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Effective interaction Hamiltonian of polaron pairs in diluted magnetic semiconductors

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The magnetic interaction of a pair of bound magnetic polarons in diluted magnetic semiconductors is analyzed via a generalized Hubbard-type Hamiltonian for two carriers in the presence of effective magnetic fields arising from the magnetic polarization of their respective polarons. For the case where the magnetic fields at the two sites have equal magnitude but are allowed to have arbitrary directions, it is shown that the energy of the two polarons is minimized for a *ferromagnetic* configuration of the carrier spins (in contrast to the case of hydrogenic centers in nonmagnetic semiconductors) if polaron fields are strong enough. A modified Heisenberg-type Hamiltonian is constructed to describe the low energy states of the resulting system.

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I. INTRODUCTION

Shallow impurities in doped semiconductors[1] can be described in terms of a hydrogenic Hamiltonian with an effective mass given by the band mass, and a Coulomb potential screened by the dielectric constant of the host semiconductor. While the ''effective mass'' equation is slightly more complicated for donors in indirect band-gap semiconductors, and for acceptors a matrix version of a generalized hydrogen problem is obtained, these differences change details, but not the basic physics. Therefore, the hydrogenic model is a useful guide for studying and understanding interactions between impurities in doped semiconductors.[2,3] At low concentrations the interactions between impurity centers can be modeled in terms of an exchange Hamiltonian involving, as the dominant term,[4] pairwise Heisenberg exchange corresponding to the hydrogen molecule problem,[5] where the exchange interactions are known to be antiferromagnetic at all distances.[6]

In diluted magnetic semiconductors (DMS), a small fraction of the nonmagnetic ions that form the lattice are replaced by magnetic ions such as Mn or Fe. Several features (such as variable band gaps, optical response, spin polarized transport, as well as the unusual magnetic behavior analyzed in this paper) have turned DMS into a topic of considerable interest during recent years. In the low doping regime (i.e., carrier density below the Mott transition), the susceptibility (i.e., dM/dH) vs magnetic field (H) curve of such a DMS displays a curious double-step feature.[7] To understand the properties of DMS with dopants, it is not only necessary to understand the direct interactions between the dopants, but also the interactions with the magnetic ions which by themselves contain low lying degrees of freedom. When the magnetic ions are dilute, their direct interactions are unimportant. Thus, for example, the problem of a single shallow impurity in a DMS is well described in terms of an exchange interaction between the bound carrier (electron or hole) and the magnetic ion, and is known from extensive studies to lead to the formation of a bound magnetic polaron (BMP).[8] The spins of the magnetic impurity ions within one effective Bohr radius of a dopant interact via a sizable exchange with the carrier, thus becoming aligned and forming large-spin polarons. The polarons align with an external magnetic field before the individual magnetic ions do, thus giving rise to the two-step susceptibility curve. By analyzing[7] the first step (fitting it to a Curie Weiss form), the susceptibility of BMPs can be deduced. It is found to exceed the susceptibility for noninteracting BMPs, implying a ferromagnetic interaction between the polarons. However, this result seems puzzling: in nonmagnetic semiconductors carrier virtual hopping invariably yields antiferromagnetism.[2] Nevertheless, similar ferromagnetic interaction has also been inferred in subsequent work, also in low doped, insulating samples.[9]

The problem was analyzed by Durst, Bhatt, and Wolff.[10,11] In their work they showed that a ferromagnetic interaction between the polarons can be obtained if one considers the overlap of two polarons formed around two dopants. The two carriers compete over the spins in the overlapping region. For certain values of the model parameters the indirect carrier-magnetic ion-carrier interaction becomes stronger than the direct carrier exchange, and the polarons align resulting in ferromagnetism.

The current work uses a different model to approach the problem from another perspective. The polarons are considered nonoverlapping, and their effect on the dopant atom is taken into account through a local magnetic field h. A system of two such polarons is analyzed via a generalized Hubbard-type Hamiltonian, where hopping (matrix element t) and Coulomb interaction (energy U) are turned on. Several cases are considered (dopants with a single bound state and with several bound excited states). Ferromagnetic behavior is seen to emerge when the carrier is allowed to hop between the ground state of one dopant atom and excited states of the other dopant. This mechanism would be another contribution to ferromagnetism in DMS. Numerical work supports the conclusion that such a ferromagnetic interaction is indeed possible in realistic conditions. We also discuss the applicability of a Heisenberg-type model for two interacting polarons. In the moderately high field domain $t \ll h \ll U$, an effective Heisenberg Hamiltonian is found which contains a mixing of the magnetic fields at the two sites.

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II. THE MODEL AND THE APPROACH

Our model consists of two identical atoms, with several bound states, in arbitrary local magnetic fields. We allow for hopping of the carriers between the two atoms. The local magnetic fields represent the exchange fields due to the magnetic ions at each site. As the number of magnetic ions around each site is large, and the doping is considered uniform, we assume that the magnitudes of the magnetic fields at the two sites are equal. However, the directions of the two fields are allowed to be arbitrary. Thus, the Hamiltonian we study has the general form:

$$H=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2)-h\hat{\mathbf{h}}(r_1)\cdot\mathbf{S}_1-h\hat{\mathbf{h}}(r_2)\cdot\mathbf{S}_2 -\frac{1}{r_{a1}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}-\frac{1}{r_{b2}}+\frac{1}{r_{12}}, \tag{1}$$

where h is the magnitude of the field, $\hat{\mathbf{h}}(\mathbf{r})$ is the (arbitrary) direction, a and b are the labels for the two hydrogenic centers and 1 and 2 are the labels for the two electrons.

