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Spin-Hamiltonian theory of orbital near-degenerate state in tetragonal field ☆

Du Maolu *

Department of Physics, Southwest University for Nationalities, Chengdu 610041, PR China

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ABSTRACT

In this paper, a Spin-Hamiltonian theory of orbital near-degenerate state in tetragonal field is presented. For orbital doublet ^{2}E, which is an orbital degenerate state in the cubic field and is a near-degenerate state in the tetragonal field, we obtain the cubic invariant form and the tetragonal invariant form of the Spin-Hamiltonian. In case of near-degeneracy (tetragonal splitting is very small) two additional *g*-factors are introduced to investigate Zeeman-splitting for tetragonal field. The two additional *g*-factors g_{2z} and g_{2xy} describe the magnetic interest between A_{1g} and B_{1g} states for a parallel magnetic field with *z*-axis and a perpendicular magnetic field with *z*-axis, respectively. The theory is based on the time-reversal invariant and the point-group symmetry invariant. The theoretical method can also be used for other orbital degenerate states $^{2S+1}\Gamma$ including $S>\frac{1}{2}$ and $\Gamma=T_1$ or T_2 and can be used for other point-group symmetry.

1. Introduction

The method of Spin-Hamiltonian is simple and powerful in treating data of electron paramagnetic resonance and fine structure of energy level of ground state. The usual Spin-Hamiltonian theory based on the perturbation theory is suitable only in cases of orbital singlet and it has been developed for the d^n configuration [1–6]. But it will in general become invalid in cases of orbital degeneracy and near-degeneracy [7]. For a long time it was a difficult problem to establish a reasonable Spin-Hamiltonian theory of the orbital degeneracy. Recently, this problem came back to interest for two reasons. One is that the investigation of the energy levels of transition metal (TM) ion in semiconductors is interesting since the semiconductors containing TM ion are widely used. For the TM ion in many semiconductors, especially in II–VI and III–V semiconductors, its local symmetry is T_d symmetry and then its orbital ground state is degenerate. Since there is no a satisfactory Spin-Hamiltonian theory of orbital degeneracy, the investigation of more properties of the TM ion in semiconductors is difficult. Another is that, in 1993, Dugdale [8] analyzed the theoretical basis of Spin-Hamiltonian theory based upon the theory of unitary transformations and showed that the condition of non-degeneracy is not a necessary one to validate the use of a Spin-Hamiltonian. Unfortunately, there is no satisfactory Spin-Hamiltonian theory of the orbital degenerate state and near-degenerate state.

Theoretically for a reasonable Spin-Hamiltonian theory the following conditions should be satisfied. The Spin-Hamiltonian must be invariant in the time-reversal operation and must be invariant to the point-group symmetry operation for the local symmetry of system [9,10]. And it must be equivalent to the real Hamiltonian in the reasonable region. We construct the Spin-Hamiltonian of orbital doublet ^{2}E on the bases of time-reversal invariance and point-group symmetry invariance and show that it is well equivalent to the real Hamiltonian by the computer-fitting calculation.

2. Spin-Hamiltonian of near-degenerate state ^{2}E in tetragonal field

The matrix of usual Spin-Hamiltonian is a (2*S*+1) dimensional with the bases $|^{2S+1}\Gamma M_s\rangle$ for a $^{2S+1}\Gamma$ state. It means that the degeneracy including both spin and orbital is (2*S*+1)-fold and that the off-diagonal matrix elements of the real Hamiltonian connecting the term of interest with others can be omitted (namely the difference between the $^{2S+1}\Gamma$ and other energy levels is more large). For the orbital singlet, above two conditions are satisfied and then the usual Spin-Hamiltonian theory is suitable. For the orbital near-degenerate state, the above second condition can not be satisfied because there is small difference between two energy levels. So we consider the near-degeneracy as an orbital degenerate one. For a orbital degenerate state $^{2S+1}\Gamma$ (its orbital

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* Tel.: +86 28 85522583.
E-mail address: duml@mail.sc.cninfo.net

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degenerate fold is Γ), the total degeneracy including both spin and orbital is $(2S+1)\times\Gamma$-fold and hence the usual Spin-Hamiltonian theory becomes invalid. The $(2S+1)\times\Gamma$-fold degeneracy makes one unable to construct Spin-Hamiltonian by using spin operators only for the orbital degenerate states. But it may be constructed by using both spin operator and orbital irreducible tensor operator [11].

