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Calculation of [g] Tensor of $3d^9$ Complexes on the Basis of Molecular Orbital Theory

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Abstract: Using molecular orbital approach, the third-order contribution tensor [G] has been calculated for the better knowledge of the [g] tensor of D_{4h} complexes formed with d^9 ions. The results have been applied to the analysis of the [g] tensor of different D_{4h} complexes, including the second-order contribution tensor [δg] coming out from the B_{2g} and E_g bonding levels. The numerical values of $G_{\parallel}$, $\delta g_{\parallel}$ and $G_{\perp}$, $\delta g_{\perp}$ indicate that, none of these tensors is negligible.

Keywords: Electron Paramagnetic Resonance, Optical Study, Molecular Orbital Coefficient

1. Introduction

The experimental spin-Hamiltonian of d^9 ions has generally been interpreted with the help of crystal field approach (CFA) [1]. In crystal field approach, the orbitals of the partly filled shell are supposed to be pure d orbitals and so the complex molecule is regarded as held by purely ionic forces. But some experimental facts [2–4] such as super hyperfine structure due to surrounding ions and the charge transfer bands in the optical absorption spectra can not be explained using the crystal field approach. Crystal field theory does not take into account the effect of interactions with the ligand electrons adequately. Moreover this theory is not fully applicable to those complexes which are characterized by strong interactions between the electronic orbitals of the central atom and ligands responsible for formation of molecular orbitals [5]. In molecular orbital (MO) approach, the structural unit for the wave function is the whole complex ion rather than single metal atom. In this approach, linear combination of atomic orbital (LCAO) [6] method is used to construct orbitals for the complex. This approach has proved most successful in explaining the complex hyperfine structure in the EPR spectra of covalently bonded metals [7].

However, for D_{4h} complexes formed with a d^9 ion, only the contributions arising from the second-order perturbation theory have been calculated till now using the MO approach. Comparing this second-order contribution with that found using the CFA, the basic hypothesis of this theory can be discussed in a reasonable way. It can be said that: (i) The reduction of the spin-orbit coefficient can be due to the covalency in the ground level B^*_{1g} as well as in the B^*_{2g} and E^*_g levels. However only one reduced spin-orbit coefficient is required for interpreting the [g] tensor when the degree of covalency of these B^*_{2g} and E^*_g π-levels is small enough. (ii) The use of a reduced *P* coefficient for the experimental hyperfine tensor is not justified, even in the cases where only a small degree of covalency exists [8].

In order to improve the understanding of the [g] tensor of D_{4h} complexes and its correlation with the optical absorption, we give here the calculation of the terms coming out from the third-order perturbation theory, using the MO approach. We were interested in knowing whether such terms contribute significantly to the [g] tensor and are reduced than the amount predicted by the theory based on the CFA [9, 10].

We apply this calculation to the D_{4h} complexes, using the second- and third-order terms as well as the possible influences of the B_{2g} and E_g bonding levels [11]. In the present paper the $[g - g_o]$ tensor ($g_o = 2.0023$) is written as the sum of three tensors, [Δg], [G] and [δg]. The first two are the second- and third-order contributions respectively due to the admixture, via spin-orbit coupling of the B^*_{1g} ground level to the B^*_{2g} and E^*_g antibonding levels; the third one is the second-order contribution coming out from the admixture of the ground level to the B_{2g} and E_g bonding levels [12, 13, 14].

2. Calculation of G Tensor for a D$_{4h}$ Complex

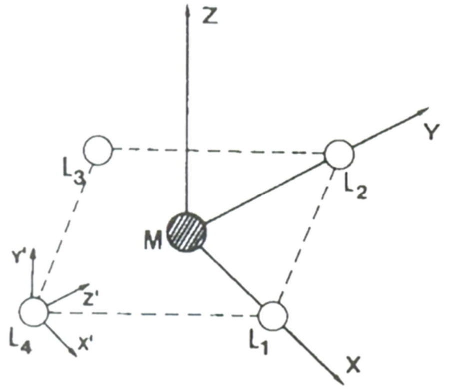

Figure 1. *The arrangement of local axis of the ligands of ML$_4$ complexes with D$_{4h}$ symmetry.*

