



## MOLECULAR ORBITAL CALCULATION OF SPIN-HAMILTONIAN PARAMETERS

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### ABSTRACT

The spin-Hamiltonian parameters [g] and A tensors for the  $d^9$  systems ( $\text{Cu}^{2+}$  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  $b_{1g}(|x^2 - y^2\rangle)$ ,  $b_{2g}(|xy\rangle)$ , and  $e_g(|xz, yz\rangle)$  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  $\text{Cu}^{2+}$  ( $d^9$  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  $D_{4h}$  (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  $d^9$  ion in a  $D_{4h}$  square-planar geometry taking bonding into account partially. Subsequently Maki and McGarvey [3] considered the covalency in the anti-bonding  $2b_{2g}$  and  $2e_g$  levels as well as the ligand hybridization in the  $3b_{1g}$  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  $3b_{1g}$  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  $\text{CuCl}_4^{2-}$  and  $\text{CuBr}_4^{2-}$  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 of a  $d^9$  square-planar complex within a 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,  $\text{CuCl}_4^{2-}$  and  $\text{CuBr}_4^{2-}$  complexes.

The aim of this work is to confirm the validity of the above mentioned expressions, to generalize them for any  $\text{Cu}^{2+}$  doped complex / diamagnetic lattice with approximate  $D_{4h}$  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  $\text{ML}_n$ ) can be described by molecular orbitals of the form

$$|\psi^i\rangle = \alpha_i |\phi_M^i\rangle - \beta_i |\chi_L^i\rangle \quad (1)$$

where  $|\phi_M^i\rangle$  is a metal orbital and  $|\chi_L^i\rangle$  is a symmetry-adapted linear combination of valence orbitals of the ligands involved and  $\alpha_i, \beta_i$  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.

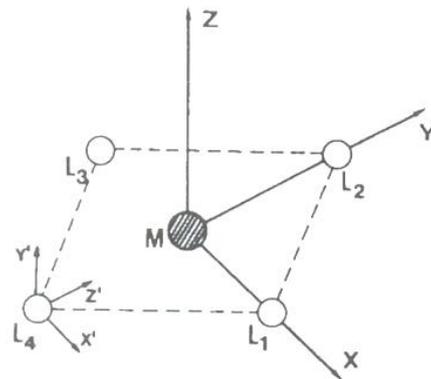


Figure 1. The arrangement of local axis of the ligands of  $\text{ML}_4$  complexes having  $D_{4h}$  symmetry

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

$$\mathcal{H} = \mathcal{H} = \beta \{g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)\} + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) + \text{shf interaction terms} \quad (2)$$

The  $3b_{1g}, 2b_{2g}, 2e_g$  (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,

$$\Delta_1 = \epsilon(3b_{1g}) - \epsilon(2b_{2g}) \quad (3)$$

$$\Delta_2 = \epsilon(3b_{1g}) - \epsilon(2e_g)$$

$$\Delta_1' = \epsilon(3b_{1g}) - \epsilon(1b_{2g}) \quad (4)$$

$$\Delta_2' = \epsilon(3b_{1g}) - \epsilon(1e_g)$$

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

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

$$\begin{aligned} |3b_{1g}\rangle &= \alpha_0 |d_{x^2-y^2}\rangle - \beta_0 \{ \mu | \chi_{p\sigma}(b_{1g})\rangle + (1-\mu^2)^{1/2} | \chi_s(b_{1g})\rangle \} \\ |2b_{2g}\rangle &= \alpha_1 |d_{xy}\rangle - \beta_1 | \chi_{p\pi}(b_{2g})\rangle \\ |2e_{g1}\rangle &= \alpha_2 |d_{xz}\rangle - \beta_2 | \chi_{p\pi}(e_{g1})\rangle \\ |2e_{g2}\rangle &= \alpha_2 |d_{yz}\rangle - \beta_2 | \chi_{p\pi}(e_{g2})\rangle \\ |1b_{2g}\rangle &= \alpha_1' |d_{xy}\rangle + \beta_1' | \chi_{p\pi}(b_{2g})\rangle \\ |1e_{g1}\rangle &= \alpha_2' |d_{xz}\rangle + \beta_2' | \chi_{p\pi}(e_{g1})\rangle \\ |1e_{g2}\rangle &= \alpha_2' |d_{yz}\rangle + \beta_2' | \chi_{p\pi}(e_{g2})\rangle \\ | \chi_{p\sigma}(b_{1g})\rangle &= \frac{1}{2} \{ -p_x(1) + p_y(2) + p_x(3) - p_y(4) \} \\ | \chi_s(b_{1g})\rangle &= \frac{1}{2} \{ s(1) - s(2) + s(3) - s(4) \} \\ | \chi_{p\pi}(b_{2g})\rangle &= \frac{1}{2} \{ p_y(1) + p_x(2) - p_y(3) - p_x(4) \} \\ | \chi_{p\pi}(e_{g1})\rangle &= 1/\sqrt{2} \{ p_x(1) - p_z(3) \} \\ | \chi_{p\pi}(e_{g2})\rangle &= 1/\sqrt{2} \{ p_x(2) - p_z(4) \} \end{aligned}$$

