

The Magnetic g-Tensors for Ion Complexes with Large Spin-Orbit Coupling

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A nonperturbative method for calculating the magnetic g-tensors is presented and discussed for complexes of transition metal ions of large spin-orbit coupling, in the ground term 2D . A numerical example for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is given.

Apresenta-se e discute-se um método não perturbativo para se calcular os tensores-g magnéticos, no caso dos complexos de ions de metais de transição com forte acoplamento spin-órbita, para o termo fundamental 2D . Dá-se um exemplo numérico que diz respeito ao $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

1. INTRODUCTION

The studies on magnetic g-tensors are usually based on the assumption that they are symmetric; hence they are diagonalizable and principal axes can be found by means of an appropriate transformation¹,

$$L g L^{-1} = g_{\text{diagonal}} \quad (1)$$

The reason for this assumption is that, as is generally believed, only for complexes with low symmetry can we expect the g-tensor to be asymmetric. Therefore, g-tensors are often described in their principal axes so that they are already diagonal^{1,2}. Lin³ derived an expression for the general case in which an arbitrary reference frame was used, and symmetry of the g-tensors not assumed. Numerical calculation of g-tensors are mostly based on perturbation approximation^{4,5,6}. A nonperturbative method has been used to obtain expressions for the g-tensor of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ by Inomata et al.⁷. They simplified the calculation by

treating the d_e orbitals of the 5D state of Fe^{2+} as a triplet with effective angular momentum $R = 1$, apart from their implicit assumption that the g-tensor is symmetric. In this paper we derive expressions for g-tensors using nonperturbative method and show that even for highly symmetric crystals the g-tensor may still be highly asymmetric, provided the spin-orbit coupling is not very much smaller than the energy splitting of the orbitals due to the crystal field.

2. THEORY

When for atomic electrons one considers besides their orbital angular momenta their spins as well, the Zeeman interaction with external magnetic field \vec{H} is

$$H_z = \beta \vec{H} \cdot (\vec{L} + g_e \vec{S}), \quad (2)$$

where β is the Bohr magneton, and g_e the g-factor for free electrons. This interaction may be represented by

$$H_z = \beta g_{ij} H_i \hat{S}_j, \quad (3)$$

where \hat{S} is called the fictitious spin, and the magnetic g-tensor being thereby defined. If we treat the spin-orbit coupling $\lambda \vec{L} \cdot \vec{S}$ as a perturbation, then up to first order in λ , we have

$$g_{ij} = g_e - \lambda \sum_n \frac{1}{E_n - E_0} \{ \langle \psi_0 | L_i | \psi_n \rangle \langle \psi_n | L_j | \psi_0 \rangle + \langle \psi_0 | L_j | \psi_n \rangle \langle \psi_n | L_i | \psi_0 \rangle \}. \quad (4)$$

Hence up to this order of approximation, the g-tensor is symmetric. However, when λ is not very small compared with the separation of energy levels $(E_n - E_0)$, the relation (4) is not expected to be a good approximation and one should not assume the g-tensor symmetric.

For the sake of simplicity, we consider the $3d^1$ electron such as in T_1^{3+} . In the absence of an external magnetic field, the Hamiltonian is

$$H = H_0 + \lambda \vec{L} \cdot \vec{S} . \quad (5)$$

The first term H_0 represents the interaction with the crystal field, and $\lambda \vec{L} \cdot \vec{S}$ the spin-orbit coupling which we shall not treat as a small perturbation. The eigenstates are at least doubly degenerate, according to Kramer's theorem. The wave function for the ground states can be written as

$$\begin{aligned} \psi_1 &= f(r) \sum_{m=-2}^2 Y_{\ell}^m(\theta, \phi) (a_m \alpha + b_m \beta), \\ \psi_2 &= f(r) \sum_{m=-2}^2 Y_{\ell}^m(\theta, \phi) (c_m \alpha + d_m \beta), \end{aligned} \quad (6)$$

with α, β being the spin wave functions for spin up and down respectively; a, b, c and d are constants. Since ψ_1 and ψ_2 are related by $\psi_2 = T\psi_1$, where T is the time reversal (antiunitary) operator of time reversal, it follows that $c_m = (-1)^m b_{-m}^*$ and $d_m = (-1)^m a_{-m}$. Within the subspace of these two degenerate states, the representation of the Hamiltonian is given by a two by two matrix. For the situation in which the external magnetic field is in the direction of the q^{th} axis of a Cartesian coordinate system arbitrarily chosen, i.e., $H_i = H\delta_{iq}$, the Hamiltonian matrix reads

$$H_z = \beta H \begin{pmatrix} g_{q_3} & g_{q_1} - ig_{q_2} \\ g_{q_1} + ig_{q_2} & -g_{q_3} \end{pmatrix} . \quad (7)$$

