The magnetopolaron effect in acceptor bound states in semimagnetic semiconductors

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We solve the problem of how the exchange interaction affects the ground state of an acceptor in a semimagnetic semiconductor with a complex valence band (the hole spin is $J = 3/2$). We show that the strong spin-orbit interaction of the bound hole implies that, in contrast to the Hamiltonian for a free particle, the Hamiltonian describing the exchange interaction between the hole and the magnetic ions in the lattice has a non-Heisenberg form; this is also true for an electron localized on a donor at the edge of a simple conduction band. The non-Heisenberg correction ensures that the maximum energy of the bound magnetic polaron corresponds to an inhomogeneous distribution of magnetization of the ions, while the ground state energy level of the acceptor is split into unequally-spaced sublevels. The cases of an acceptor center with a "zero-radius" potential and with a Coulomb potential are analyzed in detail. In solving this problem, we use the continuum approximation for the spatial distribution of magnetic ions. For both model potentials, it is found that the ground state of the polaron has axial symmetry, while the total momentum of the hole in these cases attains its maximum value, $|\langle \mathbf{F} \rangle| = 3/2$. We evaluate the polaron energy for the ground and first excited states as a function of $\gamma = m_l/m_h$, the ratio of the light to the heavy hole masses. Characterization of the splitting of the acceptor level according to projection of the total angular momentum F cannot be maintained if the discreteness in the positions of the magnetic ions is taken into account, or if a specific model of the impurity center is postulated.

1. INTRODUCTION

Recently, there have been a number of theoretical and experimental papers devoted to investigating magnetopolaron effects in semimagnetic semiconductors.[1–8] In these crystals, the strong exchange interaction between electrons, holes and magnetic ions in the lattice leads to considerable mutual alignment of their spins. Polarization of the magnetic ions causes splitting of the spin states of an electron and hole, while a charge carrier in a definite spin state in turn maintains the magnetic ions around it in a polarized state. (Analogous effects in magnetic semiconductors were studied earlier.[9–10])

The magnetopolaron effect appears, e.g., in the strong temperature-dependent shift of the luminescence line of excitons bound to acceptors[1–3], and in the gigantic Stokes shift observed in Raman scattering.[7]

In this article we investigate the problem of how the magnetopolaron effect influences acceptor states in semimagnetic semiconductors with cubic symmetry at zero temperature. In the crystals we will discuss—the A^2B^6 compounds—the energy spectrum of holes has a point of fourfold degeneracy for $p = 0$ ($\mathbf{p}$ is the hole quasimomentum). Therefore, for energies small compared to the magnitude of the spin-orbit interaction, the hole can be treated as a particle with effective spin $J = 3/2$ (Ref. 11).

In earlier attempts to construct a theory of the magnetopolaron effect, researchers used simplified models in which the complex structure of the valence band was ignored. In fact, it was assumed that the spin of a charge carrier is $J = 1/2$. This simplification leaves unexplained many qualitative peculiarities of the magnetic polaron which forms from a bound hole. Actually, the spins of the magnetic ions are always oriented along the effective exchange field, which is directed parallel or antiparallel to the carrier spin $\mathbf{J}$. In the case of an electron, the direction of this field does not change in space because the projection of the spin on the quantization axis is conserved. For the bound hole, only the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{L}$ is conserved (here $\mathbf{L}$ is the hole orbital angular momentum). Therefore, the direction of spin for the hole depends on the coordinates, and generally speaking does not coincide with the direction of the quantization axis. The exchange field of the hole varies in space both in magnitude and direction; because of these variations the orientations of the spins of the magnetic ions also change.[12,13] The ground state of a hole bound to an acceptor is split into four inequivalent sublevels; to each sublevel there corresponds a definite projection of the total orbital momentum of the hole and an axisymmetric exchange field. The state with the largest projection of total angular momentum on the axis of symmetry of the magnetic polaron ($|\langle \mathbf{F} \rangle| = 3/2$) has the lowest energy.

The calculations were carried out for two model acceptor potentials: the "zero-radius" potential and the Coulomb potential. Using these potentials, we have studied how the energy splitting of the acceptor sublevels depend on the parameters of the complex valence band.

2. HAMILTONIAN AND EXCHANGE INTERACTION ENERGY

The exchange interaction Hamiltonian for a hole with a magnetic ion has the form

$$V_{ex} = \frac{1}{3}\beta \sum_n \hat{\rho}(\mathbf{r}_n)\,(\hat{\mathbf{J}}\hat{\mathbf{I}}_n), \tag{1}$$

where $\hat{p}(\mathbf{r}_n) = \delta(\mathbf{r} - \mathbf{r}_n)$ is the density operator of the hole at the nth magnetic ion, $\mathbf{r}_n$ and $\hat{\mathbf{I}}_n$ are the radius vector and

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the spin of this ion, $\hat{\mathbf{J}}$ is the spin operator of the hole and β is the exchange interaction constant.

Usually the ground state of an acceptor in a cubic semiconductor is fourfold degenerate and has a total angular momentum $F = 3/2$ (Ref. 14). The wave function of such a state contains a spin part $\chi\sigma$ and an orbital part Y_{lm}. Because the spin of the hole is $J = 3/2$, the angular momentum of the orbital motion for a state with $F = 3/2$ can take on only two values, $1 = 2$ and $1 = 0$. The hole wave functions have the form

$$\Psi_M = 2\sum_{lm\sigma}(-1)^{l-3/2+M}\begin{pmatrix} l & 3/2 & 3/2 \\ m & \sigma & -M \end{pmatrix} R_l Y_{lm}\chi_\sigma. \qquad (2)$$