Eqs. (2) and (3) of [8] are applied here, to a D$_{4h}$ complex formed by a d^9 ion placed in the middle of a square whose corners have four identical surrounding ligands (such as N$^-$, O^{2-}, etc) as shown in Figure 1, the valence shell of these ions being an np one. From an MO point of view the unpaired electron of these complexes is placed on the highest antibonding level, the B$^*_{1g}$. In the present calculation we will only consider the contributions coming from the other antibonding levels, B$^*_{2g}$ and E$^*_g$. The [G] tensor arises from the third-order contributions due to the mixture, via spin-orbit coupling, of the B$^*_{1g}$ ground level to the B$^*_{2g}$ and E$^*_g$ antibonding levels. The orbitals can be written as:

$$\alpha_i|d_i\rangle - \beta_i|\varphi i\rangle \; (i = 0,\ 1,\ 2) \qquad (1)$$

where $i = 0$ refers to the ground level B$_{1g}$*, and $i = 1$, $i = 2$ to B$_{2g}$* and E$_g$* levels, respectively; $|d_i\rangle$ and $|\varphi i\rangle$ are the appropriate d-function and the LCAO of the ligand ions, respectively. Due to symmetry considerations, the ns-np hybridization in ligand ions is allowed only in the B$_{1g}$* level. Thus we can write:

$$|\varphi_0\rangle = \mu\, |\varphi_p\rangle + (1- \mu^2)^{1/2}|\varphi_s\rangle \; (\mu \leq 1) \qquad (2)$$

The expressions of $|\varphi_p\rangle$, $|\varphi_s\rangle$, $|\varphi_1\rangle$ and $|\varphi_2\rangle$ in terms of the atomic ns and np orbitals of the four ligand ions are obtained by the method of the group representation theory. All molecular orbitals considered are normalized. This provides the following relation:

$$\alpha_i^2 + \beta_i^2 - 2\, \alpha_i\, \beta_i\, S_i = 0 \qquad (3)$$

between α_i and β_i. Here $S_i = \langle d_i|\varphi\rangle$ is the group overlap integral. The spin-orbit operator used in the calculations has the form discussed in [8], where.

$$T= \sum_{j=0}^{4} \xi\,(r_j)\, L_j \qquad (4)$$

The index j = 0 refers to the central d^9 ion and the index j = 1- 4 to the surrounding ions. L$_j$ is the angular momentum operator, when the origin of coordinates is the position of the ion j. In calculating the matrix elements of T, the matrix elements of $\xi(r_j)\, L_j$ between two atomic orbitals are neglected if either orbital does not belong to the ion j. The diagonal elements $\langle d_o|\ \xi(r_0)\ |d_0\rangle = \xi$ and $\langle np^1|\xi(r_1)|np^1\rangle = \xi_L$ are taken as the free d^9 ion and the free ligand ion spin-orbit coefficients, respectively. Both the assumptions depend on the fact that $\xi(r_j)$ is a function decreasing rapidly with distance from the position of the ion j and, hence, the major contribution to ξ (or to ξ_L) arises from regions practically unaffected by the chemical bonding.

Taking into account all these considerations, the following expressions for the two components, G$_{II}$ and G⊥ of the [G] tensor are obtained [15, 16]

$$G_{11} = -\left(4\xi^2 / \Delta_1\Delta_2\right)\alpha_0^2\alpha_1^2\alpha_2^2K_1q_2q(1,2) - \left(\xi / \Delta_2\right)^2 \alpha_0^2\alpha_2^4q_2^2K(2,2) - g_0\left(\xi / \Delta_2\right)^2 \alpha_0^2\alpha_2^2q_2^2 \qquad (5)$$

$$G_\perp = -2g_0\left(\xi / \Delta_1\right)^2 \alpha_0^2\alpha_1^2q_1^2 - \left(2\xi^2 / \Delta_1\Delta_2\right)\alpha_0^2\alpha_1^2\alpha_2^2q_1\left[q(1,2)K_2 - q_2K(1,2)\right] - \left(\xi / \Delta_2\right)^2\left(\frac{1}{2}g_0\alpha_0^2\alpha_2^2q_2^2 - \alpha_0^2\alpha_2^4K_2q_2\right) \qquad (6)$$

