MOLECULAR ORBITAL CALCULATION OF SPIN-HAMILTONIAN PARAMETERS

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ABSTRACT
The spin-Hamiltonian parameters [g] and A tensors for the d⁹ systems (Cu²⁺ doped in different lattices) are determined using theoretical expressions containing contributions from crystal field (CF) and charge transfer (CT) excitations, up to third and second order perturbations respectively, within a molecular orbital (MO) scheme. The MO coefficients corresponding to the b₁g (|x² − y²|), b₂g (|xy|), and e_g (|xz, yz|) levels and K, the core polarization contribution to the hyperfine tensor are derived through these expressions from the experimental EPR and optical data. Finally, comparison of the spin-Hamiltonian parameters obtained by calculation with experimental EPR data shows that the perturbative approach used is quite satisfactory.
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1. INTRODUCTION
EPR method is used to determine the magnitudes and directions of spin-Hamiltonian (SH) parameters such as the g-tensor and hyperfine structure tensor associated with the central metal and ligand atoms. These are used to distinguish the type of symmetry of electric field produced by ligands around the metal ion as well as to propose the ground state of the metal ions in different systems.

EPR studies of the Cu²⁺ (d⁹ ion) doped in a variety of host lattices in different symmetry environments have been reported in literature viz. octahedral, tetrahedral, square planar, square pyramidal, trigonal bipyramidal etc. In many of such cases studied, the local symmetry of the ion is D₄h (or near to it). The interpretation of the experimental spin-Hamiltonian parameters so obtained has been guided many times by a theory based on crystal field approximation [1] (CFA).

Improving the work done by Pryce and Bleaney [1], Owen [2] first reported a theoretical expression for the [g] tensor of a d⁹ ion in a D₄h square-planar geometry taking bonding into account partially. Subsequently Maki and McGarvey [3] considered the covalency in the anti-bonding 2b₂g and 2e_g levels as well as the ligand hybridization in the 3b₁g level. However, the existence of the super hyperfine (shf) structure in EPR spectra [4,5] or the presence of charge transfer (CT) bands in the optical absorption spectra [6,7] cannot be explained on the basis of CFA. So, Kivelson and Neiman [8] further improved the expressions by including metal-ligand overlap integrals but only for 3b₁g level.

Lacroix and Emch [9] emphasized on the importance of CT excitations in interpretation of SH parameters in their work on chromium and manganese octahedral complexes. Later on Smith [10] derived a theoretical expression of [g] tensor in some square planar copper complexes by taking into account all overlap integrals and effects of spin-orbit coupling.
Chow et al. [11] analyzed their experimental EPR data on CuCl$_2$ and CuBr$_2$ complexes using theoretical expressions of Smith [10] and Kivelson and Neiman [8]. Later, second order contributions to shf tensor arising from crystal-field excitations were reported by Moreno [12].

Finally, Aramburu and Moreno [13] gave the theoretical expressions for the [$g$], hyperfine, and shf tensors which give measure of the metal molecular orbital scheme. These include crystal field contribution calculated up to third order and charge transfer excitations up to second order perturbations. Further, they obtained molecular orbital (MO) coefficients and K, the core polarization contribution to the hyperfine tensor using experimental EPR and optical data for systems namely, CuCl$_2$ and CuBr$_2$ complexes.

The aim of this work is to confirm the validity of the above mentioned expressions, to generalize them for any Cu$^{2+}$ doped complex / diamagnetic lattice with approximate D$_{3h}$ crystal field symmetry. The optical absorption data obtained experimentally is used to derive the [$g$] and hyperfine structure A tensors using MO coefficients and K and to analyze the importance of all the contributions to the SH parameters.

2. THEORY

Assuming a simple molecular orbital (MO) model for metal-ligand bonding, the one-electron levels of transition-metal complexes (say ML$_n$) can be described by molecular orbitals of the form

$$\left| \psi \right> = \alpha_i \left| \phi_{\alpha_i} \right> - \beta_j \left| \chi_{\beta_j} \right>$$

where $\left| \phi_{\alpha_i} \right>$ is a metal orbital and $\left| \chi_{\beta_j} \right>$ is a symmetry-adopted linear combination of valence orbitals of the ligands involved and $\alpha, \beta$ are MO coefficients which give measure of the metal-ligand covalency. The arrangement of the local axis of the ligands of the complexes is shown in Fig.1. Often when a significant covalency is present in several one-electron levels of the complex, the values of the MO coefficients depend much on the theoretical expressions used.

