

Bound-Magnetic-Polaron Molecule in Diluted Magnetic Semiconductors within Heitler–London Approximation

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We determine the states of a pair of bound magnetic polarons in a diluted magnetic semiconductor by taking into account both the molecular nature of the two-electron wave function in the Heitler–London approximation, as well as the thermodynamic fluctuations of magnetization due to localized $3d$ spins. We extend the theory of a single bound magnetic polaron to molecular case.

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1. Introduction

Magnetic interaction between electron on a shallow impurity and localized magnetic moments has been studied systematically in the last three decades [1–9]. In the first period, the influence of classical fluctuations of magnetization on quantum states of the impurity electron has been analyzed, thus leading to the bound magnetic polaron (BMP) formation. The main result obtained was to show that thermodynamic fluctuations produce a spontaneous spin splitting of the impurity state even without long-range magnetic order appearance, e.g. in a diluted magnetic semiconductor (DMS) [1–4]. A renewed interest was stimulated by the possibility of a ferromagnetic inter-polaron interaction [5–7], which leads to parallel alignment of polarization clouds of individual polarons.

In this paper recently developed by us [9] a microscopic theory of the bound magnetic polaron molecule (BMPM) in diluted magnetic semiconductors is reformulated in a reduced spin-state space. Namely, we solve the BMPM problem by taking into account the Heitler–London (HL) form of the two-electron wave function in the four-dimensional spin space (comprising one singlet and three triplet states) and include the thermodynamic fluctuations of the magnetization due to the localized $3d$ spins, in the Gaussian form. In this manner, simplified approaches to BMPM are evaluated and the role of covalency effect is identified and its influence analyzed in a simple workable model (for a full analysis beyond this approximation see Ref. [9]).

2. Model

We start by considering two interacting BMPs in DMS with a random distribution of localized magnetic mo-

ments (spins). Within the continuum-medium and the effective-mass approximations one can write Hamiltonian in the form

$$H = -\frac{\hbar}{2m^*}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{\varepsilon} \left(\frac{1}{r_{a1}} + \frac{1}{r_{a2}} + \frac{1}{r_{b1}} + \frac{1}{r_{b2}} - \frac{1}{r_{12}} \right) - J_c (\hat{\mathbf{S}}(\mathbf{r}_1)\hat{\mathbf{s}}_1 + \hat{\mathbf{S}}(\mathbf{r}_2)\hat{\mathbf{s}}_2), \quad (1)$$

where m^* is the effective mass, a and b label the two impurity sites, $l = 1, 2$ label the two electrons, $r_{a1}, r_{a2}, r_{b1}, r_{b2}, r_{12}, r_1, r_2$ and R_{ab} are relative distances appearing in the problem, e is the charge of the carriers, ε is the static dielectric constant, J_c is the exchange integral of the contact Fermi (s - d) interaction between localized spins and those of impurity carriers, $\hat{\mathbf{s}}_l$. $\hat{\mathbf{S}}(\mathbf{r}_l) = \sum_i \hat{\mathbf{S}}_i \delta(\mathbf{r}_l - \mathbf{R}_i)$ is the spin-density operator, with the summation running over the sites occupied by magnetic (Mn^{2+}) ions.

We assume also that the two-impurity electron wave function can be written as a product of functions which depend on spatial and spin variables separately i.e. it is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \sigma_1, \sigma_2) = \chi_S \chi_{\sigma_1 \sigma_2} \Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2), \quad (2)$$

where χ_S is the wave function of spins, and $\chi_{\sigma_1 \sigma_2}$ is the spin part of that for the carriers, whose spatial wave function is $\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2)$. In the explicit calculations we take the two-electron wave function in the Heitler–London form, for the singlet (Ψ_+) and the triplet (Ψ_-) states with $s_{\text{tot}}^z = 0$, respectively

$$\begin{aligned} \Psi_{\pm} \chi_{\sigma_1 \sigma_2}^{\mp} &= \beta_{\pm} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \chi_{\sigma_1 \sigma_2}^{\mp} \\ &\equiv \Psi_{\pm} 2^{-1/2} [\chi_{1/2}(1)\chi_{-1/2}(2) \mp \chi_{-1/2}(1)\chi_{1/2}(2)]. \end{aligned} \quad (3)$$