Where,

$$q_i = 1 - \frac{\beta_0\beta_i\xi_L}{c_i\alpha_0\alpha_i\xi}\mu, \; (i = 1, 2)\ c1 = 2,\ c2 = \sqrt{2} \qquad (7)$$

$$K_i = 1 - \frac{\beta_0}{\alpha_0}S_0 - \frac{\beta_i}{c_i\alpha_i}\left(c_iS_i + \frac{\beta_0}{\alpha_0}[\mu - V(1-\mu^2)^{1/2}]\right) \qquad (8)$$

$$q(1,2) = 1 + \frac{\beta_1\beta_2}{\sqrt{2}\alpha_1\alpha_2}\frac{\xi_L}{\xi} \qquad (9)$$

$$K(1,2) = 1 + \frac{\beta_1\beta_2}{\sqrt{2}\alpha_1\alpha_2} - \frac{\beta_1}{\alpha_1}S_1 - \frac{\beta_2}{\alpha_2}S_2 \qquad (10)$$

$$K(2,2) = 1 - 2\frac{\beta_2}{\alpha_2}S_2 \qquad (11)$$

$$V = R\left\langle ns^1\left|\frac{\delta}{\delta x^1}\right|np_x^1\right\rangle \qquad (12)$$

Here Δ_1 and Δ_2 are the B$^*_{2g}$→ B$^*_{1g}$ and E$^*_g$ → B$^*_{1g}$ optical transition energies, respectively and R is the central d^9 ion-ligand distance.

3. Calculation of [Δg] and [δg] Tensors for a D$_{4h}$ Complex

An improved calculation of the [g] tensor, based on an MO description, must consider not only the third-order contribution calculated above but also the second-order contribution due to the B_{2g} and E_g bonding levels. The calculation of this contribution is quite similar to the second-order contribution due to the B^*_{2g} and E^*_g antibonding levels [11, 17, 18].

The components of [Δg] and [δg] tensors can be written as:

$$\Delta g_{11} = \frac{8\xi}{\Delta_1}\alpha_0^2\alpha_1^2 K_1 q_1\,;\ \Delta g_{\perp} = \frac{2\xi}{\Delta_2}\alpha_0^2\alpha_2^2 K_2 q_2 \tag{13}$$

$$\delta g_{11} = \frac{8\xi}{\Delta_1^{'}}\alpha_0^2\alpha_1^{'2} K_1^{'} q_1^{'}\,;\ \delta g_{\perp} = \frac{2\xi}{\Delta_2^{'}}\alpha_0^2\alpha_2^{'2} K_2^{'} q_2^{'} \tag{14}$$

Where,

$$q_1^{'} = 1 + \frac{\beta_0\beta_i^{'}\xi_L}{c_i\alpha_0\alpha_i^{'}\xi}\mu \ \text{(i =1, 2)} \tag{15}$$

$$K_i^{'} = 1 - \frac{\beta_0}{\alpha_0}S_0 + \frac{\beta_i^{'}}{c_i\alpha_i^{'}}\left(c_iS_i + \frac{\beta_0}{\alpha_0}\left[\mu - V\left(1-\mu^2\right)^{1/2}\right]\right) \tag{16}$$

Δ'_1 and Δ'_2 are the $B_{2g} \rightarrow B^*_{1g}$, and $E_g \rightarrow B^*_{1g}$, forbidden optical transitions.

As discussed earlier [8], $q_i^{'}$ and $K_i^{'}$ are not reducing but increasing factors and give a more important contribution of the B_{2g} and E_g bonding levels to the [g] tensor.

4. Numerical Application to the Three D_{4h} Complexes

The values of MO coefficients, as well as of the other parameters, appearing in the present theory can be seen in Table 1. The values of the group overlap integrals are the same as those calculated for the value of R = 2.4 A^0 from diatomic overlap integrals [17, 18].