Here M, m and σ are projections of F, l, and J onto the quantization axis Z, and $R_l(r)$ are the radial parts of the wave functions. The coefficients in Eq. (2) are the Wigner $3j$-symbols. A truncated Hamiltonian for the exchange interaction can be constructed out of the functions (2) in the form

$$\tilde{V} = \sum_n \tilde{V}_n = \sum_n \{a_n(\hat{\mathbf{F}}\hat{\mathbf{I}}_n) + b_n[(\hat{\mathbf{F}}\mathbf{r}_n)^2(\hat{\mathbf{F}}\hat{\mathbf{I}}_n) + (\hat{\mathbf{F}}\hat{\mathbf{I}}_n)(\hat{\mathbf{F}}\mathbf{r}_n)^2] + a_{1n}(\mathbf{r}_n\hat{\mathbf{I}}_n)(\hat{\mathbf{F}}\mathbf{r}_n) + b_{1n}(\mathbf{r}_n\hat{\mathbf{I}}_n)(\hat{\mathbf{F}}\mathbf{r}_n)^3\}. \qquad (3)$$

The coefficients a_n, b_n, a_{1n}, b_{1n} can be expressed in terms of the functions

$$R_0(r_n) = R_{0n}, \quad R_2(r_n) = R_{2n},$$

e.g., as follows. Direct the Z-axis along $\mathbf{r}_n$. Then the wave function at the point $\mathbf{r}_n$ will be in its simplest form:

$$\Psi_{3/2}(r_n) = \frac{1}{(4\pi)^{1/2}}(R_{0n} - R_{2n})\chi_{3/2},$$

$$\Psi_{1/2}(r_n) = \frac{1}{(4\pi)^{1/2}}(R_{0n} + R_{2n})\chi_{1/2}. \qquad (4)$$

Let us calculate the four matrix elements of the operator $\tilde{V}_n$ using the functions (4) and the explicit expression (1). By comparing with (3) we obtain

$$\left\langle \frac{3}{2}\middle|\tilde{V}_n\middle|\frac{3}{2}\right\rangle = \frac{3}{2}\left(a_n + \frac{9}{2}b_n r_n^2 + a_{1n}r_n^2 + \frac{9}{4}b_{1n}r_n^4\right)\hat{I}_{nz} = \frac{\beta}{8\pi}(R_{0n} - R_{2n})^2\hat{I}_{nz},$$

$$\left\langle \frac{1}{2}\middle|\tilde{V}_n\middle|\frac{1}{2}\right\rangle = \frac{1}{2}\left(a_n + \frac{1}{2}b_n r_n^2 + a_{1n}r_n^2 + \frac{1}{4}b_{1n}r_n^4\right)\hat{I}_{nz} = \frac{\beta}{24\pi}(R_{0n} + R_{2n})^2\hat{I}_{nz},$$

$$\left\langle \frac{3}{2}\middle|\tilde{V}_n\middle|\frac{1}{2}\right\rangle = \left(a_n + \frac{5}{2}b_n r_n^2\right)\left\langle \frac{3}{2}\middle|\hat{F}\hat{I}_n\middle|\frac{1}{2}\right\rangle = \frac{\beta}{12\pi}(R_{0n}^2 - R_{2n}^2)\left\langle \frac{3}{2}\middle|\hat{F}\hat{I}_n\middle|\frac{1}{2}\right\rangle,$$

$$\left\langle \frac{3}{2}\middle|\tilde{V}_n\middle|-\frac{1}{2}\right\rangle = \left(a_n + \frac{1}{2}b_n r_n^2\right)\left\langle \frac{1}{2}\middle|\hat{F}\hat{I}_n\middle|-\frac{1}{2}\right\rangle = \frac{\beta}{12\pi}(R_{0n}^2 + R_{2n}^2)\left\langle \frac{1}{2}\middle|\hat{F}\hat{I}_n\middle|-\frac{1}{2}\right\rangle. \qquad (5)$$

From (5) we obtain the desired expression

$$a_n = \frac{\beta}{24\pi}(2R_{0n}^2 + 5R_{0n}R_{2n} + 3R_{2n}^2),$$

$$b_n r_n^2 = -\frac{\beta}{12\pi}R_{2n}(R_{0n} + R_{2n}), \qquad (6)$$

$$b_{1n}r_n^4 = -4a_{1n}r_n^2 = \frac{\beta}{6\pi}R_{2n}^2.$$

The Hamiltonian (3) has a much more complex structure than the corresponding Hamiltonian for a center with states close to the edge of a simple band, for which the exchange Hamiltonian contains only the first term in (3) ($3^{-1}\Sigma_n(\hat{\mathbf{F}}\hat{\mathbf{I}}_n)$). (In other words, the Bloch functions of a donor center contain only s-waves.) The additional terms containing the scalar product $(\hat{\mathbf{F}}\mathbf{r}_n)$ describe, among other things, the transfer of angular momentum from the hole to the crystal lattice. The presence of terms cubic in $\mathbf{F}$ among these additional terms leads to unequal spacing of the hole sublevels in the field of the magnetic ions.

With regard to the ion spins $\hat{\mathbf{I}}_n$, the changes in the Hamiltonian are not so noticeable. As in the simpler cases, the interaction of an ion with the spin of a localized hole is described by the scalar product of $\hat{\mathbf{I}}_n$ with an effective scalar field

$$\hat{\mathbf{B}}(\mathbf{r}_n) = \hat{\mathbf{J}}\hat{\rho}(\mathbf{r}_n)\beta/3, \qquad (7)$$

which now depends on $\mathbf{F}$ in a complicated way. It can be shown from (3) that the Hermitian matrix components of this field have an additional intrinsic symmetry

$$\mathbf{B}_{M,M'}(\mathbf{r}_n) = (-1)^{M+M'}\mathbf{B}_{-M',-M}(\mathbf{r}_n), \qquad (8)$$

where

$$\mathbf{B}_{M,M'}(\mathbf{r}_n) = \langle\Psi_M(\mathbf{r}_n)|\hat{\mathbf{J}}|\Psi_{M'}^*(\mathbf{r}_n)\rangle\beta/3, \qquad (9)$$

which considerably reduces the number of independent matrix elements of the exchange field $\mathbf{B}$. The explicit form of these matrix elements is given in Appendix I.