For completeness, we include also the triplet state with $s_{\text{tot}}^z = 1$:

$$\Psi_- [\chi_{\pm 1/2}(1)\chi_{\pm 1/2}(2)]. \quad (4)$$

In the above equations $\beta_{\pm} = (2 \pm 2\lambda^2)^{-1/2}$, where λ is the overlap integral, and $\psi_l(\mathbf{r}_j)$, $l = a, b$ and $j = 1, 2$, are:

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(i) the 1s-hydrogen-like wave functions $\varphi_l(\mathbf{r}_j)$, as in the HL approximation, and (ii) the orthogonalized molecular wave functions, which leads to a modified Heitler–London (MHL) approximation. In this manner, the covalency effect and the nonorthogonality of atomic functions φ_a and φ_b are accounted for. For the sake of simplicity,

we consider both cases (i) and (ii) using common notations Ψ_{\pm} .

Next, we determine the matrix representation of H in the defined above representation, i.e. calculate $\langle \Psi_{\tau} | H | \Psi_{\nu} \rangle$ with τ and $\nu = \pm$; it has the following explicit form:

$$\begin{pmatrix} E_+ & 0 & 0 & \Delta^{+-} \\ 0 & E_- + \Delta^{--} \cos \xi & 0 & \frac{1}{\sqrt{2}} \Delta^{--} e^{-i\phi} \sin \xi \\ 0 & 0 & E_- - \Delta^{--} \cos \xi & \frac{1}{\sqrt{2}} \Delta^{--} e^{i\phi} \sin \xi \\ \Delta^{+-} & \frac{1}{\sqrt{2}} \Delta^{--} e^{i\phi} \sin \xi & \frac{1}{\sqrt{2}} \Delta^{--} e^{-i\phi} \sin \xi & E_- \end{pmatrix}, \quad (5)$$

where ϕ and ξ are the azimuthal and the polar angles between the exchange fields $\mathbf{\Delta}^{+-}[\mathbf{M}]$ and $\mathbf{\Delta}^{--}[\mathbf{M}]$. The exchange fields, $\Delta_l^{\tau\nu}[\mathbf{M}]$ are defined as follows:

$$\Delta_l^{\tau\nu}[\mathbf{M}] = \frac{\alpha}{g\mu_B} \times \int \Psi_{\tau}^*(\mathbf{r}_1, \mathbf{r}_2) \mathbf{M}(\mathbf{r}_l) \Psi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2. \quad (6)$$

The diagonal matrix elements E_+ and E_- correspond to the singlet and the triplet states with $s_{\text{tot}}^z = 0$, respectively, whereas the remaining diagonal elements to the triplet states with $s_{\text{tot}}^z = 1$, respectively. Diagonalization of the BMPM Hamiltonian requires solution of the eigenvalue problem: $HV = EV$, where the V and E denote eigenvector and eigenvalue of H . For the four-dimensional matrix representation, this is equivalent to solving of the following fourth order equation for E :

$$\begin{aligned} & \left[\left(\left(E_- + \frac{1}{2}J \right) - E \right)^2 - \left(\frac{1}{2}J \right)^2 - (\Delta^{+-})^2 \right] \\ & \times [(E_- - E)^2 - (\Delta^{--})^2] - (\Delta^{--} \times \Delta^{+-})^2 = 0, \end{aligned} \quad (7)$$

where $J = E_+ - E_-$. This equation has simple solutions for collinear configuration of the exchange fields. In such a case, the last term vanishes and for identical BMPs the difference of the lowest energy $E(\Delta^{--} = \Delta, \Delta^{+-} = 0)$ and $E(\Delta^{--} = 0, \Delta^{+-} = \Delta)$, for parallel and antiparallel alignment of the individual polaronic exchange fields Δ , determines the nature of the ground state (thus properties at low T). Having determined the eigenvalues, we construct next the free energy of the BMP pair. Thermodynamics of this system was derived quite analogically as in Ref. [9]. In effect the physical free energy takes the form [9]:

$$F = -k_B T \ln \iint d^3\Delta^{+-} d^3\Delta^{--} P(\Delta^{+-}, \Delta^{--}), \quad (8)$$

where the probability distribution of the exchange fields Δ^{+-}, Δ^{--} is

$$\begin{aligned} P(\Delta^{+-}, \Delta^{--}) &= C \exp\left(-\frac{(\Delta^{+-})^2}{8\varepsilon_{+-}k_B T}\right) \\ &\times \exp\left(-\frac{(\Delta^{--})^2}{8\varepsilon_{--}k_B T}\right) \sum_{i=1}^4 \exp\left(-\frac{E_i}{k_B T}\right), \end{aligned} \quad (9)$$