If we consider a Hubbard-like approximation[5] with one energy level per impurity site and no magnetic fields, the Hamiltonian becomes (in second quantized form):

$$H=\sum_{\alpha=a,b}\left(\epsilon(\mathbf{n}_{\alpha\uparrow}+\mathbf{n}_{\alpha\downarrow})+U\mathbf{n}_{\alpha\uparrow}\mathbf{n}_{\alpha\downarrow}\right) +\sum_{\mathbf{s}=\uparrow,\downarrow}t(\mathbf{c}_{a\mathbf{s}}^{\dagger}\mathbf{c}_{b\mathbf{s}}+\mathbf{c}_{b\mathbf{s}}^{\dagger}\mathbf{c}_{a\mathbf{s}}), \tag{2}$$

where a,b are labels for the two impurity sites, $\mathbf{c}_{a\uparrow}$ is the annihilation operator for the state on impurity a with up-spin, $\mathbf{n}_{a\uparrow}$ is the occupation number, $\mathbf{n}_{a\uparrow}=\mathbf{c}_{a\uparrow}^{\dagger}\mathbf{c}_{a\uparrow}$, etc.

If we also introduce arbitrary number of energy levels on each impurity atom, the Hubbard Hamiltonian Eq. (2) turns into:

$$H=\sum_{i,\alpha,\mathbf{s}}\epsilon_{i\alpha}\mathbf{n}_{i\alpha\mathbf{s}}+\sum_{i<j,\mathbf{s}_1,\mathbf{s}_2,\alpha}U_{ij}\mathbf{n}_{i\alpha\mathbf{s}_1}\mathbf{n}_{j\alpha\mathbf{s}_2} +\sum_{i,\alpha}U_{ii}\mathbf{n}_{i\alpha\uparrow}\mathbf{n}_{i\alpha\downarrow}+\sum_{i,j,\mathbf{s}}t_{i,j}(\mathbf{c}_{jb\mathbf{s}}^{\dagger}\mathbf{c}_{ia\mathbf{s}}+\mathbf{c}_{ia\mathbf{s}}^{\dagger}\mathbf{c}_{jb\mathbf{s}}), \tag{3}$$

where $\alpha\in\{a,b\}$ indexes the impurity sites; i,j the atomic levels on each impurity; $\mathbf{s}_1,\mathbf{s}_2\in\{\uparrow,\downarrow\}$ the spin degree of freedom; ϵ_i the energy of level i; and U_{ij} the Coulomb interaction energy of electrons in states i and j on the same impurity atom.

Finally, if at each site we consider the arbitrary magnetic fields $\mathbf{h}_a,\mathbf{h}_b$, and we quantize spin along the axes of the local magnetic fields (i.e., $\mathbf{c}_{ia\uparrow}^{\dagger}$ creates an electron in the ith state on impurity a with spin parallel to $\mathbf{h}_a$), the Hubbard Hamiltonian becomes

$$H=\sum_{i,\alpha,\mathbf{s}}\epsilon_{i\alpha}\mathbf{n}_{i\alpha\mathbf{s}}+\sum_{i<j,\mathbf{s}_1,\mathbf{s}_2,\alpha}U_{ij}\mathbf{n}_{i\alpha\mathbf{s}_1}\mathbf{n}_{j\alpha\mathbf{s}_2}+\sum_{i,\alpha}U_{ii}\mathbf{n}_{i\alpha\uparrow}\mathbf{n}_{i\alpha\downarrow} +\sum_{i,\alpha}h_{\alpha}(\mathbf{n}_{i\alpha\uparrow}-\mathbf{n}_{i\alpha\downarrow})+\sum_{i,j,\mathbf{s}_1,\mathbf{s}_2}t_{i\mathbf{s}_1,j\mathbf{s}_2} \times(\mathbf{c}_{jb\mathbf{s}_1}^{\dagger}\mathbf{c}_{ia\mathbf{s}_2}+\mathbf{c}_{ia\mathbf{s}_2}^{\dagger}\mathbf{c}_{jb\mathbf{s}_1}). \tag{4}$$

We caution the reader that in this case the transition matrix elements $t_{i\mathbf{s}_1,j\mathbf{s}_2}$ become dependent on the angle Θ between the two magnetic fields $\mathbf{h}_a,\mathbf{h}_b$. We will discuss the relationship between Eqs. (4), (3), (2), and Eq. (1) in more detail in the concluding section.

Several models of increasing complexity were considered: atoms with a single bound state and without magnetic fields (Sec. III A), atoms with a single bound state in arbitrary magnetic fields (Sec. III B), atoms with several excited states in arbitrary magnetic fields (Sec. IV A). The ground state of the two-center system is shown to undergo a transition from an antiferromagnetic state (singlet) to a fully ferromagnetic (triplet) configuration with the increase of the effective polaron magnetic field (Sec. IV B). The results for a regular Heisenberg Hamiltonian where the two spins are in arbitrary fixed fields are calculated as well and compared with those derived from our model (Sec. III C). Finally we find a modified Heisenberg-type Hamiltonian that agrees with our model in the moderately high field regime (Sec. V).