Despite the complex form of the matrix (3), we can find its eigenvalues for any configuration of magnetic ion spins. The corresponding secular equation is found to be biquadratic, and has the form of a pair of eigenvalues with equal absolute values but opposite signs:

$$\varepsilon_1 = -\varepsilon_3, \quad \varepsilon_2 = -\varepsilon_4,$$

$$\varepsilon_{1,2}^2 = \frac{1}{2}[f_1^2 + f_2^2 + f_3^2 + f_4^2 + f_5^2 + f_6^2 + 2(f_7^2 + f_8^2 + f_9^2 + f_{10}^2)] \pm \Big\{\frac{1}{4}(f_1^2 + f_3^2 + f_4^2 - f_2^2 - f_5^2 - f_6^2)^2 + [(f_1 + f_2)f_8 + (f_3 + f_5)f_{10} + (f_4 + f_6)f_9]^2 + [(f_1 + f_2)f_7 + (f_5 - f_3)f_9 + (f_6 - f_4)f_{10}]^2 + [(f_1 - f_2)f_9 + (f_3 + f_5)f_7 + (f_4 - f_6)f_8]^2 + [(f_1 - f_2)f_{10} + (f_5 - f_3)f_8 + (f_4 + f_6)f_7]^2\Big\}^{1/2}. \qquad (10)$$

Here

$$f_i=\sum_n \mathbf{B}_i(\mathbf{r}_n)\mathbf{I}_n,$$

$$\begin{aligned}
\mathbf{B}_1&=\mathbf{B}_{1/2\,1/2}, \quad \mathbf{B}_2=\mathbf{B}_{1/2\,1/2},\\
\mathbf{B}_3&=\mathrm{Re}(\mathbf{B}_{-1/2\,1/2}), \quad \mathbf{B}_4=\mathrm{Im}(\mathbf{B}_{-1/2\,1/2}),\\
\mathbf{B}_5&=\mathrm{Re}(\mathbf{B}_{-1/2\,1/2}), \quad \mathbf{B}_6=\mathrm{Im}(\mathbf{B}_{-1/2\,1/2}),\\
\mathbf{B}_7&=\mathrm{Re}(\mathbf{B}_{1/2\,1/2}), \quad \mathbf{B}_8=\mathrm{Im}(\mathbf{B}_{1/2\,1/2}),\\
\mathbf{B}_9&=\mathrm{Re}(\mathbf{B}_{-1/2\,1/2}), \quad \mathbf{B}_{10}=\mathrm{Im}(\mathbf{B}_{-1/2\,1/2}).
\end{aligned} \tag{11}$$

However, in view of the immense number of possible spin configurations, such a calculation by itself cannot give information about the observed characteristics of the center at nonzero temperatures. In the next section, we will discuss how to analyze the simplest situation, in which we bypass the thermodynamic averaging over the various spin configurations of magnetic ions, and find the configuration corresponding to the most tightly bound hole level.

3. GROUND STATE OF A HOLE ON AN ACCEPTOR AT $T=0$ K

3.1. In order to find the state with the largest magnetopolaron energy directly, i.e., by using Eq. (3), we would have to optimize this equation for an infinite number of arguments (the angles of the vectors $\hat{\mathbf{I}}_n$). It is more convenient to proceed in another way.

First, given an arbitrary hole wave function

$$\Psi=\sum_M c_M\Psi_M \tag{12}$$

let us find the spin configuration of magnetic ions which corresponds to the maximum value of the magnetopolaron energy

$$\langle\varepsilon(c)\rangle=\sum_{MM'} c_M c_{M'}{}^*\langle M|\hat{V}|M'\rangle. \tag{13}$$

To do this, we must align the spin of each ion $\mathbf{I}_n$ parallel to the local field acting on it:

$$\langle\mathbf{B}(\mathbf{r}_n)\rangle=\sum_{MM'} c_M c_{M'}{}^*\mathbf{B}_{MM'}(\mathbf{r}_n). \tag{14}$$

(Here and henceforth we will denote a quantum-mechanical average over the wave function Ψ by the angular brackets). Then

$$\langle\varepsilon(c)\rangle=\left(\sum_n|\mathbf{B}(\mathbf{r}_n)|\right)I \tag{15}$$

is a function of four complex arguments in all, which satisfy the normalization condition $\Sigma_M|c_M|^2=1$.[1)]

In analogy with the problem of an impurity center with states near a simple conduction band edge, it is natural to assume that the largest value of the correlation energy $\langle\varepsilon(c)\rangle$ corresponds to large average values of angular momentum which are close to the maximum possible value the hole can have, i.e., $|\langle\mathbf{F}\rangle|=3/2$. As we will show below, it is just this situation which obtains in the case of a center described by a "zero-radius" potential or by a Coulomb potential. However, in the general case such an assumption can turn out to be erroneous.

In Eq. (15), we assume that the ion spin is parallel to $\langle\mathbf{B}(\mathbf{r}_n)\rangle$. In doing this, we approximated the magnetic ion spin as a classical vector. Let us also make use of a second important simplification: we replace the summation over magnetic ions in the Hamiltonian by a volume integration. Both approximations are useful when $Na_h{}^3\gg 1$, where N is the concentration of magnetic ions and a_h is the acceptor radius.

Actually, the exchange interaction energy is additive in the number of magnetic ions $Na_h{}^3$ within the polaron; therefore, the relative error in determining this energy is of order $\delta_n\approx(Na_h{}^3)^{-1/2}$. The additivity of the polaron energy in fact implies that the spin of the hole interacts with the total spin of the magnetic ions, i.e., $Na_h{}^3I$. The quantum-mechanical indeterminacy of the length of this spin is of order $(Na_h{}^3)^{1/2}$, while the relative error in replacing the spins of the magnetic ions by a classical vector is $\delta_{cl}\approx(Na_h{}^3)^{-1/2}$. A numerical estimate of the error in this approximation will be given below for specific materials.