**Figure 1. The arrangement of local axis of the ligands of ML$_n$ complexes having D$_{3h}$ symmetry**

The spin-Hamiltonian of metal (d$^9$) ion–ligand complex is given by,

$$\mathcal{H} = \mathcal{H} - \mathcal{H}_e = \beta_g (g_1 H_1 S_1 + g_2 H_2 S_2 + H_1 S_3 + H_2 S_3) + A_0 S L_0 + A_\perp (S L_z + S L_z) + \text{shf interaction terms}$$

The 3b$_{2g}$, 2b$_{2g}$, 2e$_{g}$ (anti-bonding) and 1b$_{2g}$, 1e$_{g}$ (bonding) levels correspond to the ground state $^2B_{1g}$ of the complex. These are important since EPR properties are governed by the following transitions,

$$\Delta \epsilon = \epsilon (3b_{2g}) - \epsilon (2b_{2g})$$

(3)

$$\Delta \epsilon = \epsilon (3b_{2g}) - \epsilon (2e_g)$$

(4)

Here only the crystal field and charge transfer excitations are considered.

Molecular orbitals characteristic of the antibonding 3b$_{2g}$, 2b$_{2g}$, 2e$_{g}$ levels and of the bonding 1b$_{2g}$, 1e$_{g}$ levels are given in the box below,

$$\begin{align*}
|3b_{2g}>& = \alpha_1 & |2b_{2g}>& = \alpha_1 \\
|2e_{g1}>& = \alpha_2 & |2e_{g2}>& = \alpha_2 \\
|1b_{2g}>& = \alpha_1 & |1e_{g1}>& = \alpha_2 \\
|1e_{g2}>& = \alpha_1 & |1e_{g2}>& = \alpha_2 \\
|X_{cm} (b_{1g})>& = \frac{1}{2} \{ p_1 (1) + p_2 (2) + p_3 (3) - p_4 (4) \} \\
|X_{cm} (b_{2g})>& = \frac{1}{2} \{ s_1 (1) - s_2 (2) + s_3 (3) - s_4 (4) \} \\
|X_{cm} (e_{g1})>& = \frac{1}{2} \{ p_1 (1) + p_2 (2) - p_3 (3) \} \\
|X_{cm} (e_{g2})>& = \frac{1}{2} \{ p_1 (1) - p_2 (2) \}
\end{align*}$$

The two components of the [$g$-$g_0$] tensor where $g_0 = 2.0023$ (value for free ion) are written as a sum of three contributions [13],

$$\begin{align*}
g_1 - g_0 &= \Delta^2 g_{||} (CF) + \Delta^2 g_{\perp} (CT) + \Delta^2 g_1 (CF) \quad (5) \\
g_{\perp} - g_0 &= \Delta^2 g_{\perp} (CF) + \Delta^2 g_{\perp} (CT) + \Delta^2 g_{\perp} (CF) \quad (6)
\end{align*}$$
Similarly, the theoretical contributions to $A_{||}$ and $A_{\perp}$ are given as,

$$
A_{||} = -K + A_{||}^1 + A_{||}^2 (CF) + A_{||}^3 (CT) + A_{||}^4 (CF) \\
A_{\perp} = -K + A_{\perp}^1 + A_{\perp}^2 (CT) + A_{\perp}^3 (CT) + A_{\perp}^4 (CF)
$$

(7)

(8)

The expressions for each contribution is as follows [13],

$$
\Delta g^2 g_{||}(CF) = 8 \alpha_0^2 \alpha_1^2 q_1 K_1 \xi_M / \Delta_1 \\
\Delta g^2 g_{||}(CT) = 2 \alpha_0^2 \alpha_2^2 q_2 K_2 \xi_M / \Delta_2 \\
\Delta g^2 g_{||}(CF) = 8 \alpha_0^2 \alpha_2^2 \xi_1^2 q_1 K_2 \xi_M / \Delta_1 \\
\Delta g^2 g_{||}(CT) = 2 \alpha_0^2 \alpha_2^2 q_2 K_2 \xi_M / \Delta_2
$$

(9)

(10)

(11)

(12)

$$
\Delta \xi g_{||}(CF) = -4 \alpha_0^2 \alpha_2^2 \alpha_2^2 q_2 K_1 q_1 (1,2) \xi_M / \Delta_2 \\
\Delta \xi g_{||}(CT) = -2 \alpha_0^2 \alpha_2^2 \alpha_2^2 q_2 \left[ q_1 (1,2) K_2 - q_2 K_1 (2,1) \right] \xi_M / \Delta_2 \\
\Delta \xi g_{||}(CF) = -2 \alpha_0^2 \alpha_2^2 \alpha_2^2 q_2 \left[ q_1 (1,2) K_2 - q_2 K_1 (2,1) \right] \xi_M / \Delta_2
$$

(13)

(14)

where $K_1 = 1 - (\beta_0 / \alpha_0) S_0$ - $(\beta_1 / 2 \alpha_0) S_1 / \Delta_1$.

