SPIN-DEPENDENT INTERACTION OF A BAND ELECTRON WITH PARAMAGNETIC IMPURITIES*

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A band electron interacting with N electrons in a d-shell of a paramagnetic impurity in zinc-blende type semiconductors was considered. The hybridization of band and d-states in the crystal field and the nonorthogonality mechanisms of interaction were examined in addition to the standard direct exchange. The Heisenberg- type form was derived for the interaction between a Γ_8-electron and an impurity with a half-filled d-shell. The domination of the hybridization mechanism explains the observed sign of the effective exchange constant for Γ_8 electrons in diluted magnetic semiconductors (DMS) and the difference in magnitude of this constant for Mn^{2+} and Fe^{3+} ions in HgSe.

PACS numbers:75.50.Pp, 75.30.-m,71.70.-d

It is generally believed that the spin-dependent interaction of band electrons with paramagnetic ions in DMS can be described by an effective Heisenberg type Hamiltonian proportional to the product $S \cdot J$, where S is the total spin operator of d-electrons and J is the appropriate quasi-angular momentum for the band electron. Such a Hamiltonian has been rigorously derived from the direct exchange interaction for an electron in s-like bands (whatever the number of electrons in the d-shell of the paramagnetic ion) [1] and for an electron in Γ_8 bands in zinc-blende type crystals [2], but only in the case of a half filled d-shell. Incompatible with the direct exchange mechanism, experimental results for DMS gave a negative effective exchange constant β for Γ_8 bands.

Guided by the results of [3], concerning a band electron interacting with an electron from a single *d*-orbital hybridized with the band, Bhattacharjee et al. [4] suggested that the antiferromagnetic interaction for a *p* band was due to strong *p–d* hybridization. In a more recent paper [5] Larson et al. gave support to this idea. They considered several *d*-orbitals hybridizing with the *p*-type Bloch functions but they used the band with well defined spin and a single hybridization matrix element independent of *d*- and *p*-orbitals involved. On the other hand, Semenov and Shanina [6] ascribed the antiferromagnetic interaction to the nonvanishing overlaps between the *p*-band and localized *d*-states.

It can be shown, that Γ_6 bands do not hybridize and have vanishing overlaps with *d*-orbitals, so that the direct exchange remains the only mechanism for *s–d* interaction.

Inspired by the controversy on the origins of the negative exchange constant β and by the new experimental results [7] indicating that β for Fe^{3+} ions in HgSe is much bigger than that for Mn^{2+} in the same compound, we decided to examine in detail the *p–d* interaction in zinc-blende type crystals. To account properly for the symmetry of the many-electron wave functions we use the occupation number representation. Our one-electron model Hamiltonian has the form $H = H_0 + H_1$

$$H_0 = \sum_{m,\sigma} \varepsilon_d \hat{n}_{m\sigma} + \sum_{n,k} \varepsilon_n(k) \hat{n}_{nk} \qquad (1)$$

and

$$H_1 = \sum_{n,k,m,\sigma} \left[L_{m\sigma nk} \hat{a}_{m\sigma}^+ \hat{a}_{nk} + h.c. \right], \qquad (2)$$

where $m = -2, -1, 0, 1, 2$ and $\sigma = \pm 1/2$ specify the states of a *d*-electron, whereas n and k define the Bloch functions of the band electron. The hybridization matrix elements are defined as $L_{m\sigma nk} = < m\sigma \mid V_{cf} \mid nk >$, where V_{cf} is a crystal field potential, which in the range of localization of the *d*-electrons can be expressed as [8]

$$V_{cf} = F(r) \left\{ Y_{40}(\vartheta, \varphi) + \sqrt{5/14} [Y_{44}(\vartheta, \varphi) + Y_{4-4}(\vartheta, \varphi)] \right\} \qquad (3)$$

$Y_{lm}(\vartheta, \varphi)$ are the spherical harmonics and $F(r)$ is the radial function.