Let us investigate the interaction energy of the hole $d\varepsilon$ with the ions located in a thin spherical layer of radius r. From the explicit form of the Hamiltonian (3) we can obtain the following expression for the vector $\langle\mathbf{B}(\mathbf{r})\rangle$:

$$\begin{aligned}
\langle\mathbf{B}(\mathbf{r})\rangle=\{&(5+4\eta-\eta^2)\langle\mathbf{F}\rangle+6(\eta^2-2\eta)(\langle\mathbf{F}\rangle\mathbf{e})\mathbf{e}\\
&+(\eta+\eta^2)\mathbf{k}-\eta^2(\mathbf{k}\mathbf{e})\mathbf{e}\}\frac{\beta R_0{}^2(r)}{40\pi},
\end{aligned} \tag{16}$$

where $\eta=R_2(r)/R_0(r)$; $\mathbf{e}=\mathbf{r}/r$ is a unit vector along $\mathbf{r}$, while the components of the vector $\mathbf{k}$ are expressed through the components of the octupole moment tensor of the hole (see Ref. 15, p. 305):

$$\langle T_q{}^3\rangle=\sum_{MM'} c_M c_{M'}{}^*\begin{pmatrix}3/2 & 3 & 3/2\\ -M' & q & M\end{pmatrix}(-1)^{3/2-M'} \tag{17}$$

using the equation

$$k_\gamma=42\sqrt{5}\left(\frac{4\pi}{3}\right)^{1/2}(-1)^\gamma\begin{pmatrix}2 & 1 & 3\\ -m & -\gamma & q\end{pmatrix}Y_{-m}{}^2\langle T_q{}^3\rangle. \tag{18}$$

Here, $Y_m{}^l$ is the spherical harmonic of order l, whose arguments are the angles of the radius vector $\mathbf{r}$.

The general expression for the magnitude of this field is rather cumbersome:

$$\begin{aligned}
|\langle\mathbf{B}\rangle|=\frac{\beta R_0{}^2(r)}{40\pi}&[d_1(\langle\mathbf{F}\rangle\langle\mathbf{F}\rangle)\\
&+d_2(\langle T^3\rangle\langle T^3\rangle)+d_3\{\langle\mathbf{F}\rangle,\langle\mathbf{F}\rangle,Y^2\}\\
+d_4\{\langle T^3\rangle,\langle\mathbf{F}\rangle,Y^2\}&+d_5\{\langle T^3\rangle,\langle\mathbf{F}\rangle,Y^4\}+d_6\{\langle T^3\rangle,\langle T^3\rangle,Y^2\}\\
&+d_7\{\langle T^3\rangle,\langle T^3\rangle,Y^4\}+d_8\{\langle T^3\rangle,\langle T^3\rangle,Y^6\}]^{1/2},
\end{aligned} \tag{19}$$

and its integral over solid angle

$$d\varepsilon=Nr^2\,dr\int d\Omega\,|\langle\mathbf{B}\rangle|I \tag{20}$$

is difficult to obtain analytically. The coefficients d_i in Eq. (19) are

$$\begin{aligned}
&d_1=(25+42\eta^2-32\eta^3+9\eta^4), \quad d_2=60(7\eta^2+8\eta^3+4\eta^4),\\
&d_3=12\sqrt{2}(-10\eta+9\eta^2-6\eta^3+2\eta^4),\\
&d_4=12\sqrt{5}(35\eta+12\eta^2+27\eta^3-4\eta^4),\\
&d_5=24\sqrt{15}(17\eta^2-2\eta^3-\eta^4), \quad d_6=360\sqrt{7}(2\eta^2+2\eta^3+\eta^4),\\
&d_7=-60\sqrt{42/11}(11\eta^2+4\eta^3+2\eta^4), \quad d_8=-1800\sqrt{7/11}(2\eta^3+\eta^4).
\end{aligned} \tag{21}$$

The rounded brackets denote the scalar product of two equal-rank spherical tensors (see Ref. 15, p. 336):

$$(\hat{A},\hat{B})=\sum_{q}(-1)^{q}A_{q}B_{-q}, \tag{22}$$

while the curly brackets define a scalar formed by contracting the direct product of two tensors with the corresponding spherical functions:

$$\{A^{l_1},B^{l_2},Y^{l_3}\}=\left(\frac{4\pi}{3}\right)^{1/2}\sum_{\alpha,\beta,\gamma}A_{\alpha}^{l_1}B_{\beta}^{l_2}Y_{\gamma}^{l_3}\begin{pmatrix}l_1 & l_2 & l_3\\ \alpha & \beta & \gamma\end{pmatrix}. \tag{23}$$

Keeping in mind the approximate character of (20), it is expedient for purposes of estimation to make use of a simple analytic expression which approximates (20) to within a few percent:

$$\int d\Omega|\langle\mathbf{B}\rangle|\approx\left[4\pi\int d\Omega|\langle\mathbf{B}\rangle|^{2}\right]^{1/2}=\frac{\beta R_0^{2}}{2\sqrt{35}}[6(7\eta^{2}+8\eta^{3}+4\eta^{4})$$
$$+g(\eta)|\langle F\rangle|^{2}]^{1/2},\quad g(\eta)=35+42\eta^{2}-64\eta^{3}+3\eta^{4}. \tag{24}$$

To derive this equation we make use of the fact that for states described by a few arbitrary superpositions of the functions Ψ_M, the following equation holds (see Appendix II):

$$(\langle T^{3}\rangle,\langle T^{3}\rangle)=\frac{1}{14}-\frac{1}{35}(\langle\mathbf{F}\rangle,\langle\mathbf{F}\rangle). \tag{25}$$

As an example, in Fig. 1 we present the dependence of the energy $d\varepsilon$ on the structure of the hole wave function for three values of η; the hole wave function is cast in the form

$$\Psi=\Psi_{3/2}\cos\alpha+\Psi_{-3/2}\sin\alpha. \tag{26}$$

The dotted curves correspond to a calculation using Eq. (24), while the continuous curves are results of a numerical calculation using the exact relations (19)–(23). It is clear that the results for the exact and the approximate calculations are in rather good agreement. Using Eq. (26), we find that whereas for $\eta=1$ the maximum correlation energy is attained for $\alpha=0$ (i.e., when $|\langle\mathbf{F}\rangle|=3/2$), for $\eta=2$ the largest interaction energy with the magnetic ions corresponds to a spinless state ($\alpha=\pi/4$ and $|\langle\mathbf{F}\rangle=0$). We can show that the average spin of a hole in such a state, averaged over a sphere, equals zero ($\int d\Omega\langle\mathbf{J}\rangle=0$); however, from what was said earlier, the same spherical average of the absolute value of the spin is a maximum ($\int d\Omega|\langle\mathbf{J}\rangle|$).