Table 1. *Numerical values of the parameters involved in the calculation of the [g] tensor of the $[CuCl_4]^{2-}$ D_{4h} Complex.*

α_0= 0.834	β_0= 0.677	q_1= 0.916	k_1= 0.807
α_1=0.973	β_1= 0.294	q_2= 0.905	k_2= 0.807
α_2= 0.982	β_2= 0.235	q'_1 = 2.146	k'_1= 1.984
α'_1= 2.38	β'_1 = 0.956	q'_2 = 3.050	k'_2= 2.628
α'_2= 1.93	β'_2 = 0.974	$q_{(1,2)}$ = 1.036	$k_{(1,2)}$ = 1.024
S_0 = 0.136	S_1=0.058	S_2=0.041	V =1.85

The values of the optical transitions involved are taken as, Δ_1 = 1.17 eV and Δ_2 =1.36 eV [13]. However, from the position of the three charge transfer absorption bands observed, we can reasonably take $\Delta_1^{'} = \Delta_2^{'}$ = 35000 cm^{-1} [14]. Table 2 gives the experimental g and R values for different D_{4h} complexes. Table 3 shows the numerical values of each of three tensors considered.

Table 2. *The experimental g and R values for different D_{4h} complexes.*

S.N.	Reference Distance R (A^0)	System	Experimental g Value g_x	g_y	g_z	Reference
1.	2.26	Bis(L-asparaginato) zinc(II)	2.0341	2.0649	2.2390	[19]
2.	2.32	Tris-sarcosine calcium chloride				[20]
		Site I	2.0276	2.0517	2.4019	
		Site II	2.0231	2.0368	2.5294	
3.	2.27	Cadmium (II) formate dihydrate				[21]
		Site I	2.0970	2.1166	2.2887	
		Site II	2.0843	2.1045	2.2742	

Table 3. *The values of the components of three [Δg], [δg] and [G] tensors involved in the determination of [g] tensor of D_{4h} complexes.*

S.N.	Reference Distance R (A^0)	System G_{11}	Component of [g] Tensor $G_\perp$	Δg_{11}	$\Delta g_\perp$	δg_{11}	$\delta g_\perp$	$g-g_0$	Ref. $(g-g_0)_e$
1.	2.26	Bis(L-asparaginato) zinc(II)							[19]
		-0.0240	-0.0167	0.3421	0.0739	0.0317	0.0098	0.1612	0.1103
2.	2.32	Tris-sarcosine calcium chloride Site I							[20]
		-0.0231 Site II	-0.0153	0.3412	0.0735	0.0342	0.0084	0.1618	0.1581
		-0.0241	-0.0154	0.3416	0.0687	0.0346	0.0095	0.1592	0.1941
3.	2.27	Cadmium (II) formate dihydrate SiteI							[21]
		-0.0229 Site II	-0.0146	0.3354	0.0779	0.0353	0.0091	0.1642	0.1651
		-0.0253	-0.0145	0.3471	0.0667	0.0356	0.0085	0.1596	0.1520

$_e$ = experimental

5. Discussion

The [g-g_0] tensor calculated using formulae (5), (6), (13) and (14) and the excitation energies obtained for crystal field and charge transfer transitions by optical absorption spectrum of various D_{4h} complexes are given in Table 3.

Different contributions to [g-g_0] tensor are also given in Table 3. Comparison of theoretical and experimental [g-g_0]

shows that the perturbative approach used for calculating the SH parameters gives satisfactory results. As seen in Table 3, even the contribution to [g-g_0] tensor arising from charge transfer levels [δg] is not negligible. However, second order contribution from crystal field levels [Δg] is dominant. Also, the third order term [G] is negative. From these facts it is seen that no contribution can be neglected in any careful analysis of the [g] tensor of these D_{4h} complexes.

6. Conclusion

The results of the present work show that the perturbative procedure for deriving the spin-Hamiltonian parameter g using MO coefficients is quite satisfactory for the present complexes.

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