III. REGULAR HUBBARD MODEL

A. Regular Hubbard model in zero field

The Hubbard model of the hydrogen molecule[5] [see Eq. (2)] consists of two hydrogenic (one-electron) centers, each with one single electron bound state of energy ϵ. Electrons are allowed to hop between the two sites, subject to the restrictions imposed by the Pauli principle with a hopping matrix element t. Each center also has one two-electron state, with energy $2\epsilon+U$, where U represents the interaction energy between two electrons on the same atom.

In this case we can decouple the spin-1 and spin-0 subspaces (since there is no connection between states of different spin). It turns out that the spectrum of eigenvalues is 2ϵ (triple degenerate) for spin-1 and $2\epsilon-(4t^2/U)$, $2\epsilon+U$ and $2\epsilon+U+(4t^2/U)$ for spin-0. The ground state therefore has spin 0 (i.e., the interaction between the electrons can be thought of as antiferromagnetic).

B. Regular Hubbard model with arbitrary fields

If two arbitrary fixed fields (of strengths h_a and h_b and making an angle Θ) are applied at the two sites, the analysis becomes more complicated [see Eq. (4), and consider that there is a single level, $i=1$, on each impurity]. We can quantize the spins along the axes of the fields, and we can pick as a basis:

$$\{a\uparrow a\downarrow, a\uparrow b\uparrow, a\uparrow b\downarrow, a\downarrow b\uparrow, a\downarrow b\downarrow, b\uparrow b\downarrow\}.$$

Each element in the basis is antisymmetrized, for example,

$$a\uparrow b\downarrow \equiv \frac{1}{\sqrt{2}}(|\psi_a(x_1)\uparrow\rangle|\psi_b(x_2)\downarrow\rangle - |\psi_b(x_1)\downarrow\rangle|\psi_a(x_2)\uparrow\rangle).$$

This basis obviously is not formed of eigenstates of the total spin, but only of the z component of the spin.

The new Hamiltonian matrix (ignoring μ_B, the Bohr magneton, for simplicity) is shown in Eq. (5) below:

$$H_1 = \begin{pmatrix} 2\epsilon+U & it\sin\frac{\Theta}{2} & t\cos\frac{\Theta}{2} & -t\cos\frac{\Theta}{2} & -it\sin\frac{\Theta}{2} & 0 \\ -it\sin\frac{\Theta}{2} & 2\epsilon+\frac{h_a+h_b}{2} & 0 & 0 & 0 & -it\sin\frac{\Theta}{2} \\ t\cos\frac{\Theta}{2} & 0 & 2\epsilon+\frac{h_a-h_b}{2} & 0 & 0 & t\cos\frac{\Theta}{2} \\ -t\cos\frac{\Theta}{2} & 0 & 0 & 2\epsilon-\frac{h_a-h_b}{2} & 0 & -t\cos\frac{\Theta}{2} \\ it\sin\frac{\Theta}{2} & 0 & 0 & 0 & 2\epsilon-\frac{h_a+h_b}{2} & it\sin\frac{\Theta}{2} \\ 0 & it\sin\frac{\Theta}{2} & t\cos\frac{\Theta}{2} & -t\cos\frac{\Theta}{2} & -it\sin\frac{\Theta}{2} & 2\epsilon+U \end{pmatrix}. \tag{5}$$

We next make the simplifying assumption that $h_a = h_b = h$. For the case of DMS, since the magnetic ion distribution is random, this can be justified if each polaron has several (N) magnetic ions producing the exchange field on the carrier, so $|h_a - h_b| = h/\sqrt{N} \ll h$. In this case we obtain two pairs of degenerate states $\{a\uparrow a\downarrow, b\uparrow b\downarrow\}$ and $\{a\uparrow b\downarrow, a\downarrow b\uparrow\}$. By making a 45 degree rotation within each of the degenerate subspaces, and by multiplying some of the basis vectors by i when necessary, we single out two of the eigenvalues (2ϵ and $2\epsilon+U$), the rest of the matrix having the simpler form in Eq. (6) below:

$$H_1 \rightarrow \begin{pmatrix} 2\epsilon+h & 0 & 0 & \sqrt{2}t\sin\frac{\Theta}{2} \\ 0 & 2\epsilon & 0 & -2t\cos\frac{\Theta}{2} \\ 0 & 0 & 2\epsilon-h & \sqrt{2}t\sin\frac{\Theta}{2} \\ \sqrt{2}t\sin\frac{\Theta}{2} & -2t\cos\frac{\Theta}{2} & \sqrt{2}t\sin\frac{\Theta}{2} & 2\epsilon+U \end{pmatrix}. \tag{6}$$