As $\eta\to\infty$ ($r\to\infty$), Eq. (24) gives a very weak dependence of $d\varepsilon$ on $(\langle\mathbf{F}\rangle,\langle\mathbf{F}\rangle)$. Under these conditions, small corrections to (24) can markedly affect the character of the behavior of $d\varepsilon$. In point of fact, the results of numerical calculations make clear that the maximum correlation energy in this case is attained for $\alpha\approx\pi/8$, so that $0\neq|\langle\mathbf{F}\rangle|\neq3/2$.

The coefficient $g(\eta)$ in front of $(\langle\mathbf{F}\rangle,\langle\mathbf{F}\rangle)$ in Eq. (24) changes sign twice in the region of positive η, so that it is negative in the region

$$1.14\leqslant\eta\leqslant20.65 \tag{27}$$

and is positive outside it. If for some reason or other values of η from the region (24) play a fundamental role in the formation of the magnetic polaron, then the spin of the ground state of a bound hole will be zero.

3.2. The radial functions $R_0(r)$ and $R_2(r)$, and consequently the function $\eta(r)$, are determined by the form of the impurity center potential. For a Coulomb center, no analytic expressions for these functions are known, so we found them numerically.[16,17] In what follows we will investigate the simpler situation of a "zero-radius" center, for which

$$R_0=\frac{A}{\rho}[\gamma e^{-\gamma^{1/2}\rho}+e^{-\rho}],$$
$$R_2=\frac{A}{\rho}\left[\left(\gamma+\frac{3}{\rho}\gamma^{1/2}+\frac{3}{\rho^{2}}\right)e^{-\gamma^{1/2}\rho}-\left(1+\frac{3}{\rho}+\frac{3}{\rho^{2}}\right)e^{-\rho}\right], \tag{28}$$

where (Eq. G) is a normalization factor , $\varkappa_l=(2m_l\varepsilon_0/\hbar^2)^{1/2}$ and $\varkappa_h=(2m_h\varepsilon_0/\hbar^2)^{1/2}$ are the characteristic wave vectors for particles with the light and heavy hole masses bound to the center with energy ε_0, $\rho=r\varkappa_h$ is the radius measured in Bohr radii of the heavy hole, and $\gamma=m_l/m_h$. If $\gamma=1$, then $R_2\equiv0$ and

$$R_0=\exp(-\varkappa_h r)\varkappa_h^{1/2}/r,$$

the spin of the hole does not interact with its orbital motion and there are no qualitative differences between magnetic polarons in the valence and conduction bands. In particular, the maximum magnetopolaronic energy is achieved for $|\langle\mathbf{J}\rangle|=|\langle\mathbf{F}\rangle|=3/2$.

If $\gamma\neq1$, however, then the form of the ground state is not known *a priori*. In Fig. 2 we show the dependence of the

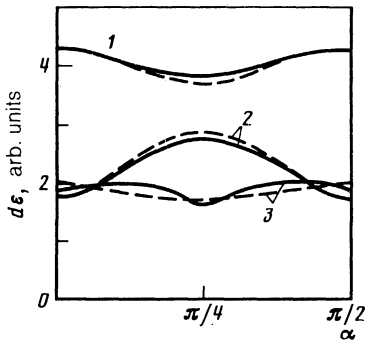

FIG. 1. Dependence of the magnetopolaron energy of a thin spherical shell of magnetic impurities on the form of the hole wave function at an acceptor: $\Psi=\Psi_{3/2}\cos\alpha+\Psi_{-3/2}\sin\alpha$. Dashed curves: calculated using the approximation in Eq. (24), continuous curves: based on the exact relations (19)–(23). Curve 1—$\eta=R_2/R_0=1$; 2—$\eta=2$; 3—$\eta=\infty$ ($r\to\infty$).

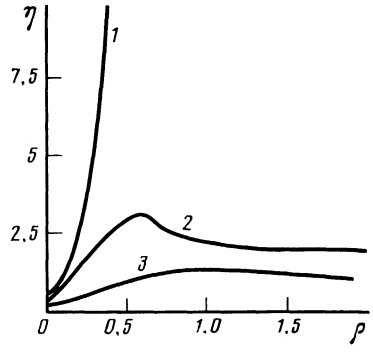

FIG. 2. Dependence of the ratio of the radial wave functions $\eta=R_2/R_0$ on the distance out to the acceptor center in the "zero-radius" model potential ($\rho=r\varkappa_h$), curve 1—$\gamma=0$; 2—$\gamma=0.1$; 3—$\gamma=0.5$.

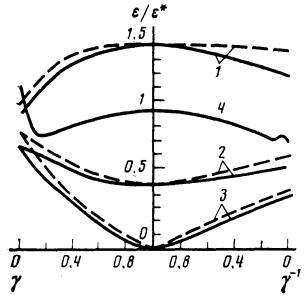

FIG. 3. Dependence of the energy of a magnetic polaron localized at an acceptor center on the light hole-heavy hole ratio. The energy is measured in units of $\varepsilon^* = 1/3\,\beta\,\mathrm{NI}$ in such a way that its value is numerically equal to the "effective spin" of the hole in a given state. The continuous curves are calculated using the exact relations (19)–(23), the dashed curves are the approximate relation (24). Curve 1—magnetopolaron energy for a hole state described by the functions $\Psi_1 = \Psi_{3/2}(|\langle \mathbf{F}\rangle| = 3/2)$; curve 2—by the functions $\Psi_2 = \Psi_{1/2}(|\langle \mathbf{F}\rangle| = 1/2$; curve 3—by the functions $\Psi_3 = (\Psi_{3/2} + \Psi_{-3/2})/2^{1/2}$ and $\Psi_4 = (3^{1/2}\Psi_{-1/2} + \Psi_{3/2})/2(|\langle \mathbf{F}\rangle| = 0)$. It is clear that for any value γ the maximum magnetopolaron energy corresponds to the maximum possible value of the total angular momentum of the hole $|\langle \mathbf{F}\rangle| = 3/2$. Curve 4 illustrates the ratio $\xi = \varepsilon_{3/2}/3\varepsilon_{1/2}$ as a function of γ. The quantity ξ differs from 1 because of the unequal spacing of the polaron sublevels.