We assume that matrix of the Spin-Hamiltonian H_S on the base $|^{2S+1}\Gamma M_s\rangle$ is

$$\langle SM_s|H_s|SM'_s\rangle = \langle \alpha^{2S+1}\Gamma\gamma M_s|H_{\rm eff}|\alpha^{2S+1}\Gamma\gamma' M'_s\rangle \tag{1}$$

where the Spin-Hamiltonian $H_S = \langle \alpha\Gamma\gamma|H_{\rm eff}|\alpha\Gamma\gamma'\rangle$ is a Γ-fold matrix. Hence H_S is a 2×2 matrix for the orbital doublet ^{2S+1}E.

It is convenient to introduce irreducible spin operator $S_\alpha^{(K)}$ as that

$$\begin{aligned} S_0^{(0)} &= 1, \quad S_{+1}^{(1)} = -1/\sqrt{2}(S_x + iS_Y) \\ S_{-1}^{(1)} &= 1/\sqrt{2}(S_x - iS_Y), \quad S_0^{(0)} = S_z \end{aligned} \tag{2}$$

Similarly magnetic field H can be written as that

$$H_{+1} = -\frac{1}{\sqrt{2}}(H_x + iH_Y), \quad H_{-1} = \frac{1}{\sqrt{2}}(H_x - iH_Y), \quad H_0 = H_z \tag{3}$$

The effective Hamiltonian can be written as a linear combination of the product of the spin operator $S_\alpha^{(K)}$, the orbital irreducible tensor operator $X_{\bar\gamma}(\bar\Gamma)$ and the magnetic field H_β

$$H_{\rm eff} = \sum_{K,\alpha,\bar\gamma,\bar\Gamma} D_{K\alpha\bar\gamma}(\bar\Gamma) S_\alpha^{(K)} X_{\bar\gamma}(\bar\Gamma) + \beta \sum_{K,\alpha,\beta,\bar\gamma,\bar\Gamma} g_{K\alpha\beta\bar\gamma}(\bar\Gamma) S_\alpha^{(K)} H_\beta X_{\bar\gamma}(\bar\Gamma) \tag{4}$$

Since in the Spin-Hamiltonian there are only spin operators but not orbital operators, we should make integrals for the orbital part of the effective Hamiltonian as in the usual Spin-Hamiltonian theory of the orbital singlet. We write that

$$X_{\gamma\gamma'\bar\gamma}(\bar\Gamma) = \langle \Gamma\alpha\gamma|X_{\bar\gamma}(\bar\Gamma)|\Gamma\alpha\gamma'\rangle \tag{5}$$

Then Spin-Hamiltonian can be written as

$$H_s = \sum_{K,\alpha,\bar\gamma,\bar\Gamma} D_{K\alpha\bar\gamma}(\bar\Gamma) S_\alpha^{(K)} X_{\gamma\gamma'\bar\gamma}(\bar\Gamma) + \beta \sum_{K,\alpha,\beta,\bar\gamma,\bar\Gamma} g_{K\alpha\beta\bar\gamma}(\bar\Gamma) S_\alpha^{(K)} H_\beta X_{\gamma\gamma'\bar\gamma}(\bar\Gamma) \tag{6}$$

where $D_{K\alpha\bar\gamma}(\bar\Gamma)$ denotes zero-field splitting and $g_{K\alpha\beta\bar\gamma}(\bar\Gamma)$ denotes Zeeman splitting (g-factor). Since $S_0^{(0)} = 1$ and $D_{K\alpha\bar\gamma}(\bar\Gamma) = 0$ for the orbital degenerate state, K is started from 1 in first term and is started from 0 in second term.