This Hamiltonian can be solved by perturbation theory (PT). In the limit $h \rightarrow 0$ the upper three states become degenerate and the problem needs to be handled by degenerate perturbation theory. We will not investigate this limit any further. In the high field limit however, the magnetic field removes the degeneracy and we can obtain the eigenvalues to second order by regular PT. Thus we obtain for the lowest eigenvalues

$$\left(2\epsilon+h-\frac{2t^2\sin^2\frac{\Theta}{2}}{U-h},\; 2\epsilon, 2\epsilon-\frac{4t^2\cos^2\frac{\Theta}{2}}{U},\right. \\ \left. 2\epsilon-h-\frac{2t^2\sin^2\frac{\Theta}{2}}{U+h}\right). \tag{7}$$

C. Heisenberg Hamiltonian with arbitrary fields

By solving the same problem (two atoms in fixed external fields) using a Heisenberg Hamiltonian, and comparing the eignevalues with the results obtained above in Eq. (7), one can see how the effective exchange parameter in the Heisenberg Hamiltonian is affected by external magnetic fields. We start with[12]

$$H_{H1} = \mathbf{h_a}\cdot\mathbf{s_a} + \mathbf{h_b}\cdot\mathbf{s_b} + J\mathbf{s_a}\cdot\mathbf{s_b}. \tag{8}$$

We can again quantize the spins along the axes of the two fields, and work in the basis

$$\{a\uparrow b\uparrow, a\uparrow b\downarrow, a\downarrow b\uparrow, a\downarrow b\downarrow\}$$

which yields the Hamiltonian matrix:

$$H_{H1}=\begin{pmatrix} -h+\frac{J}{4}\cos\Theta & -\frac{J}{4}\sin\Theta & \frac{J}{4}\sin\Theta & -\frac{J}{4}(1-\cos\Theta) \\ -\frac{J}{4}\sin\Theta & -\frac{J}{4}\cos\Theta & \frac{J}{4}(1+\cos\Theta) & -\frac{J}{4}\sin\Theta \\ \frac{J}{4}\sin\Theta & \frac{J}{4}(1+\cos\Theta) & -\frac{J}{4}\cos\Theta & \frac{J}{4}\sin\Theta \\ -\frac{J}{4}(1-\cos\Theta) & -\frac{J}{4}\sin\Theta & \frac{J}{4}\sin\Theta & h+\frac{J}{4}\cos\Theta \end{pmatrix}. \tag{9}$$

After we do a rotation by 45 degrees in the $\{a\uparrow b\downarrow, a\downarrow b\uparrow\}$ subspace we can apply perturbation theory (considering J as a small parameter), which yields (after subtracting J) the eigenvalues:

$$\left(h-\frac{J}{2}\sin^2\frac{\Theta}{2}, 0, -J\cos^2\frac{\Theta}{2}, -h-\frac{J}{2}\sin^2\frac{\Theta}{2}\right). \tag{10}$$

By matching the results in Eq. (7) to those in Eq. (10) in the $h \ll U$ limit $[$ignoring $O(t^2h/U^2)]$ we can make the identification

$$J=\frac{4t^2}{U}. \tag{11}$$

However, when the field is increased, the matching is not perfect anymore, and the effective exchange parameter for the ground state is reduced to

$$J=\frac{4t^2}{U+h}. \tag{12}$$

Thus the appearance of polarons decreases the effective antiferromagnetic exchange between the carriers.

IV. GENERALIZED HUBBARD MODEL

A. Two-level Hubbard model with random fields

One can improve this analysis by considering a more realistic model. The next simplest case is to consider two energy levels 1 and 2 (energies ϵ_1 and ϵ_2) on each atom, and to allow hopping $1\leftrightarrow 1$, $1\leftrightarrow 2$ and $2\leftrightarrow 2$ between sites. Again we consider arbitrary fields h_a and h_b. The Hamiltonian is still given by Eq. (4) with the summation for i going over 1, 2. The number of states increases dramatically: we are dealing now with a 28×28 matrix $[28=6\times(3+1)+4\times 1$ since there are 6 pairs of different spatial states which each can have spin 0 or 1, and 4 pairs of identical states which can only have spin 0]. We need to concentrate on the lowest energy states only, treating the rest perturbatively. We ignore the $2\leftrightarrow 2$ hopping, since it affects the lowest eigenvalues only to higher order in PT. We are using again the simplifying assumption $h_a=h_b=h$.

The lowest energy subspace can be identified as being spanned by $\{a1\uparrow b1\uparrow, a1\uparrow b1\downarrow, a1\downarrow b1\uparrow, a1\downarrow b1\downarrow\}$. By applying second order degenerate PT in this subspace, we obtain the following expressions for the eigenvalues

$$\begin{pmatrix} 2\epsilon_1+h-\dfrac{2t_{12}^2\cos^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}}-\dfrac{2t_{12}^2\sin^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}-h}-\dfrac{2t_{11}^2\sin^2\frac{\Theta}{2}}{U_{11}-h} \\ 2\epsilon_1-\dfrac{2t_{12}^2\cos^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}}-\dfrac{t_{12}^2\sin^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}-h}-\dfrac{t_{12}^2\sin^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}+h} \\ 2\epsilon_1-\dfrac{4t_{11}^2\cos^2\frac{\Theta}{2}}{U_{1a}}-\dfrac{2t_{12}^2\cos^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}}-\dfrac{t_{12}^2\sin^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}-h}-\dfrac{t_{12}^2\sin^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}+h} \\ 2\epsilon_1-h-\dfrac{2t_{12}^2\cos^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}}-\dfrac{2t_{12}^2\sin^2\frac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}+h}-\dfrac{2t_{11}^2\sin^2\frac{\Theta}{2}}{U_{11}+h} \end{pmatrix}. \tag{13}$$

TABLE I. The couplings of the ground state of the many-level Hubbard model to various excited states.