ratio $R_2/R_0 = \eta$ on the spacing ρ for certain values of γ. It is clear that there is a region of values of ρ in which condition (27) is fulfilled. For those magnetic ions whose distance from the impurity center falls within this interval, the exchange interaction energy is a maximum for $|\langle \mathbf{F}\rangle| = 0$. However, it is clear from Fig. 3 that averaging over all the magnetic ions leads immediately to the conclusion that the maximum magnetopolaron energy is achieved for $|\langle \mathbf{F}\rangle| = 3/2$.

In Fig. 4 we show the spatial distribution of the polarization of magnetic ions for $\gamma = 0$ in the neighborhood of a given center. The tangents to the curves shown in this figure coincide at each point with the direction of $\langle \mathbf{B}\rangle$ and $\mathbf{I}$. It is clear that, in contrast to the magnetic polaron for a simple band, the maximum energy for the acceptor case corresponds to an inhomogeneous distribution of impurity magnetization.

Using the form $\mathbf{I}(\mathbf{r})$ of the distribution we have found for a hole in its ground state ($\Psi = \Psi_{3/2}$), it is not difficult to determine both the energy of the ground state ($M = 3/2$)

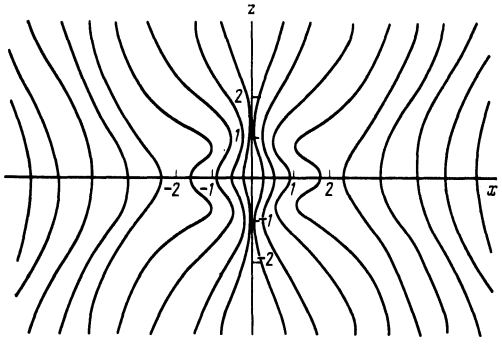

FIG. 4. Spatial distribution of the polarization of magnetic ions in the neighborhood of an acceptor center with a "zero-radius" potential ($\gamma = m_e/m_h = 0$). The tangents to the curves at each point coincide with the directions of $\langle \mathbf{B}\rangle$ and $\mathbf{I}$ at that point. The calculation was carried out for $|\langle \mathbf{F}\rangle| = 3/2$. The axes are numbered in units of the heavy-hole Bohr radius.

and the three excited sublevels ($M = \pm 1/2, \pm 3/2$):

$$\varepsilon_M = IN \int d^3r\, |\mathbf{B}_{\psi_h\psi_h}|^{-1} \sum_{\alpha} B_{\psi_h\psi_h\alpha} B_{M M\alpha}. \tag{29}$$

Thus, the energy of the ground state is

$$\varepsilon_{\psi_h} = {}^1/_2\beta IN \int_0^\infty dr\, r^2 R_0^2 \int_0^1 dt\,[\,(1+2\eta+\eta^2) + t^2(-6\eta-2\eta^2-4\eta^3+\eta^4) + t^4(7\eta^2+2\eta^3+\eta^4) - t^6(2\eta^3+\eta^4)\,]^{1/2}. \tag{30}$$

These energies are needed, e.g., for interpreting experiments involving Raman scattering of light. The results of such experiments are shown in Fig. 3. Curve 4 of this figure shows the dependence of the parameter $\xi = \varepsilon_{3/2}/3\varepsilon_{1/2}$ on γ. The extent to which ξ differs from 1 is a measure of how unequally spaced the energies of the four polaron sublevels are, since $\varepsilon_M = \varepsilon_{-M}$, and the sublevels are equidistant for $\varepsilon_{3/2} = 3\varepsilon_{1/2}$. This latter condition is fulfilled only for $\gamma = 1$. For almost all $\gamma \neq 1$, we have $\xi < 1$, and only in the small region $0 < \gamma \lesssim 0.04$ do we have $\xi \geqslant 1$; it reaches 1.18 for $\gamma = 0$.

It is important to emphasize that the maximum magnetopolaron splitting is attained for $\gamma = 1$, for which $R_2 = 0$ and $|\langle \mathbf{J}\rangle| = 3/2$ for all values of r.

3.3. Analogous results are obtained for a Coulomb center with $\gamma = 0$, and of course for $\gamma = 1$. As in the case of a center described by the "zero radius" potential, the hole ground state here corresponds to an axisymmetric distribution of polarization of magnetic ions; the average value of the angular momentum of a hole in this state is a maximum; $|\langle \mathbf{F}\rangle| = 3/2$. The unequal spacing of the excited sublevels is also preserved. The value of the parameter ξ for $\gamma = 0$ is 0.93 for a Coulomb center.