The Spin-Hamiltonian H_S must be invariant in the time-reversal operation. We consider transformation of $S_\alpha^{(K)}$, H_β and $X_{\gamma\gamma'\bar\gamma}(\bar\Gamma)$ under the time-reversal operation. Since the signs of the three components of the spin operator are changed under time reversal, the signs of the components of $S_\alpha^{(K)}$ are changed when $K=$ odd and are invariable when $K=$ even under time reversal. The signs of the three components of the magnetic field H_β are changed under time reversal. Since the direct product of irreducible representation E of O group is $E\otimes E = A_1\oplus A_2\oplus E$ (similarly T_d or D_4 group), we consider orbital irreducible tensor operator $X_{\bar\gamma}(\bar\Gamma)$ only: $X(A_1), X(A_2), X_{\bar\gamma}(E)$ in the effective Hamiltonian. The sign of $X_{\gamma\gamma'\bar\gamma}(A_1)$ and $X_{\gamma\gamma'\bar\gamma}(E)$ is invariable and the sign of $X_{\gamma\gamma'\bar\gamma}(A_2)$ is changed under time reversal. We consider $S_\alpha^{(0)}$ and $S_\alpha^{(1)}$ only because $S=\frac{1}{2}$ for ^{2}E state. Then the time-reversal invariant H_S can be written as

$$\begin{aligned} H_s = &\sum_{\alpha,\bar\gamma} D_{1\alpha\bar\gamma}(A_2) S_\alpha^{(1)} X_{\gamma\gamma'\bar\gamma}(A_2) + \beta \sum_{\alpha,\beta,\bar\gamma} [g_{1\alpha\beta\bar\gamma}(A_1) S_\alpha^{(1)} H_\beta X_{\gamma\gamma'\bar\gamma}(A_1) \\ &+ g_{00\beta\bar\gamma}(A_2) S_0^{(0)} H_\beta X_{\gamma\gamma'\bar\gamma}(A_2) + g_{1\alpha\beta\bar\gamma}(E) S_\alpha^{(1)} H_\beta X_{\gamma\gamma'\bar\gamma}(E)] \end{aligned} \tag{7}$$

where $X_{\gamma\gamma'\bar\gamma}(A_1)$ is a 2×2 unit matrix and can be written as I_0.

The Spin-Hamiltonian must be invariant in the point-group symmetry operation. It is convenient taking C_4-axis as main axis and using the appropriate base [12]. In this base the two components of the irreducible representation E are θ and ε. By considering the C_4 and C'_2 operations of the O-group the invariant form of the Spin-Hamiltonian is obtained as

$$\begin{aligned} H_S = &\beta g_z H_Z S_Z I_0 - \beta g_{xy}(H_{+1}S_{-1}^{(1)} + H_{-1}S_{+1}^{(1)}) I_0 \\ &+ \sqrt{2}\beta[g_{1z}H_Z S_Z - g_{1xy}(H_{+1}S_{-1}^{(1)} + H_{-1}S_{+1}^{(1)}] X_{\gamma\gamma'\theta}(E) \\ &+ \sqrt{2}\beta[g_{2z}H_Z S_Z - g_{2xy}(H_{+1}S_{-1}^{(1)} + H_{-1}S_{+1}^{(1)})] X_{\gamma\gamma'\varepsilon}(E) \end{aligned} \tag{8}$$

where $g_z = g_{100}(A_1)$, $g_{xy} = -g_{1+1-1}(A_1) = -g_{1-1+1}(A_1)$, $\sqrt{2}\ g_{1z} = g_{100\theta}(E)$, $\sqrt{2}\ g_{1xy} = -g_{1+1-1\theta}(E) = -g_{1-1+1\theta}(E)$, $\sqrt{2}\ g_{2z} = g_{100\varepsilon}(E)$, $\sqrt{2}\ g_{2xy} = -g_{1+1-1\varepsilon}(E) = -g_{1-1+1\varepsilon}(E)$. Taking the value of $X_{\gamma\gamma'\bar\gamma}(E)$, the Spin-Hamiltonian of the orbital doublet ^{2}E in tetragonal field can be written as