If we denote $\vec{K} = \vec{L} + g_e \vec{S}$, then the Hamiltonian matrix can also be written as

$$H_z = \beta H \begin{pmatrix} (K_q)_{11} & (K_q)_{12} \\ (K_q)_{21} & (K_q)_{22} \end{pmatrix} , \quad (8)$$

where $(K_q)_{ij} = \int \psi_i K_q \psi_j dx$, which can be calculated in terms of the coefficients in Eq.(4). From (5) and (6), we have

$$\begin{aligned} g_{q1} &= (K_g)_{12} + (K_g)_{21} , \\ g_{q2} &= i \left[(K_q)_{12} - (K_q)_{21} \right] , \\ g_{q3} &= 2 (K_q)_{11} = -2 (K_g)_{22} . \end{aligned} \quad (9)$$

Hence the components of the g-tensor in terms of the coefficients in ψ_1 and ψ_2 are

$$\begin{aligned} g_{xx} - ig_{xy} &= \sum_m (-1)^m \{ \sqrt{6-m(m+1)} (a_{m+1}^* b_{-m}^* - a_{-m}^* b_{m+1}^*) \\ &\quad + \sqrt{6-m(m-1)} (a_{m-1}^* b_{-m}^* - a_{-m}^* b_{m-1}^*) \\ &\quad - g_e (a_m^* a_{-m}^* - b_m^* b_{-m}^*) \} , \\ g_{xz} &= 2 \operatorname{Re} \sum_m \{ \sqrt{6-m(m+1)} (a_{m+1}^* a_m^* + b_{m+1}^* b_m^*) + g_e a_m^* b_m^* \} , \\ g_{yx} - ig_{yy} &= i \sum_m (-1)^{m+1} \{ \sqrt{6-m(m+1)} (a_{m+1}^* b_{-m}^* - a_{-m}^* b_{m+1}^*) \\ &\quad + a_m^* b_{-m-1}^* - b_m^* a_{-m-1}^* \} \\ &\quad - g_e (a_m^* a_{-m}^* + b_m^* b_{-m}^*) \} , \\ g_{yz} &= 0 , \\ g_{zx} - ig_{zy} &= 4 \sum_m (-1)^m (m + \frac{1}{2} g_e) a_m^* b_{-m}^* , \\ g_{zz} &= \sum_m 2m (|a_m|^2 + |b_m|^2 + g_e (|a_m|^2 - |b_m|^2)) , \end{aligned} \quad (10)$$

where summations are carried out with m varying from -2 to 2 .

As can be seen from the above expressions, $g_{i,j}$ does not necessarily equal $g_{j,i}$, and their values depend on the choice of wave functions ψ_1 and ψ_2 . This means that the g-tensor as defined through Equation (1) and calculated by using expressions (7) cannot be compared with experimental measurements directly. On the other hand, the eigenvalues of the Hamiltonian are $\pm\beta \sqrt{(g^2)_{ij} H_i H_j}$, where

$$(g^2)_{ij} = \sum_{k=1}^3 g_{ik} g_{jk} . \quad (11)$$

Hence, only $(g^2)_{ij}$ are experimentally **measurable quantities**, and they transform under rotation of coordinate axes as components of a tensor². The g^2 -**tensor** is not only symmetric but is also independent of the choice of the basis states ψ_1 and ψ_2 . This can be seen by noting that from Eqs. (9) and (11), we have

$$\begin{aligned} (g^2)_{ij} &= \left[(K_i)_{12} + (K_i)_{21} \right] \left[(K_j)_{12} + (K_j)_{21} \right] \\ &\quad - \left[(K_i)_{12} - (K_i)_{21} \right] \left[(K_j)_{12} - (K_j)_{21} \right] \\ &\quad + 4 (K_i)_{11} (K_j)_{11} \\ &= \text{tr} (K_i K_j) . \end{aligned} \quad (12)$$

As the **coefficients** in Eqs. (6) are expected to be real, it follows from Eqs.(10) that

$$g_{xy} = g_{yx} = g_{zy} = 0 \quad (13)$$

since the components of the g-tensor are real numbers.

3. A NUMERICAL EXAMPLE

Here we study, as an example, the paramagnetic effect of the $3d^3$ **electron shell** of the Cu^{2+} in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Liu and Peixoto⁸ have calculated

the wave functions and the energy levels of the positive hole in the shell of the Cu^{2+} ion by using a point charge model plus spin-orbit coupling. Their results are shown in Table I and Fig.1. Since the spin-orbit coupling constant is about 800 cm^{-1} , which is of the same order of magnitudes as the energy separations, one therefore cannot use a perturbative approximation. Substituting the values shown in Table I into Equations (10), one obtains

$$g = \begin{pmatrix} -0.6466 & 0 & -1.3641 \\ 0 & -0.7270 & 0 \\ -0.3902 & 0 & 2.4130 \end{pmatrix} \quad (14)$$

This gives

$$(g^2) = \begin{pmatrix} 2.2789 & 0 & -3.0393 \\ 0 & 0.5285 & 0 \\ -3.0393 & 0 & 5.9750 \end{pmatrix} \quad (15)$$

