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Indirect exchange in dilute magnetic semiconductors

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A generalized Ruderman-Kittel-Kasuya-Yosida (RKKY) approach is used to calculate indirect exchange interactions between localized spins in doped magnetic semiconductors. The exchange is mediated by electron or hole states centered around shallow impurities. The states hybridize and may or may not form a narrow band, but in both cases, the exchange is obtained from the hybridized states by second-order perturbation theory. As in the free-electron RKKY model, both positive and negative exchange interactions occur, but the strength J_{ij} of the exchange is no longer a unique function of the distance between the localized spins. A closed expression with simple geometric interpretation is obtained in the dilute limit of exchange mediated by two overlapping orbitals. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2159394]

I. INTRODUCTION

Motivated by the search for materials for spin electronics, dilute magnetic semiconductors have recently attracted renewed attention. One aspect is the explanation and prediction of Curie temperature T_C by models such as the Ruderman-Kittel-Kasuya-Yosida (RKKY) model and by numerical simulations.[1–5] Naturally, the different approaches have specific advantages and shortcomings,[1,2,6] but here we do not attempt to discuss and judge them in this paper. Our focus is on the sign and magnitude of RKKY-type interactions J_{ij} between localized spins i and j in magnetic semiconductors that contain shallow impurities. From the J_{ij} the Curie temperature is readily estimated by site-averaged[1] or site-resolved[2,7,8] mean-field approximations. In the latter approach, the Curie temperature is obtained by diagonalizing the matrix J_{ij}, similar to the determination of the mean-field Curie temperature in ferrimagnets.[9]

By definition, Ruderman-Kittel exchange is a perturbative indirect exchange between localized spins labeled i and j. In the widely known original theory, the exchange is mediated by free electrons. A key feature of the free-electron RKKY exchange[10] is long-range oscillations $J_{ij} \sim \cos(2k_F r)/r^3$, where k_F is the Fermi wave vector and $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the spins. The origin of the oscillations is the sharp Fermi surface, which means that spatial features smaller than about $1/k_F$ cannot be resolved with the available wave functions.

However, as remarked long ago,[11] the assumption of free electrons is rather unessential. The essence of the RKKY interactions is the perturbative treatment of the interactions mediated by a system of electrons, and the free-electron gas may well be replaced by a more complicated system. In the following, we make the reasonable assumption that the exchange between localized spins (magnetic ions) is mediated by orbitals that originate from shallow donors or acceptors. Since the diameters of shallow orbitals are much bigger than the interatomic distance, each orbital may contain one (or more) atoms carrying a local magnetic moment. At some impurity concentration, the orbitals overlap and start to form clusters of hybridized orbitals, and these orbitals give rise to an exchange interaction similar to that mediated by free electrons. In general, clusters of shallow orbitals do not yield a sharp Fermi surface, and the question arises what determines the transition between positive and negative exchanges, if there is any.

II. CALCULATION AND RESULTS

The basic idea is to place two localized spins into an electron system and to evaluate the total energy for parallel and antiparallel spin orientations $s_i = \pm s_j$. The corresponding energy contribution is

$$E_{\pm} = \Sigma_{\mu} \frac{|\langle \Psi_{\mu} | V(s_i) \pm V(s_j) | \Psi_0 \rangle|^2}{E_{\mu} - E_0}, \tag{1}$$

where $|\Psi_{\mu}\rangle$ is the many-body wave function of the mediating electron system. In a simple approximation, the neglect of correlations reduces $|\Psi_{\mu}\rangle$ to Slater determinants of one-electron wave functions $|\psi\rangle$, and the evaluation of Eq. (1) simplifies considerably. In the following calculations, we will focus on this one-electron approximation but return to correlations in the last section. The interaction potential V is of the well-known s-d-type

$$V_i(\mathbf{r}) = \pm V_0 s_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{2}$$

where the sign indicates whether the mediating electron is $\uparrow$ or $\downarrow$. Figure 1 illustrates the nature of the shallow orbitals and the position of the localized magnetic spins (magnetic atoms). If two spins are located in one shallow orbital occupied by one electron, then the exchange is *ferromagnetic*.[5] This is a direct consequence of Eq. (2).

With increasing impurity concentration, the shallow orbitals $|\phi_m\rangle = \phi(|\mathbf{r} - \mathbf{R}_m|)$ overlap and finally percolate. Figure 2 shows the geometry of the problem. In a tight-binding approximation, the hybridization yields one-electron wave functions $\psi_n(\mathbf{r}) = \Sigma_m c_{nm} \phi(|\mathbf{r} - \mathbf{R}_m|)$, where the c_{nm} are linear combination of atomic-orbital (LCAO) coefficients. Since