(15)

$$
\Gamma(\mu) = \mu - (1 - \mu^2)^{1/2} S_1 / \Delta_1
$$

(25)

And $S_0$, $S_1$ and $S_2$ are the group overlap integrals.

Table 1. Spin-Hamiltonian parameters and the excitation energies of various crystal systems

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>g-tensor</th>
<th>A-tensor</th>
<th>Optical absorption data (in cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{</td>
<td></td>
<td>}$</td>
</tr>
<tr>
<td>L-Threonine:Cu$^{2+}$</td>
<td>2.260</td>
<td>2.056</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rubidium cadmium sulphate:Cu$^{2+}$</td>
<td>2.423</td>
<td>2.071</td>
<td>105.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium malonate:Cu$^{2+}$</td>
<td>2.236</td>
<td>2.0152</td>
<td>54.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium citrate:Cu$^{2+}$</td>
<td>2.445</td>
<td>2.118</td>
<td>78.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium cadmium acetate:Cu$^{2+}$</td>
<td>2.36</td>
<td>2.06</td>
<td>119.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium tartrate:Cu$^{2+}$</td>
<td>2.449</td>
<td>2.099</td>
<td>73.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-asparaginato zinc(II):Cu$^{2+}$</td>
<td>2.239</td>
<td>2.0495</td>
<td>169.0</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Here, $\alpha_1$, $\beta_1$ and $\mu$ are MO coefficients, K is the core polarization contribution, $P$ is the hyperfine interaction parameter, $\Delta_1$ and $\Delta_2$ are the excitation energies & $\xi_1$ and $\xi_2$ are given by the spin-orbit coupling operators, $H^m_{SO} = \xi_1 (r) L_s$ and $H^{\perp}_{SO} = \xi_2 (r \cdot \tau_L) I_p s$ for central metal ion and ligand respectively.

They have been used to obtain different terms using the optical absorption data of crystal systems given in Table 1.
3. RESULTS AND DISCUSSION

The spin-Hamiltonian parameters, $[g]$ and $A$ tensors calculated by EPR technique and the excitation energies obtained for CF and CT transitions by optical absorption spectrum of various crystal systems namely, Cu$^{2+}$ doped L-threonine [14], rubidium cadmium sulphate [15], calcium malonate [16], sodium citrate [17], calcium cadmium acetate [18], ammonium tartrate [19] and L-asparaginato zinc(II) [20] are given in Table 1.

The different contributions to $[g_{0}g_{0}]$ and A tensor are calculated using formulae (9-26) and (31-38), respectively. The value of metal-ligand distance $R$ has been taken as 2.265 Å. The corresponding values of overlap integrals given by (27-30) are $S_1 = 0.095$, $S_{2g} = 0.116$, $S_1 = 0.090$ and $S_2 = 0.063$. The values of MO coefficients used are taken from Table 2 of Aramburu and Moreno's work [13] as $\alpha_0 = 0.827$, $\beta_0 = 0.686$, $\alpha_1 = 0.934$, $\beta_1 = 0.451$, $\alpha_2 = 0.937$, $\beta_2 = 0.412$, $\alpha_3 = 0.368$, $\beta_3 = 0.897$, $\alpha_3 = 0.354$, $\beta_3 = 0.913$. Atomic parameters included in the theoretical expressions $\xi_M = 790$ cm$^{-1}$ and $\xi_L = 515$ cm$^{-1}$. Also, $\mu = 0.966$ and $P = 0.036$ cm$^{-1}$.

Different contributions to $[g_{0}g_{0}]$ tensor are given in Table 2. Comparison of Tables 1 & 2 shows that the perturbative approach used for calculating the SH parameters give satisfactory results. As seen in Table 2, even the contribution to $[g_{0}g_{0}]$ tensor arising from charge transfer levels $\Delta g$(CT) is not negligible. However, second order contribution from crystal field levels $\Delta g$(CF) is dominant. Also, the term $\Delta g$(CF) is negative.