$$H_S = \begin{array}{c} \begin{array}{cc} \quad\theta & \qquad\qquad\varepsilon \end{array} \\ \begin{bmatrix} \beta(g_z - g_{1z})HS_z & \beta g_{2z}HS_z \\ \beta g_{2z}HS_z & \beta(g_z + g_{1z})HS_z \end{bmatrix} \end{array} \tag{9.1}$$

for $\vec{H}\parallel Z$ and

$$H_S = \begin{array}{c} \begin{array}{cc} \quad\theta & \qquad\qquad\varepsilon \end{array} \\ \begin{bmatrix} \beta(g_{xy} - g_{1xy})HS_x & \beta g_{2xy}HS_x \\ \beta g_{2xy}HS_x & \beta(g_{xy} + g_{1xy})HS_x \end{bmatrix} \end{array} \tag{9.2}$$

for $\vec{H}\parallel X$. Eqs. (9.1) and (9.2) is a tetragonal invariant Spin-Hamiltonian since it is invariant form under C_4 and C'_2 operation. From Eq. (9.1), the equivalent energy matrix of H_S with bases $|^2E\bar\gamma M_s\rangle$ in tetragonal field is obtain as (for $\vec{H}\parallel Z$)

$$\frac{1}{2}\begin{array}{c} \begin{array}{cccc} \theta^+ & \qquad\theta^- & \qquad\varepsilon^+ & \qquad\varepsilon^- \end{array} \\ \begin{bmatrix} \beta(g_z - g_{1z})H & 0 & \beta g_{2z}H & 0 \\ 0 & -\beta(g_z - g_{1z})H & 0 & -\beta g_{2z}H \\ \beta g_{2z}H & 0 & \beta(g_z + g_{1z})H & 0 \\ 0 & -\beta g_{2z}H & 0 & -\beta(g_z + g_{1z})H \end{bmatrix} \end{array} \tag{10}$$

where θ^+, θ^-, ε^+ and ε^- denotes $|^2E_\theta 1/2\rangle|^2E_\theta{-}1/2\rangle|^2E_\varepsilon 1/2\rangle$ and $|^2E_\varepsilon{-}1/2\rangle$, respectively. In the tetragonal field, the ^{2}E, which is an orbital doublet in the cubic field, is split into two orbital singlets. In the D_4 symmetry field, for example, the ^{2}E is split into A_{1g} and B_{1g} corresponding to θ and ε component of ^{2}E [13]. So Zeeman splitting of θ and ε from Eq. (10) correspond to that of A_{1g} and B_{1g}, respectively. When the tetragonal splitting μ between A_{1g} and B_{1g} is large enough, the off-diagonal elements can be omitted. And then one can use one g-factor ($g_z{-}g_{1z}$) for θ and one g-factor ($g_z{+}g_{1z}$) for ε as in usual Spin-Hamiltonian theory of orbital singlet. But in cases of near-degeneracy, which means that the tetragonal splitting μ between A_{1g} and B_{1g} is small, the contribution of the off-diagonal elements between θ and ε can not be omitted. So one should use the Spin-Hamiltonian theory of orbital degeneracy (Eqs. (9.1) and (9.2)) to investigate Zeeman splitting of A_{1g} and B_{1g}. We calculate Zeeman splitting using Eq. (10) and $\beta(g_z \pm g_{1z})H$ with different tetragonal splitting μ. The result is given in Fig. 1. From Fig. 1, one can find that the Zeeman splitting obtained from Eq. (10) is more different with that from $\beta(g_z \pm g_{1z})H$ when $\mu < 3\,\mathrm{cm}^{-1}$. It means that one should introduce factor g_{2z}, which describes the magnetic interest between A_{1g} and B_{1g}, besides factors ($g_z{-}g_{1z}$) and ($g_z{+}g_{1z}$) in case of near-degeneracy.