coefficients $a_{0\pm}$, which determine the spin state of a conduction electron in the case of an inhomogeneous distribution of spins of the d (f) electrons may—in general—depend on the coordinate.[2] However, it is natural to assume that this dependence is weak compared with the dependence on $\mathbf{r}$ of the coordinate parts of the wave function $\varphi_0(\mathbf{r})$, i.e., the coefficients $a_{0\pm}$ are constant to within one unit cell and vary only from cell to cell. The integration ranges of α_j in Eq. (2), l_j in Eq. (6), β_j in Eq. (10), and $\langle j|V_H|0\rangle$ are governed by the localization of the d (f) electrons, so that the spin parts of the wave functions can be taken outside the integral in every one of these expressions. Therefore, the sum in the denominator of the second term of Eq. (8) can be rewritten as follows:

$$\frac{1}{N}\sum_{j=1}^{zN}|l_{j,\sigma_0,\sigma_j}|^2=\frac{1}{N}\sum_{j=1}^{zN}|a_{0+}{}^*a_{j+}+a_{0-}{}^*a_{j-}|^2|l_j|^2, \tag{13}$$

where l_j is still given by the integral (6) but this integral relates only to the coordinate wave functions. Next, we shall assume that, on the basis of the Bloch theorem, $|l_j|^2$ is independent of the unit cell number, so that

$$|a_{0+}{}^*a_{j+}+a_{0-}{}^*a_{j-}|^2=2(\mathrm{s}_0\mathrm{s}_j+{}^1/_4), \tag{14}$$

where s_j and s_0 are the average values of the spins of the d (f) electrons and conduction electron, respectively, and that the intraatomic Hund coupling is stronger than the exchange interaction of a d (f) electron with a conduction electron; consequently, instead of Eq. (13), we obtain

$$\frac{2l^2}{N}\sum_{j=1}^{N}\left[\mathrm{s}_0(\mathbf{R}_j)\mathrm{S}_j+\frac{z}{4}\right], \tag{15}$$

where $S_j=zs_j$ is the total spin of the j-th atom, l^2 is the average over the unit cell:

$$l^2=\frac{1}{z}\sum_{j=1}^{z}|l_j|^2. \tag{16}$$

Exactly the same procedure can be used to transform all the terms in the numerator of the second term in Eq. (8), so that the required expression for the energy becomes

$$E=\langle 0|\hat{V}_H|0\rangle+E_{\mathrm{exch}},$$

$$E_{\mathrm{exch}}=-\frac{2I}{N}\left\{1-\frac{2l^2}{N}\sum_{j=1}^{N}\left(\mathrm{s}_0\mathrm{S}_j+\frac{z}{4}\right)\right\}^{-1}\sum_{j=1}^{N}\left(\mathrm{s}_0\mathrm{S}_j+\frac{z}{4}\right), \tag{17}$$

$$I=\alpha_j-l_j\beta_j+l\langle j|\hat{V}_H|0\rangle-l^2\langle 0|\hat{V}_H|0\rangle, \tag{18}$$

where the terms in the expression for I are defined as in Eq. (16).

In the case when we can ignore l^2 compared with unity, Eq. (17) gives the familiar expression which, obviously, can be obtained using the Heisenberg Hamiltonian without allowance for the Pauli principle and using I defined by Eq. (18):

$$E=\left\langle\prod_{i=0}^{zN}\psi_i{}^*(\mathbf{r}_i\sigma_i)\,\middle|\,\hat{V}_H-\frac{Iz}{2}-\mathscr{H}_{\mathrm{Hb}}\,\middle|\,\prod_{i=0}^{zN}\psi_i(\mathbf{r}_i,\sigma_i)\right\rangle. \tag{19}$$

In general, when s_0 and $\mathbf{S}_j$ do not have eigenvalues at the same time (this is a typical situation in the interaction between the conduction and localized electrons at $T\neq 0$), it is impossible to obtain a complete expression for E_{exch} allowing for the denominator by some spin Hamiltonian. However, if $\mathbf{s}_0$ and $\mathbf{S}_j$ have eigenvalues at the same time, then E_{exch} can be regarded as representing the eigenvalues of the following effective Hamiltonian:

$$\mathscr{H}_{\mathrm{eff}}=-\frac{2Iz}{N}\sum_{m=0}^{\infty}\left\{\left(\frac{zl^2}{N}\right)^m\left[\sum_{j=1}^{zN}\left(\hat{\mathrm{s}}_0\hat{\mathrm{s}}_j+\frac{3}{4}\right)\right]^{m+1}\right\}. \tag{20}$$

It should be noted that the eigenvalues of the Hamiltonian containing the operator $\hat{\mathrm{s}}_0\cdot\hat{\mathrm{S}}_j$ (for $z\neq 1$) cannot be identical with E_{exch}.