For the hyperfine A-tensor, the main contributions are $-K$, $A_1$, $A^2$(CF), $A^2$(CT); $A^2$(CF) is the smallest one. In the present analysis, different values of core polarization contribution $K$ are obtained. As pointed out by Simanek and Muller [21], an increase in the covalency tends to decrease the value of $K$. So, it is clear from Table 1 that covalency of calcium malonate, sodium citrate and ammonium tartrate is large owing to their smaller values of $K$ which is even less than half of the value $K = 130 \times 10^{-4}$ cm$^{-1}$ obtained theoretically from free Cu$^{2+}$ ion [22] and less than $K = 68 \times 10^{-4}$ cm$^{-1}$ calculated by Bencini and Gatteschi [23]. The order of covalency in the complexes studied may thus be given as, Cu$^{2+}$/sodium citrate > Cu$^{2+}$/calcium malonate, Cu$^{2+}$/ammonium tartrate > Cu$^{2+}$/calcium cadmium acetate > Cu$^{2+}$/L-threonine > Cu$^{2+}$/L-asparaginato zinc(II) > Cu$^{2+}$/rubidium cadmium sulphate. There is a general trend of decrease of covalency with increase of metal-ligand distance [24, 25]. In all the systems studied here, the results indicate that covalency is higher in the σ-level 3b$_{1g}$ than in the π-levels 2b$_{2g}$ and 2e$_g$. This is consistent with the theoretical results of earlier workers [26, 27]. Keeping in view the calculations of Bencini and Gatteschi [23], our results show that for every one of the 3b$_{1g}$, 2b$_{2g}$ and 2e$_g$ levels electronic charge lies mainly on copper as in case of CuCl$_2$ [13].

Table 2. Different contributions to $[g_{0}g_{0}]$ tensor of various crystal systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>$\Delta g$(CF)</th>
<th>$\Delta g$(CT)</th>
<th>$\Delta g$(CF)</th>
<th>Total $K$</th>
<th>$A_1$</th>
<th>$A_2$(CF)</th>
<th>$A_2$(CT)</th>
<th>$A_4$(CF)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Threonine</td>
<td></td>
<td></td>
<td></td>
<td>A$_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-0.197881</td>
<td>0.09132</td>
<td>-0.0881</td>
<td>2.826023</td>
<td>A$_1$</td>
<td>-1.28</td>
<td>-1.40694</td>
<td>109.854</td>
<td>21.1928</td>
</tr>
<tr>
<td>Rubidium</td>
<td>-0.038023</td>
<td>0.03127</td>
<td>-0.01434</td>
<td>0.054953</td>
<td>A$_1$</td>
<td>-1.28</td>
<td>70.34698</td>
<td>15.86775</td>
<td>4.110061</td>
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<tr>
<td>Cadmium</td>
<td>-0.301577</td>
<td>0.145874</td>
<td>-0.02153</td>
<td>0.425921</td>
<td>A$_1$</td>
<td>-1.55</td>
<td>-1.40694</td>
<td>167.933</td>
<td>31.82765</td>
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<td>Sulphate</td>
<td>-0.06007</td>
<td>0.046962</td>
<td>-0.03386</td>
<td>0.073172</td>
<td>A$_1$</td>
<td>-1.55</td>
<td>70.34698</td>
<td>25.06878</td>
<td>6.172563</td>
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<td>Calcium</td>
<td>-0.156086</td>
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<td>A$_1$</td>
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<td>86.9371</td>
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<td>Malonate</td>
<td>-0.031381</td>
<td>0.027654</td>
<td>-0.00908</td>
<td>0.049751</td>
<td>A$_1$</td>
<td>-0.40</td>
<td>70.34698</td>
<td>13.0126</td>
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<td>Sodium</td>
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<td>83.45358</td>
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<td>0.068035</td>
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<td>0.052582</td>
<td>A$_1$</td>
<td>-0.40</td>
<td>70.34698</td>
<td>14.63229</td>
<td>3.627673</td>
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</table>
CONCLUSION

The results show that a good understanding of the SH parameters in terms of the MO scheme requires one to be careful with respect to the theoretical framework used. The value of K obtained indicates that it depends not only on the equatorial covalency but also on bonding with axial ligands. The results of the present work show that the perturbative procedure for deriving the spin-Hamiltonian parameters using MO coefficients and core polarization contribution K is quite satisfactory for the present complexes. The order of covalency in the complexes studied is obtained as: Cu$^{2+}$/sodium citrate $>$ Cu$^{2+}$/calcium malonate, Cu$^{2+}$/ammonium tartrate $>$ Cu$^{2+}$/calcium cadmium acetate $>$ Cu$^{2+}$/L-threonine$>$ Cu$^{2+}$/L-asparaginato zinc $>$ Cu$^{2+}$/rubidium cadmium sulphate.

REFERENCES