The value of the sublevel energies of the magnetic polaron were found using the truncated Hamiltonian (3), constructed from the wave functions (2). This, however, does not imply that we are limited to perturbation theory. The radial wave functions $R_0(r)$ and $R_2(r)$ can contain variational parameters. Thus, e.g., for the most nontrivial case $\gamma = 0$, two single-parameter wave functions can be chosen for the Coulomb center in the form

$$R_0 = (2/a^3)^{1/2} e^{-r/a}, \qquad R_2 = (2/a^3)^{1/2} \frac{1}{(r/a)^3}\left[6 - e^{-r/a}\left(\left(\frac{r}{a}\right)^3 + 3\left(\frac{r}{a}\right)^2 + 6\left(\frac{r}{a}\right) + 6\right)\right], \tag{31}$$

where a is a variational parameter. Such functions constitute a good description of the acceptor ground state in a semiconductor with a complex valence band ($\gamma = 0$) when

$$a = a_h = 1.5\hbar^2\varkappa/e^2 m_h.$$

Here $\varkappa$ is the dielectric permittivity, e is the electron charge, and $\hbar$ is Planck's constant. The factor 1.5 appears because of the difference between the hole wave function and a hydrogenic function. It is found that the sublevel energies ε_M of the polaron at $T = 0$ K do not depend on the value of the variational parameter a. This comes about because the magnetic ions at zero temperature are aligned along whatever direc-

tion the exchange field ends up pointing, while the increase in volume of the wave function is compensated by the decrease in hole density at each magnetic ion. Thus, the single-parameter variational procedure does not lead to a change in the acceptor radius. This assertion is correct for any γ. For $\gamma = 1$ the particle spin is a conserved quantity; therefore the exchange interaction does not change the wave function of the hole. For $\gamma \neq 1$ the answer could perhaps be made more precise by using a two-parameter variational procedure. A further error comes from replacing (1) in Eq. (3) with the invariant functions (2). However, this error is not large and is of order $\delta_V \approx (\varepsilon_{3/2\max} - \varepsilon_{3/2})^2/\varepsilon_0^2$. Here, $\varepsilon_{3/2\max} = \varepsilon_{3/2}(\gamma = 1)$, where ε_0 is the energy of the bound acceptor.

Because the results for the two basic impurity center models are so similar, we can assume that within the continuum approximation for the magnetic ion distribution the ground state always corresponds to the maximum value of angular momentum $|\langle \mathbf{F} \rangle| = 3/2$.

3.4. Let us discuss the applicability of the models we have developed here to specific semiconductors. In the crystal $Cd_{1-x}Mn_xTe$ the ratio of the light to heavy hole masses $\gamma \approx 0.1$, $\beta N_0 \approx 880$ meV. The FCC sublattice has a period of $a_0 = 6.46$ Å, in which there are 4 atoms per unit cell, i.e., the concentration of ions in this sublattice is $N_0 = 4/a_0^3$. The concentration of magnetic Mn ions equals $N = N_0 x$, $\varkappa = 10$, and $m_h/m_0 \approx 0.4$ (m_0 is the free-electron mass); $a_B = 0.53$ Å is the electron Bohr radius. Thus, the heavy-hole radius in $Cd_{1-x}Mn_xTe$ is $a_h = 1.5 a_B \varkappa m_0/m_h \approx 20$ Å. The quantity of magnetic ions in the neighborhood of the center for $x = 0.05$ is $\bar{n} = (4\pi/3) N a_h^3 \approx 24$. The applicability of the continuum approximation is limited by fluctuations in the number of ions, which leads to a relative error $\delta_n \approx (\bar{n})^{-1/2} \approx 0.2$. The spin of the magnetic Mn ion is $I = 5/2$. The error related to the replacement of the magnetic ion spins by classical vectors (see above) is $\delta_{\text{cl}} \approx (\bar{n}I)^{-1/2}$ 0.13. For $\gamma = 1$, we have $|\langle J \rangle| = 3/2$ and the magnetopolaron shift is maximal:

$$\varepsilon_{3/2\,max} = {}^1/_2 \beta N I \approx 55 \text{ meV}.$$

For $\gamma = 0.1$ we have $\varepsilon_{3/2}$ 37 meV. The acceptor binding energy $\varepsilon_0 \approx 53$ meV.[4] The relative error associated with replacing (1) by the truncated Hamiltonian (3) (see above) comes to $\delta_v \approx 0.11$.

The calculations were carried out assuming an antiferromagnetic interaction between magnetic ions. This approximation is satisfactory until the exchange interaction energy of an acceptor with one Mn ion $\varepsilon_1 = \varepsilon_{3/2}/\bar{n}$ is large compared to the antiferromagnetic exchange energy of two neighboring magnetic ions $\varepsilon_{1\text{-}2}$. For $\varepsilon_1 \lesssim \varepsilon_{1\text{-}2}$, however, the hole does not interact with paired spins. According to the data in Ref. 19, for $x = 0.05$ the effective fraction of magnetic ions x' amounts to only 60% of the original concentration. For $Cd_{0.95}Mn_{0.05}Te$, without taking into account the antiferromagnetic interaction, we have $\varepsilon_1 \approx 1.5$ meV and $\varepsilon_{1\text{-}2} \approx 1$ meV. The relative error in this approximation is

$$\delta_{AF} \approx (\varepsilon_{1\text{-}2}/\varepsilon_1)^2 (x - x')/x \approx 0.18.$$

Thus, the principal inaccuracy in this model ($\sim 20\%$) is connected with the continuum approximation.

In the crystal $Hg_{1-x}Mn_xTe$ all the parameters are close to the corresponding parameters for $Cd_{1-x}Mn_xTe$ and only the dielectric constant is different, i.e., $\varkappa = 15$. Correspondingly, the radius of the hole bound state is 1.5 times larger: $a_h \approx 30$ Å while $\bar{n} = 84$. The continuum approximation is good to an accuracy of $\delta_n \approx 0.11$, while the classical vector approximation for the Mn spins is good to 0.07. The increase in the size of the wave function implies that it is necessary to include the antiferromagnetic interaction of the Mn ions for small fractions x. For $x = 0.05$ we have $\varepsilon_1 \approx 0.44$ meV $< \varepsilon_{1\text{-}2} \approx 1$ meV, $x'/x \approx 0.6$. Therefore the value of the polaron shift must be less by a factor of 0.6, i.e., the real magnetopolaron shift equals $\varepsilon_{3/2} \approx 22$ meV. The polaron energy calculated in this manner has a relative error, due to the antiferromagnetic interactions of the Mn ions, of order

$$\delta_{AF} \approx (\varepsilon_1/\varepsilon_{1\text{-}2})^2 (x - x')/x \approx 0.08.$$

The effective average number of magnetic ions in the polaron is $\bar{n}' = \bar{n}x'/x \approx 50$. The continuum approximation error $\delta_n \approx 0.14$. Thus, even for the crystal $Hg_{0.95}Mn_{0.05}Te$ the principal error ($\sim 14\%$) is a consequence of the continuum approximation.