The usually employed one-particle Schrödinger equation for a conduction electron is obtained from Eq. (19) by the standard Hartree–Fock procedure. The corresponding Euler–Lagrange equation is

$$\left[\hat{V}_H-\frac{2I}{N}\sum_{j=1}^{N}\left(\mathrm{s}_0\mathrm{S}_j+\frac{z}{4}\right)\right]\psi_0(\mathbf{r},\sigma)=\varepsilon\psi_0(\mathbf{r},\sigma). \tag{21}$$

In principle, the above equation can be used to find $\psi_0(\mathbf{r},\sigma)$ and, in particular, the most interesting coordinate dependence of the direction of the conduction electron spin. We shall not be interested in this problem; for some special cases (specific distributions of $\mathbf{S}_j$), it is considered by a variety of methods in published papers.[12-15] We must draw attention to just one circumstance. In those cases when the second term on the left-hand side of Eq. (21) can be regarded as a perturbation, the zeroth-approximation wave function is the eigenfunction of the Hartree operator and, in the first order, the expression for I given by Eq. (18) reduces to the very simple form

$$I=\alpha-l\beta, \tag{22}$$

which resembles the well-known expression for the exchange constant of the hydrogen molecule. The second term in the above equation naturally differs from the corresponding term for the hydrogen molecule because the zeroth-approximation is the Hartree Hamiltonian rather than the atomic one. The criterion of validity of the perturbation theory in the case of Eq. (21) and an arbitrary distribution of $\mathbf{S}_j$ requires a separate discussion. However, in the case of a homogeneous distribution, this criterion is

$$I/(1-zl^2)\ll W,$$

where W is the allowed band width.

3. The coefficient I of Eq. (18) and the overlap integral l of Eq. (6) contain the wave function of a conduction electron, which depends on its quasimomentum $\mathbf{k}$ and, therefore, the exchange potential energy should depend on $\mathbf{k}$. In the case of ferromagnetic metals, this dependence has been investigated numerically[7] and observed experimentally.[16] It is not possible to obtain some analytic expression for this dependence.

In the case of semiconductors, we can assume approximately that the dependence $E_{\mathrm{exch}}(\mathbf{k})$ is linear because the range of integration for l of Eq. (6) and I of Eq. (18) is, in fact, governed by the size of the localization region d (f) electrons, which is of the order of the lattice constant a, so that throughout this region we find that $\mathbf{k}\cdot\mathbf{r}\ll 1$ for the filled states in the conduction band. Making allowance for this point, we can obviously write the one-particle spectrum of the conduction electron in a wide-gap magnetic semiconductor with $l^2 \ll 1$ in the form

$$\mathscr{E}=\frac{\hbar^2k^2}{2m}-\frac{2}{N}[a\mathbf{k}\mathbf{I}_1+I_0]\sum_{j=1}^{N}\left(\mathbf{s}_0\mathbf{S}_j+\frac{z}{4}\right), \qquad (23)$$

where I_0 and $\mathbf{I}_1$ are the coefficients of the expansion of I of Eq. (18) in terms of $a\mathbf{k}$. For real ferromagnetic semiconductors the total energy of the exchange interaction of a carrier with the d (f) electrons represents a few tenths and may even approach 1 eV. This is probably proved most directly by the published experiments,[17,18] so that a typical value of the quantity $a\mathbf{k}\cdot\mathbf{I}_1$ should represent a few hundreds of degrees, which—for nondegenerate semiconductors—is considerably greater than the kinetic energy of the conduction electrons and, therefore, this term should have a strong influence on the behavior of the other terms. For example, it is clear that allowance for this term cardinally alters the nature of certain transport effects in these materials.

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[1] In principle, this influence can be allowed for in the appropriate one-particle Hartree-Fock equation using the perturbation theory, which in this case should work well because usually the localized-electron spectrum depends weakly on the degree of magnetic ordering of a crystal.

[2] It should be noted that this term differs slightly from that considered by Eremin and Khaliullin [9] although it is of the same order of magnitude; Eremin and Khaliullin consider (in our notation) terms of the $\mathcal{L}\alpha=\mathcal{L}\langle 0,j\,|\,V(\mathbf{r},\mathbf{r}')\,|\,j,0\rangle$ type [compare with Eqs. (8) and (11)], which cannot appear in our treatment because we have assumed right from the beginning that $\mathcal{L}\approx 0$.

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Thermal ionization of impurities in strong electric fields

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It is shown that the well-known Poole–Frenkel formula, describing the dependence of the thermal ionization coefficient β on the electric field $\mathscr{E}$ in a semiconductor, should be modified. In addition to the exponential dependence of β on $\mathscr{E}$, which appears because of the reduction in the ionization energy of an impurity in the applied field, allowance should be made for the electric-field dependence of the preexponential factor, associated with the change in the rate of diffusion of electrons over highly excited impurity states in the presence of the field. The Pitaevskiĭ method is used to obtain an expression for the coefficient of thermal ionization from a Coulomb impurity center in an electric field in the specific case when the ionization is due to the interaction of electrons with acoustic phonons.

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1. The probability of thermal ionization of an impurity center in strong electric fields is known to rise exponentially with the field intensity. This is known as the Poole–Frenkel effect, named in this way because Poole was the first to observe an exponential increase in the conducitvity of an insulator in the prebreakdown state[1] and Frenkel explained this effect theoretically.[2]

The Frenkel idea was that the application of an elec-