We proved that even in the case of a nonorthogonal one-electron basis defining the occupation number representation, the one-particle Hamiltonian has only terms involving one creation and one annihilation operator. All terms proportional to matrix elements of the one-electron potential in [6] which involve two creation and two annihilation operators are incorrect. In fact they resulted from an arbitrary partial selection of terms in the one-electron Hamiltonian artificially expressed in the apparent form of a two particle operator. As a result of the same procedure the hybridization terms H_1 were lost in [6]. We proved that to the first order in overlap integrals the nonorthogonality of the one-electron basis gives only some corrections to hybridization matrix elements without changing the form of the Hamiltonian. Thus, in the following we will neglect these corrections.

H_1 couples the states of N *d*-electrons and 1 band electron with the states of $N+1$ (or $N-1$) *d*-electrons and 0 (or 2) band electrons. To describe properly the

energy differences between the coupled many particle states one should complete H_0 by the Coulomb interaction within the d-shell. The dominant effect of this interaction, i.e. the repulsion of opposite-spin electrons located on the same orbital, can be accounted for by the Anderson term [8]

$$(1/2)\sum_{m\sigma}U\hat{n}_{m\sigma}\hat{n}_{m-\sigma} \tag{4}$$

We eliminate H_1 to the first order in L adapting the canonical transformation of [3] to the case of 5 d-orbitals. To the second order in L the part of the transformed Hamiltonian, which depends on the state of d-electrons and is responsible for $\Gamma_8 \to \Gamma_8$ transitions in the vicinity of the Γ point, has the form

$$H_2 = \sum_{m\sigma,\sigma',m_J,k,m'_J,k'} L_{m\sigma m_J o}L_{m\sigma'm'_J o}\left[\frac{1}{\varepsilon_p - \varepsilon_d} - \frac{1}{\varepsilon_p - \varepsilon_d - U}\right]$$
$$\times \left(\delta_{\sigma\sigma'}\hat{n}_{m-\sigma} + \delta_{-\sigma\sigma'}\hat{a}^+_{m\sigma}\hat{a}_{m-\sigma}\right)\hat{a}^+_{m_Jk}\hat{a}_{m'_Jk'}. \tag{5}$$

Here we passed to the Luttinger representation for the Γ_8 states, ε_p is the energy of the Γ_8 bands at $k = 0$.

To discuss sp–d interaction it is in the most cases enough to consider only the subspace of the lowest states of the paramagnetic ion given by Hund's rules. For ions like Mn^{2+} and Fe^{3+} with the half-filled d-shell (i.e. ^6S ground term) the Hund's subspace is spanned by the vectors

$$|\,0,S> = C\hat{S}_-^{5/2-S}\prod_{m=-2}^{2}\hat{a}^+_{m\uparrow}\,|\,0>, \quad S = \mp\frac{5}{2}, \mp\frac{3}{2}, \mp\frac{1}{2}; \tag{6}$$

where $\hat{S}_- = \sum_{m=-2}^{2}\hat{a}^+_{m\downarrow}\hat{a}_{m\uparrow}$ is the spin lowering operator, $|\,0>$ is the vacuum state and C is the normalization constant depending on S.

We established that the Hamiltonian (5) leads to the Heisenberg-type p–d interaction only for the ^6S ions. The obtained negative effective exchange constant

$$J_{ex} = -(2/5)L_{2\uparrow,\frac{1}{2}o}^2\left[\frac{1}{\varepsilon_p - \varepsilon_d} + \frac{1}{\varepsilon_d + U - \varepsilon_P}\right] \tag{7}$$

has a similar form to that proposed in [4] and [5] but the present formula gives a precise definition for the vaguely defined there hybridization matrix element V_{kd}.

We notice, that the first energy denominator in formula (7) represents the energy which has to be supplied when one electron is taken from the half-filled d-shell and put into the band. The second one is the energy required when transferring the band electron into the already half-filled d-shell. As the latter energy is particularly small for iron impurities in HgSe [10], one can easily conclude that the observed difference in magnitude of the exchange constants for Mn^{2+} and Fe^{3+} in HgSe can result from the changes in energy denominators in formula (7).

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