State	Coupling	Energy diff.
$a(b)\psi_0\downarrow a(b)\psi_0\uparrow$	$\pm i t_{00}\sin(\frac{\Theta}{2})$	$U_{00}+h$
$a(b)\psi_i\uparrow a(b)\psi_0\downarrow, a(b)\psi_i\downarrow a(b)\psi_0\uparrow$	$\pm i t_{0i}\sin(\frac{\Theta}{2})$	$\epsilon_i-\epsilon_0+U_{0i}+h$
$a(b)\psi_i\downarrow a(b)\psi_0\downarrow, a(b)\psi_i\uparrow a(b)\psi_0\uparrow$	$\pm t_{0i}\cos(\frac{\Theta}{2})$	$\epsilon_i-\epsilon_0+U_{0i}$

One can see that in the limit $t_{12}\rightarrow 0$ we obtain the same results as in the one-level Hubbard model analyzed in the beginning. This is a good consistency check.

B. Magnetic properties of the ground state

By applying second order perturbation theory to the two-level Hubbard model (and considering $h \gg t^2/U$), we therefore obtain the following expression for the ground-state energy:

$$E_{\mathrm{GS}}=2\epsilon_1-h-\frac{2t_{12}^2\cos^2\dfrac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}}-\frac{2t_{12}^2\sin^2\dfrac{\Theta}{2}}{\epsilon_2-\epsilon_1+U_{12}+h}-\frac{2t_{11}^2\sin^2\dfrac{\Theta}{2}}{U_{11}+h}. \tag{14}$$

The angle Θ between the two fields was regarded up to this point as an external parameter. All the calculations so far were done under the assumption that the magnetic field was fixed externally. We must take, however, into account the fact that the field is generated by the actual polaron, and that although the magnitude of the field is fixed by the size of the polaron, the direction is free to change. Therefore, when $T\rightarrow 0\,\mathrm{K}$, Θ takes the value that minimizes the energy. Since $E_{\mathrm{GS}}(\Theta)=\mathrm{const.}+A(h)\sin^2(\Theta/2)$, with

$$A(h)=\frac{2t_{12}^2}{\epsilon_2-\epsilon_1+U_{12}}-\frac{2t_{12}^2}{\epsilon_2-\epsilon_1+U_{12}+h}-\frac{2t_{11}^2}{U_{11}+h}$$

the two values that minimize the value of the energy are $\Theta=0$ and $\Theta=\pi$, depending on the sign of the factor $A(h)$. We can regard A, which represents the energy difference between the ferromagnetic and the antiferromagnetic configurations, as an effective exchange constant. For small values of the polaron field it is the antiferromagnetic state that dominates, whereas if we increase the polaron field the ground state of the system becomes ferromagnetic.

In order to get an idea of what parameters are essential for the transition, let us solve $A(h)=0$, which is just a quadratic equation. The critical field is given by the only acceptable (positive) root:

$$h_c=U_{11}\frac{-1+\alpha\beta+\sqrt{1-2\alpha\beta+\alpha^2\beta^2+4\alpha\beta^2}}{2}, \tag{15}$$

where we have defined $\alpha=(t_{11}/t_{12})^2$ and $\beta=(U_{12}+\epsilon_2-\epsilon_1/U_{11})$. In the one-level limit, thus, the transition disappears (we have $\alpha\rightarrow\infty\Rightarrow h\rightarrow\infty$). The ferromagnetic configuration happens then as a consequence of the local magnetic fields *and* of the hopping to excited states. As a side remark we observe that while β depends entirely on the type of dopant used, α depends both on the type of dopant *and* on the dopant density (since all the transition probabilities depend on the separation of the atoms). Thus we may have a transition from a polaron ferromagnetic to an antiferromagnetic ground state configuration as the density is varied. It turns out that for the two-level (hydrogenic ground state and any excited state) approximation, α can take virtually any value from $\alpha=0$ for 0 separation, to $\alpha\rightarrow\infty$ when the separation becomes infinite.

C. Many-level Hubbard model

One can generalize the results presented above about the ground state of a two-level Hubbard model to the case where any number of bound excited states exists. Consider $|\psi_i\uparrow\rangle$ and $|\psi_i\downarrow\rangle$ (with energies ϵ_i) to be the one-electron states, indexed by the subscript i ($i=0$ for the ground state). We consider the ground state to be nondegenerate, however, allowing arbitrary degeneracies for all the other states. The ground state of the two-electron system in a magnetic field is then: $a\psi_0\downarrow b\psi_0\downarrow$, with energy (in the zeroth order) $2\epsilon_0-h$. We allow the hopping of an electron from the ground state of one atom to any state of the other atom, the coupling constants between $a\psi_0$ and $b\psi_i$ being given by t_{0i}. Expression (4) gives the right Hamiltonian with the summation for α being over a,b, corresponding to only two interacting polarons.