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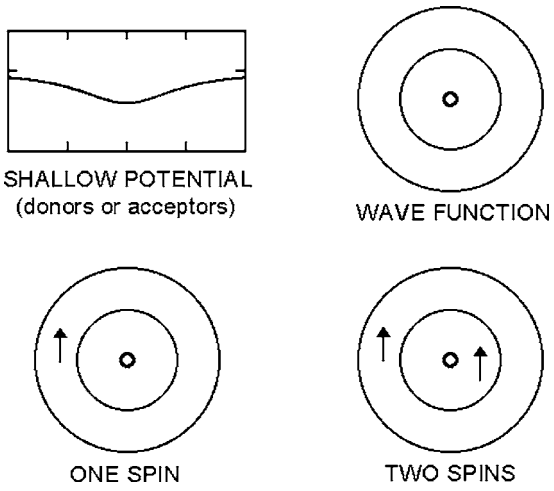

FIG. 1. Localized spins (arrows) in the vicinity of a shallow donor or acceptor. One method of calculating shallow orbitals is the envelope function method well known in semiconductor physics.

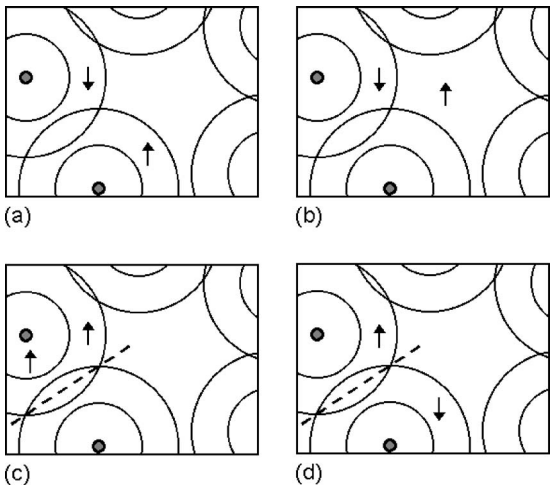

FIG. 3. Exchange mediated by two shallow orbitals: (a) basic geometry, (b) zero exchange due to isolation of one spin, (c) ferromagnetic exchange, and (d) antiferromagnetic exchange.

the shallow orbitals have a radius of the order of 1 nm, the percolation happens at relatively low concentrations. The physics of the percolation transition is nontrivial, involving electron localization and critical fluctuations. However, we are not concerned with long-range phenomena and restrict ourselves to a length scale of a few nanometers, where the exchange is particularly strong. This is inconsistent with the implied use of mean-field theory to determine T_C.

Figure 2 indicates that the exchange J_{ij} depends not only on the positions $\mathbf{r}_i$ and $\mathbf{r}_j$ of the localized spins but also on the positions of the impurities. For example, a spin at $\mathbf{r}_i$ may be isolated (not close to any of the mediating orbitals), so that $J_{ij}=0$ for all j. This is in striking contrast to free-electron RKKY exchange, where the duties of the impurities are performed by a homogeneous background (jellium) and J_{ij} is a simple function of $|\mathbf{r}_i-\mathbf{r}_j|$. For this reason, we cannot expect to obtain simple expressions for J_{ij}.

One exception is the exchange mediated by two overlapping shallow orbitals located at $\mathbf{R}_1$ and $\mathbf{R}_2$. Here the hybridized wave functions have the character of bonding or antibonding states, and the level splitting is determined by the hopping integral t. The unperturbed ground state is bonding, but the interaction with the localized spin yields some admixture of antibonding character. The degree of admixture and therefore the energy of the system depend on the relative spin orientation $s_i=\pm s_j$. The calculation is straightforward and yields, in second-order perturbation theory,

$$J_{ij}=-\frac{{V_0}^2}{8t}[\rho(\mathbf{r}_i-\mathbf{R}_1)-\rho(\mathbf{r}_i-\mathbf{R}_2)] \times[\rho(\mathbf{r}_j-\mathbf{R}_1)-\rho(\mathbf{r}_j-\mathbf{R}_2)], \quad (3)$$

where $\rho(\mathbf{r})=\phi^*(\mathbf{r})\phi(\mathbf{r})$. Here the involvement of ${V_0}^2$ reflects the second-order perturbation character of the theory, whereas the level splitting $E_\mu-E_0\sim t$ originates from the denominator in Eq. (1). Note that the second-order RKKY-type exchange adds to any lowest-order exchange of order V_0.

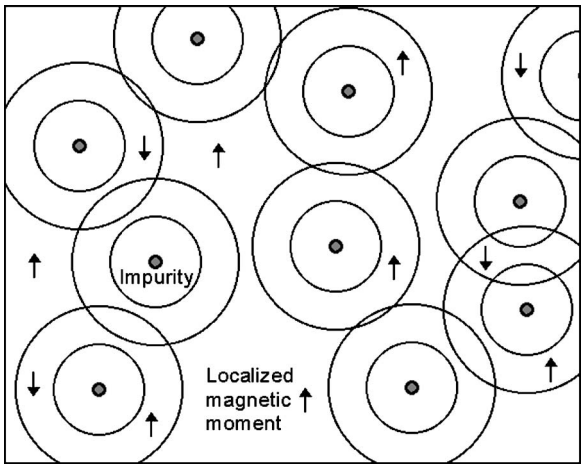

FIG. 2. Indirect exchange in dilute semiconductors. The mechanism is similar to free-electron RKKY interactions, but due to the essential involvement of shallow impurities, $J(\mathbf{r}_i,\mathbf{r}_j)$ can no longer be written as $J(|\mathbf{r}_i-\mathbf{r}_j|)$. For example, some ions may not overlap with the shallow orbitals, so that $J_{ij}=0$ for all $|\mathbf{r}_i-\mathbf{r}_j|$.