As in Ref.8, we have taken the crystal axes (a, b, c^*) as the x, y and z coordinate axes. The principal values of the g^2 - tensor are 7.6083, 0.5285 and 0.5457, with direction cosines $(-0.4954, 0, 0.8687)$, $(0, 1, 0)$ and $(0.8687, 0, 0.4954)$ respectively. These give $g_a = 1.5096, g_b = 0.7270$ and $g_c = 2.4444$ or $g_c = 2.4843$. These are not in good agreement with the experimental result of Gerritsen et al.⁹: $g_a = 2.187, g_b = 2.037, g_c = 2.252$. This disagreement perhaps indicates the inadequacy of the simple point-charge model for the calculation of electronic wave functions of the Cu^{2+} ion, or probably the spin-orbit coupling constant for Cu^{2+} imbedded in the crystal should be much smaller than -829 cm^{-1} , which is the free ion value. Indeed, when one puts $h = 0$, the ground state wave functions are as indicated in Table II, which then gives

$$g = \begin{pmatrix} -0.200232 & 0 & -0.000014 \\ 0 & 2.00233 & 0 \\ 0 & 0 & 2.00234 \end{pmatrix}$$

ℓ_3	S_3	ψ_1	ψ_2
2	$\frac{1}{2}$	-0.80620	-0.11054
	$\frac{1}{2}$	0.21611	-0.19953
1	$\frac{1}{2}$	0.42064	-0.03548
	$\frac{1}{2}$	-0.13479	0.10619
0	$\frac{1}{2}$	-0.20896	-0.00263
	$\frac{1}{2}$	0.00263	-0.20896
-1	$\frac{1}{2}$	-0.10620	-0.13478
	$\frac{1}{2}$	-0.03548	-0.42064
	$\frac{1}{2}$	-0.19953	-0.21611
	$\frac{1}{2}$	0.11054	-0.80620

Table I. The coefficient of the degenerate ground state wave functions of Cu^{2+} in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in terms of $\psi_{1^3 S_2}$ obtained from calculation with point-charge model with spin orbit coupling $\lambda = -829 \text{ cm}^{-1}$.

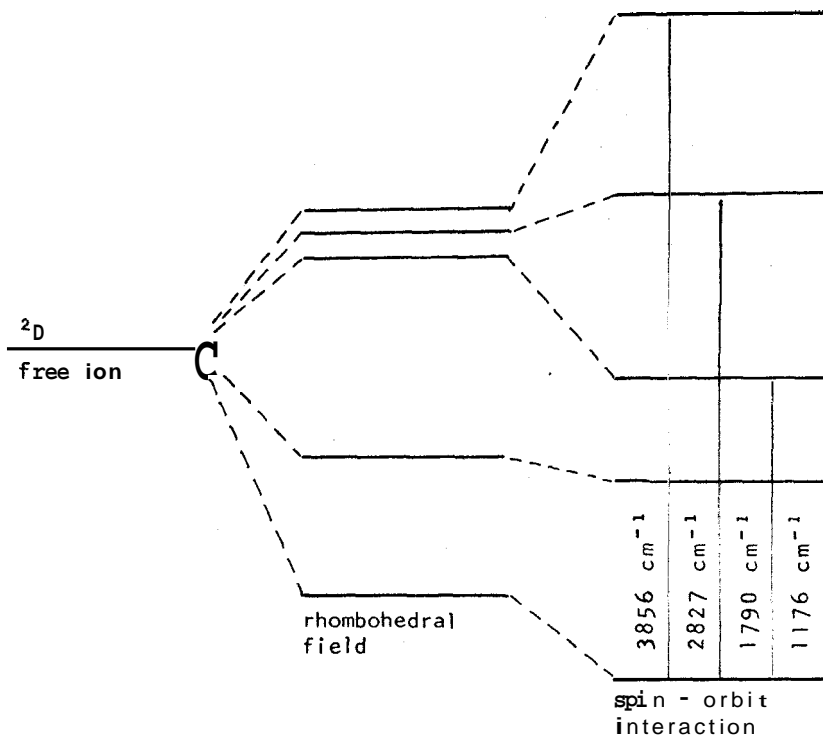


Fig. 1. Energy levels diagram of the hole in the 3d shell of Cu^{2+} .

l_3	S_3	ψ_1	ψ_2
2	$\frac{1}{2}$	-0.68266	0
	$\frac{1}{2}$	0	-0.68266
1	$\frac{1}{2}$	0.18432	0
	$\frac{1}{2}$	0	0.18432
0	$\frac{1}{2}$	-0.24861	0
	$\frac{1}{2}$	0	-0.24861
-1	$\frac{1}{2}$	0.18432	0
	$\frac{1}{2}$	0	0.18432
-2	$\frac{1}{2}$	0.68266	0
	$\frac{1}{2}$	0	0.68266

Table II. Same as Table I, except $h = 0$.

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