The couplings of the groundstate $a\psi_0\downarrow b\psi_0\downarrow$ to various other states are given in Table I. Applying second order nondegenerate PT, we obtain for the ground-state energy:

$$E_{\mathrm{GS}}=2\epsilon_0-h-\frac{2t_{00}^2\sin^2\dfrac{\Theta}{2}}{U_{00}+h}-\left(\sum_i\frac{2t_{0i}^2}{\epsilon_i-\epsilon_0+U_{0i}}\right)\cos^2\frac{\Theta}{2}-\left(\sum_i\frac{2t_{0i}^2}{\epsilon_i-\epsilon_0+U_{0i}+h}\right)\sin^2\frac{\Theta}{2}. \tag{16}$$

We can apply the same kind of analysis as for the two-level case above, however, $A(h)$, the effective exchange constant whose sign dictates the magnetic configuration now becomes

$$A(h)=\sum_i\frac{2t_{0i}^2}{\epsilon_i-\epsilon_0+U_{0i}}-\sum_i\frac{2t_{0i}^2}{\epsilon_i-\epsilon_0+U_{0i}+h}-\frac{2t_{00}^2}{U_{00}+h}. \tag{17}$$

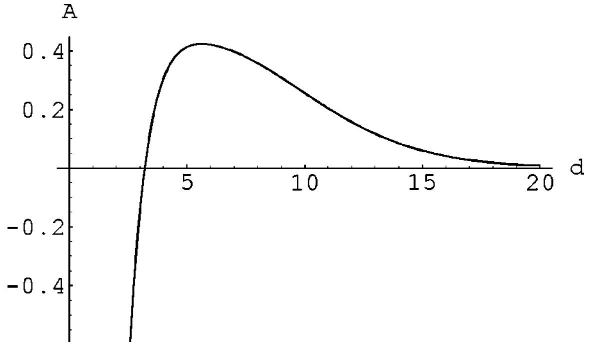

FIG. 1. The effective exchange A as a function of the dopant separation d. The polaron field was taken as $h=0.3$ Ry.

The value of the critical field above which the ferromagnetic configuration becomes energetically favorable is again given by the equation $A(h_c)=0$, however, this cannot be solved analytically anymore.

D. Application to hydrogenic centers

We can understand the details of this change of magnetic configuration better if we derive the actual couplings and Coulomb terms from a simplified model of the dopant. As discussed in the Introduction, one can use simple hydrogenic models: two H atoms separated by a distance ρ in magnetic fields $\mathbf{h_a},\mathbf{h_b}$. We obtained the two-center overlap integrals (t_{0i}) by using explicit machine-readable formulas that have been constructed by applying symbolic calculation to the ζ-function method of Barnett and Coulson. The mathematical formalism has been described originally here.[13] The symbolic calculations are described here[14,15] and the work cited therein. The evaluation of one-center Coulomb integrals (U_{0i}) was done following an approach described in some textbooks.[16]

We considered hydrogenic centers, and included transitions and Coulomb interaction energies between the ground-state $1s$ and the states $1s$, $2s$, $2p_z$, $3s$, $3p_z$, and $3d$. Figure 1 plots the effective exchange A as a function of separation d between the two centers, for a fixed value of the polaron effective field, $h=0.3$ Ry, which is still small compared to the Rydberg [$A(d)$ obtained from Eq. (17), with $t_{0i}(d)$ calculated from the integrals given in Refs. 13,14]. It can be seen that the effective exchange A becomes positive at a certain dopant separation d_c and thus the favorable configuration becomes ferromagnetic. The existence of the transition from antiferromagnetic to ferromagnetic behavior is independent on the choice of h, the polaron field. Also, the critical separation d_c is quite insensitive to the choice of h (the only parameter of the model). As an example, for $h=0.1$ Ry, $d_c=3.91a_B$; for $h=0.3$ Ry, $d_c=3.20a_B$ and for $h=1$ Ry, $d_c=2.48a_B$. All of these figures are within typical experimental range. Figure 2 plots the critical field h_c as a function of the dopant separation d. For $d>4a_B$, which is true for typical experimental doping densities, the minimal value of the polaron field that will provide a ferromagnetic interaction becomes reasonable (a few tenth of a Rydberg) and therefore we can conclude that our model predicts ferromagnetic interractions between polarons in DMS.

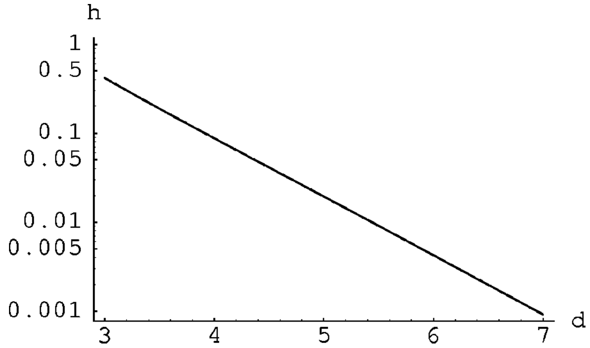

FIG. 2. The critical field h_c (in Ry) vs the dopant separation d (in a_B). The log-linear plot reveals the exponential behavior of the critical field on the dopant separation.