Figure 3 shows the meaning of Eq. (3). Aside from the trivial case of isolated spins (b), the exchange is ferromagnetic if the magnetic ions are located in the same shallow s orbital (c) and antiferromagnetic if they are in different s orbitals (d). The dashed line in the figure provides an alternative criterion. Spins on the *same side* of the line couple ferromagnetic, whereas spins *separated* by the dashed line exhibit antiferromagnetic coupling. Figure 4 is a contour plot of the exchange J_{ij} as a function of the position $\mathbf{r}_j$ of one of the spins. Due to the multiplicative character of Eq. (3), the position of the other spin, $\mathbf{r}_i$, affects the magnitude of J_{ij} but does not change the contour lines of constant J_{ij} in Fig. 4. However, when the second spin crosses the $J_{ij}=0$ line, then the ferromagnetic half plane becomes the antiferromagnetic half plane and vice versa.

III. DISCUSSION AND CONCLUSIONS

The dashed line in Fig. 3 helps us to understand why there are no simple expressions for exchange interactions involving three or more coupled orbitals. Each pair of orbitals creates a dashed separation line, and with increasing im-

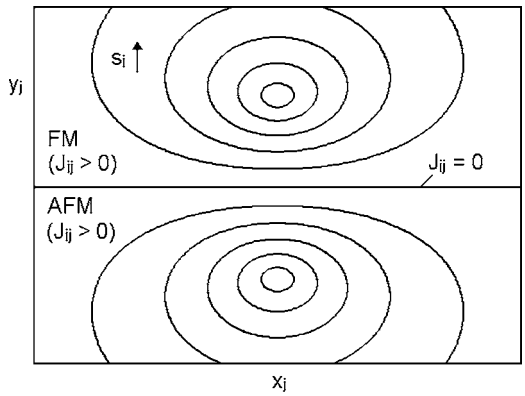

FIG. 4. Exchange J_{ij} as a function of the position of the second spin (j). The arrow shows the position of the first spin s_i. In this figure, we have used hydrogenlike orbitals.

purity density, the number of lines increases. Each line gives amounts of one prediction, but some of the predictions may contradict each other. In addition, the lines "interact" with each other, because clusters comprising three or more orbitals have complicated level splittings. In terms of Eq. (1), this leads to a complicated summation over $1/(E_\mu - E_0)$, as compared to a common factor $1/t$.

In a general sense, RKKY interactions are restricted to s-type orbitals.[12] When applied to d orbitals, the exchange depends on the direction $\mathbf{r}_i - \mathbf{r}_j$. This bond anisotropy is magnetically *isotropic*, in contrast to magnetic anisotropies created by spin-orbit coupling. The latter mechanism includes not only the ordinary magnetic anisotropy but also a generally anisotropic orbital contribution to the magnetic moment.[13]

Equation (3) predicts a $1/t$ dependence of the exchange, but this does not mean that the exchange diverges for large separations between impurities, where $t=0$. The reason is the perturbative character of Eqs. (1) and (3), which requires $V_0 < t$ and excludes the limit of zero hopping. Furthermore, Eq. (3) ignores correlations, very similar to the failure of the LCAO approach in the small-hopping limit of large interatomic separations. The correlation effects are akin to the Coulomb blockade in quantum dots. As we will show elsewhere, correlations reduce the exchange but leave the qualitative picture unchanged.

As mentioned above, the present theory focuses on the highly diluted limit which may be called "dilute magnetic dielectrics."[14] The percolation transition, the formation of impurity bands, and the accompanying changes in conductivity and magnetism go far beyond the scope of this paper. For example, below percolation, there is no long-range magnetic order, but the J_{ij} yield short-range order, a situation similar to that in other inhomogeneous magnets.[1,8,15] There are, however, links between the isolating and free-electron limits. In metals, $1/k_F$ scales as the average interelectronic distance, so that the oscillation period is proportional to the interatomic distance. The same is true for the present model, even if there is no sharp k_F. In our case, there is one electron per shallow orbital, and the interelectronic distance is determined by the impurity density. Since J_{ij} changes sign between two impurities, Figs. 3(c) and 3(d), this amounts to changes of the sign of J_{ij} on a length scale of the electronic distance.

In conclusion, we have found a simple solution for indirect exchange mediated by two orbitals. Depending on the locations of the impurities and spins, the net exchange may be ferromagnetic or antiferromagnetic. The present mechanism interpolates between the traditional RKKY exchange and the exchange caused by a single donor or acceptor.

ACKNOWLEDGMENTS

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