The authors are grateful to V. I. Perel' for useful discussions of the results obtained here.

APPENDIX I

An explicit form for the independent matrix elements of the exchange field $B_{MM'}(r_n)$ (9) in spherical coordinates

To simplify the notation, we will omit the subscript n from the coordinates r_n, θ_n and φ_n of a point, and also from the coefficients a_n, b_n and a_{1n} which depend on r_n. We also introduce the following notation: $(B_\pm)_{MM'} = (B_x)_{MM'} \pm i(B_y)_{MM'}$. Thus, we obtain

$$(B_z)_{MM} = M\{a + 5/2 br^2 - 12 a_1 r^2 \cos^2\theta + 8 a_1 r^2 \cos^4\theta + (M^2 - {}^5/_4)[3br^2 \cos^2\theta - br^2 + 6a_1 r^2 \cos^2\theta - 10 a_1 r^2 \cos^4\theta]\},$$

$$(B_+)_{MM} = 3e^{i\varphi} \cos\theta \sin\theta [br^2 + a_1 r^2 (\cos^2\theta - 3) - (M^2 - {}^5/_4) 2 a_1 r^2 \cos\theta],$$

$$(B_-)_{MM} = 3e^{-i\varphi} \cos\theta \sin\theta [br^2 + a_1 r^2 (\cos^2\theta - 3) - (M^2 - {}^5/_4) 2 a_1 r^2 \cos^2\theta],$$

$$(B_z)_{-3/2\,3/2} = -ie^{-3i\varphi} a_1 r^2 3 \sin^3\theta \cos\theta,$$

$$(B_+)_{-3/2\,3/2} = 3ie^{-2\varphi} \sin^2\theta (-br^2 + a_1 r^2 \sin^2\theta),$$

$$(B_-)_{-3/2\,3/2} = 3ie^{-4i\varphi} a_1 r^2 \sin^4\theta,$$

$$(B_z)_{-1/2\,1/2} = -9ie^{-i\varphi} a_1 r^2 \sin^3\theta \cos\theta,$$

$$(B_+)_{-1/2\,1/2} = i[2a + br^2 (6\sin^2\theta + 1) - 9 a_1 r^2 \sin^4\theta],$$

$$(B_-)_{-1/2\,1/2} = 3ie^{-2i\varphi} \sin^2\theta (br^2 - 3 a_1 r^2 \sin^2\theta),$$

$$(B_z)_{1/2\,3/2} = i\sqrt{3} e^{-i\varphi} \cos\theta \sin\theta (2br^2 - 3a_1 r^2 (1 + \cos^2\theta)),$$

$$(B_+)_{1/2\,3/2} = i\sqrt{3}[a + {}^5/_2 br^2 - 3a_1 r^2 (1 + \cos^2\theta) \sin^2\theta],$$

$$(B_-)_{1/2\,3/2} = i\sqrt{3} e^{-2i\varphi} \sin^2\theta (br^2 - 3a_1 r^2 (1 + \cos^2\theta)),$$

$$(B_z)_{-1/2\,3/2} = -\frac{\sqrt{3}}{2} e^{-2i\varphi} \sin^2\theta (br^2 - 6 a_1 r^2 \cos^2\theta),$$

$$(B_+)_{-1/2\,3/2} = \frac{\sqrt{3}}{2} e^{-i\varphi} \sin 2\theta (-2br^2 + 3 a_1 r^2 \sin^2\theta),$$

$$(B_-)_{-1/2\,1/2} = \frac{3\sqrt{3}}{2} e^{-3i\varphi} a_1 r^2 \sin 2\theta \sin^2\theta.$$

APPENDIX II

Let us prove that the relation between the square of the absolute value of the octupole moment and the average angular momentum of a hole on an acceptor has the form

$$(\langle T^3\rangle, \langle T^3\rangle)=\frac{1}{14}-\frac{1}{35}(\langle \mathbf{F}\rangle, \langle \mathbf{F}\rangle), \tag{A1}$$

where

$$\langle T_q^{\varkappa}\rangle=\sum_{MM'} c_M c_{M'}^{*}\begin{pmatrix} 3/2 & \varkappa & 3/2 \\ -M & q & M' \end{pmatrix}(-1)^{3/2-M} \tag{A2}$$

is the octupole moment of the hole in a state with wave function

$$\Psi=\sum_M c_M \Psi_M. \tag{A3}$$

Using the definition of the scalar product of two tensors of the same rank [see Eq. (22)], and also the condition of orthogonality of the $3j$ symbols (Ref. 15, p. 313), we obtain

$$(\langle T^0\rangle, \langle T^0\rangle)+3(\langle T^1\rangle, \langle T^1\rangle)+5(\langle T^2\rangle,$$

$$\langle T^2\rangle)+7(\langle T^3\rangle, \langle T^3\rangle)=1. \tag{A4}$$

We can show that

$$(\langle T^0\rangle, \langle T^0\rangle)=1/4, \quad (\langle T^2\rangle, \langle T^2\rangle)=1/20. \tag{A5}$$

Therefore it follows from Eq. (A4) that

$$3(\langle T^1\rangle, \langle T^1\rangle)+7(\langle T^3\rangle, \langle T^3\rangle)=1/2. \tag{A6}$$

Equation (A6) is equivalent to (A1), because the first rank tensor defined by (A2) is proportional to the angular momentum $\langle T^1\rangle = \langle \mathbf{F}\rangle/\sqrt{15}$, which completes the proof.

[1)] We can decrease the number of variables still more if we take into account the fact that the energy $\langle \varepsilon(c)\rangle$ is invariant under arbitrary rotations of the system of coordinates and premultiplication of all the coefficients by an overall phase factor. Thus, e.g., without loss of generality we can assume that the average angular momentum of the hole $\langle \mathbf{F}\rangle$ is directed along the Z axis ($\langle F_x\rangle = \langle F_y\rangle = 0$).

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