V. SPIN HAMILTONIAN FOR MODERATE FIELDS

Coming back to our fixed magnetic field model, we note that both the one- and two-level Hubbard models agree with the Hamiltonian of Eq. (8), containing the standard Heisenberg exchange and Zeeman terms when contributions of order $O(t^2h/U^2)$ are ignored. However, when those contributions are taken into account, Eq. (8) does not provide the right solutions anymore. The question to be asked is whether it is possible to modify the Hamiltonian so as to have agreement up to $O(t^2h/U^2)$. It turns out that this is indeed possible.

If we expand the terms in Eq. (7) we obtain the energies

$$\left(2\epsilon+h-\frac{2t^2\sin^2\frac{\Theta}{2}}{U}-\frac{2t^2h\sin^2\frac{\Theta}{2}}{U^2},\ 2\epsilon,\ 2\epsilon-\frac{4t^2\cos^2\frac{\Theta}{2}}{U},\right.$$

$$\left.2\epsilon-h-\frac{2t^2\sin^2\frac{\Theta}{2}}{U}+\frac{2t^2h\sin^2\frac{\Theta}{2}}{U^2}\right). \tag{18}$$

We need to add some small correction to Eq. (8) that is linear in the fields and reproduces the above structure. There are several ways of doing this, the simplest being to add a term of the form $\mathbf{h_a}\cdot\mathbf{s_b}+\mathbf{h_b}\cdot\mathbf{s_a}$ or $\mathbf{h}\cdot\mathbf{s_a}\times\mathbf{s_b}$ or $\mathbf{h_a}\cdot\mathbf{s_a}+\mathbf{h_b}\cdot\mathbf{s_b}$ (or any linear combination thereof). It turns out that the Hamiltonian

$$H_{H2}=(1-\alpha)(\mathbf{h_a}\cdot\mathbf{s_a}+\mathbf{h_b}\cdot\mathbf{s_b})+J\mathbf{s_a}\cdot\mathbf{s_b}+\alpha(\mathbf{h_a}\cdot\mathbf{s_b}+\mathbf{h_b}\cdot\mathbf{s_a}) \tag{19}$$

reproduces the right structure. In the basis $\{a\uparrow b\uparrow, a\uparrow b\downarrow, a\downarrow b\uparrow, a\downarrow b\downarrow\}$ it becomes

$$\begin{pmatrix} -(1-\alpha)h+\left(\frac{J}{4}-\alpha h\right)\cos\Theta & -\left(\frac{J}{4}-\frac{\alpha h}{2}\right)\sin\Theta & \left(\frac{J}{4}-\frac{\alpha h}{2}\right)\sin\Theta & -\frac{J}{4}(1-\cos\Theta) \\ -\left(\frac{J}{4}-\frac{\alpha h}{2}\right)\sin\Theta & -\frac{J}{4}\cos\Theta & \frac{J}{4}(1+\cos\Theta) & -\left(\frac{J}{4}+\frac{\alpha h}{2}\right)\sin\Theta \\ \left(\frac{J}{4}-\frac{\alpha h}{2}\right)\sin\Theta & \frac{J}{4}(1+\cos\Theta) & -\frac{J}{4}\cos\Theta & \left(\frac{J}{4}+\frac{\alpha h}{2}\right)\sin\Theta \\ -\frac{J}{4}(1-\cos\Theta) & -\left(\frac{J}{4}+\frac{\alpha h}{2}\right)\sin\Theta & \left(\frac{J}{4}+\frac{\alpha h}{2}\right)\sin\Theta & (1-\alpha)h+\left(\frac{J}{4}+\alpha h\right)\cos\Theta \end{pmatrix}.$$

After doing the necessary 45 degree rotation in the $\{a\uparrow b\downarrow, a\downarrow b\uparrow\}$ subspace the matrix becomes suitable for PT and it yields the eigenvalues (to first order in J and α and after subtracting a common J):

$$\left(h-\frac{J}{2}\sin^2\frac{\Theta}{2}-2\alpha h\sin^2\frac{\theta}{2},\ 0,\ -J\cos^2\frac{\Theta}{2},\right.$$
$$\left.-h-\frac{J}{2}\sin^2\frac{\Theta}{2}+2\alpha h\sin^2\frac{\theta}{2}\right). \tag{20}$$

By matching the results in Eq. (20) to Eq. (18) we obtain for the parameters of the modified Hamiltonian

$$J=\frac{4t^2}{U},\qquad \alpha=\frac{t^2}{U^2}. \tag{21}$$

One can also expand the result for the two-level Hubbard model to get a better estimate for the parameters. In that case one obtains

$$J=\frac{4t_{11}^2}{U_{11}},\qquad \alpha=\frac{t_{11}^2}{U_{11}^2}+\frac{t_{12}^2}{(\epsilon_2-\epsilon_1+U_{12})^2}. \tag{22}$$

VI. CONCLUSION

The calculations presented above lead us to two conclusions:

(I) They confirm once more the fact that the polarons formed in dilute magnetic semiconductors can interact ferromagnetically for certain dopant densities and types. This extends the results obtained by Refs. 10,11 in the limit that the polarons have an important overlap to the situation where the two polarons do not overlap at all. Thus, the two qualitatively distinct effects combine in order to generate an effective ferromagnetic interaction of the bound magnetic polarons in a DMS.