and the eigenvalues E_i are the roots of Eq. (7), whereas the two parameters, ε_{+-} and ε_{--} , are defined as follows:

$$\begin{aligned} \varepsilon_{\tau\nu}(R_{ab}) &= \frac{1}{4} \frac{\alpha\chi}{(g\mu_B)^2} \int (\Psi_{\tau}^* \Psi_{\nu})^2 d^3r \\ &\equiv \frac{1}{4} \frac{\alpha\chi}{(g\mu_B)^2} f_{\tau\nu}(R_{ab}). \end{aligned} \quad (10)$$

This form is written down for the orthogonal as well as for nonorthogonal (atomic) wave functions. We stress that the parameters ε_{+-} and ε_{--} are material dependent and correspond to the single particle parameter ε_p of single polaron theory [1]. Their distance (R_{ab}) dependence is crucial, as it affects the magnitudes of both $\mathbf{\Delta}^{+-}$ and $\mathbf{\Delta}^{--}$.

3. Results

In Fig. 1 we plot their distance dependence for the MHL (dashed line) and the HL (solid lines) approximations. One can see that HL highly underestimates ε_{+-} for inter-polaron distances $R_{ab} < 4a_B$. Let us note also that the functions f_{--} and f_{+-} are the same for MHL and the full approach considered in Ref. [9]. Presented results in Fig. 1 reveal an impact influence of the nonorthogonality of electron wave functions on magnitude of fluctuating exchange fields. In order to demonstrate the covalency effect we compare in Fig. 2 temperature dependence of the averaged values of $\mathbf{\Delta}^{+-}$ and $\mathbf{\Delta}^{--}$ calculated for the weakly interacting strong polaron fields case with the same values of parameters, as used in Ref. [9] ($R_{ab} = 3.65a_B$, $\kappa = k\kappa_0$, where $\kappa = \alpha^2 \chi \varepsilon^2 m_e / (g\mu_B)^2 m^*$, $k = 25$ and the value κ_0 is taken for $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$: $\varepsilon = 9.4$, $m^*/m_e = 0.13$), using the MHL approximation and the BMPM theory of Ref. [9]. Let us note that for the p -type DMS the s - d

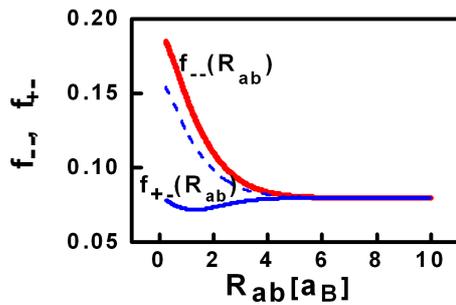


Fig. 1. Interpolaron distance dependence of the functions $f_{--}(R_{ab})$ and $f_{+-}(R_{ab})$ describing the fluctuating exchange fields, as defined in Eq. (10).

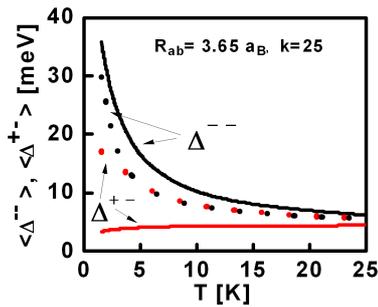


Fig. 2. Average exchange fields Δ_{--} and Δ_{+-} for hypothetical n -type semiconductor with the enhancement factor $k = 25$ of κ_0 obtained for $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ to emulate p -type BMPM. Δ_{--} stands for the value of the molecular polaron splitting in the triplet state; Δ_{+-} is for the non-magnetic states. Solid lines — MHL case; dotted lines taken from a full approach, from Ref. [9].

exchange integral is about 4–5 times stronger, which justifies such increased value of κ taken. The p -BMPM is

emulated by taking the parameter $k = 25$ ($k = 1$ for $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$). In conclusion, the results displayed in Fig. 2 confirm that BMPs can interact ferromagnetically and that nature of the ground state (low T limit) remain unchanged irrespective on the approximation used. Influence of ionic states occupation, accounted for within the full approach of [9], on Δ_{+-} and Δ_{--} is clearly visible at low temperatures by comparison within the MHL results (covalency effect).

Acknowledgments

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