(II) For the case where two one-electron atoms are placed in fixed, but nonparallel external magnetic fields, the standard model with Heisenberg exchange and Zeeman terms is not a suitable approximation. Instead, the calculations above give a correction, with which we are able to reproduce the correct spectrum in the moderately high field domain ($t \ll h \ll U$). The correction represents an effective mixing of the fields at the two sites, which can be intuitively understood as a ‘‘transfer’’ of the field from one site to the other by the hopping electron. In the high field domain ($h<U$), this correction is not valid anymore and the correct model is a Heisenberg Hamiltonian with a field-dependent exchange constant.

We will return now to Conclusion (I) with a few remarks. The change from antiferromagnetic to ferromagnetic effective coupling in the presence of strong local fields in the generalized Hubbard model naturally leads one to the question whether this would actually occur in an exact calculation. We believe it does, though the parameter values for the change are likely to be different. To explain our ‘‘belief,’’ we consider the case of the hydrogen molecule problem in zero field, where the issue of the effective Heisenberg Hamiltonian has been thoroughly discussed.[17,18,6,19]

In Fig. 3 we plot the effective exchange parameter as a function of $d=(r/a_B)$ in the range 1–8, as calculated in four different ways. The solid line represents the Herring–Flicker[6] (HF) result, $J_{\mathrm{HF}}(r)=1.636(r/a_B)^{5/2}\exp(-2r/a_B)$ Ry, which is asymptotically exact [in the sense that $J_{\mathrm{HF}}(r)/J_{\mathrm{exact}}(r)\rightarrow 1$ as $r/a_B\rightarrow\infty$], while the dots are the numerically converged results of Kolos and Wolniewicz[20] (KW). Both show that $J(r)$ is positive (antiferromagnetic) for all r. The dashed line is the result of the Heitler–London[18] (HL) approximation, which, though clearly not exact, works reasonably well on this logarithmic plot for the range shown. It should be noted, however, that

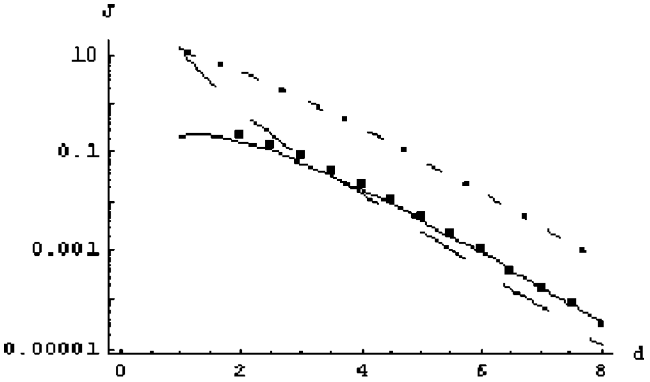

FIG. 3. The effective exchange parameter as a function of reduced distance (r/a_B) for Herring–Flicker (solid), Kolos–Wolniewicz (dots), Heitler–London (dashed), and Hubbard model (dot–dashed).

while the HL result has the right sign of $J(r)$ for the range of r/a_B shown, it incorrectly predicts a negative $J(r)$ at large r/a_B because it does not take into account polarization corrections to the ground state hydrogenic wave function. Finally, as the dot-dashed curve, is the standard Hubbard model result, $J(r)=4t^2(r)/U$, with $t(r)=2(1+r/a_B)\exp(-r/a_B)$ Ry and $U=5/4$ Ry, calculated within the ground-state approximation for the hydrogen wave functions (the generalized Hubbard model would give the same result in this case without external fields, as adding excited states does not alter the second order splitting between the lowest singlet and triplet states).

As can be clearly seen, the Hubbard approximation overestimates $J(r)$ by a large factor [this qualitative fact does not change with more refined estimates for $t(r)$ and U]. The reason for the larger exchange is that Hubbard, and Hubbard-like approximations, consider only the kinetic exchange (due to the hopping process), which is antiferromagnetic, and neglect Coulomb exchange which tends to favor ferromagnetism. (Such a split is often used in literature[21]). The latter *is* included in the ''exact'' HF/KW treatment, as well as the HL approximation, resulting in a much lower value net (antiferromagnetic) exchange.

We expect that inclusion of local magnetic fields h_i of equal magnitude (h), which couple only to the electron spin is properly captured on a qualitative/semiquantitative level by the extended Hubbard model. Therefore inclusion of such fields in a more accurate model will also result in a movement of the kinetic exchange towards ferromagnetism; consequently, the overall exchange will change over to ferromagnetic at some value of h. If we just add a field independent (ferromagnetic) Coulomb term to the kinetic exchange of the generalized Hubbard model, the change from antiferromagnetism to ferromagnetism would be expected at lower values of h than we have calculated, and make the effect we consider more relevant for DMS systems.

We caution, though, that for the purely hydrogenic problem with local fields, one must take into account the effect of the magnetic field on the orbital wave function as well, and that will certainly affect the results, at least quantitatively. In the case of DMS, the local fields represent exchange fields due to interaction of hydrogenic states with local atomic states of the magnetic ion (Mn), and therefore their orbital effect is not the same as that of external magnetic fields in the H_2 problem. Nevertheless, we expect these to have some effect on the orbital part of the wave function of the hydrogenic impurity,[22] which would have at least a quantitative effect on our results.

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