The two components of the [g-g<sub>0</sub>] tensor where  $g_0 = 2.0023$  (value for free ion) are written as a sum of three contributions [13],

$$g_{\parallel} - g_0 = \Delta^2 g_{\parallel}(\text{CF}) + \Delta^2 g_{\parallel}(\text{CT}) + \Delta^3 g_{\parallel}(\text{CF}) \quad (5)$$

$$g_{\perp} - g_0 = \Delta^2 g_{\perp}(\text{CF}) + \Delta^2 g_{\perp}(\text{CT}) + \Delta^3 g_{\perp}(\text{CF}) \quad (6)$$

Similarly, the theoretical contributions to  $A_{\parallel}$  and  $A_{\perp}$  are given as,

$$A_{\parallel} = -K + A_{\parallel}^1 + A_{\parallel}^2 (CF) + A_{\parallel}^2 (CT) + A_{\parallel}^3 (CF) \quad (7)$$

$$A_{\perp} = -K + A_{\perp}^1 + A_{\perp}^2 (CF) + A_{\perp}^2 (CT) + A_{\perp}^3 (CF) \quad (8)$$

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

$$\Delta^2 g_{\parallel}(CF) = 8 \alpha_0^2 \alpha_1^2 q_1 K_1 \xi_M / \Delta_1 \quad (9)$$

$$\Delta^2 g_{\perp}(CF) = 2 \alpha_0^2 \alpha_2^2 q_2 K_2 \xi_M / \Delta_2 \quad (10)$$

$$\Delta^2 g_{\parallel}(CT) = 8 \alpha_0^2 \alpha_1^2 q_1' K_1' \xi_M / \Delta_1' \quad (11)$$

$$\Delta^2 g_{\perp}(CT) = 2 \alpha_0^2 \alpha_2^2 q_2' K_2' \xi_M / \Delta_2' \quad (12)$$

$$\Delta^3 g_{\parallel}(CF) = -4 \alpha_0^2 \alpha_1^2 \alpha_2^2 q_2 K_1 q(1,2) \xi_M^2 / \Delta_1 \Delta_2 - \alpha_0^2 \alpha_2^4 q_2^2 K(2,2) \xi_M^2 / \Delta_2^2 - g_0 \alpha_0^2 \alpha_2^2 q_2^2 \xi_M^2 / \Delta_2^2 \quad (13)$$

$$\Delta^3 g_{\perp}(CF) = -2 \alpha_0^2 \alpha_1^2 \alpha_2^2 q_1 \{q(1,2)K_2 - q_2 K(1,2)\} \xi_M^2 / \Delta_1 \Delta_2 - 2 g_0 \alpha_0^2 \alpha_1^2 q_1^2 \xi_M^2 / \Delta_1^2 - \{g_0/2 \alpha_0^2 \alpha_2^2 q_2^2 - \alpha_0^2 \alpha_2^4 q_2 K_2\} \xi_M^2 / \Delta_2^2 \quad (14)$$

$$\text{where } K_1 = 1 - (\beta_0 / \alpha_0) S_0 - (\beta_1 / 2\alpha_1) \{2S_1 + (\beta_0 / \alpha_0) \Gamma(\mu)\} \quad (15)$$

$$K_2 = 1 - (\beta_0 / \alpha_0) S_0 - (\beta_2 / \sqrt{2}\alpha_2) \{\sqrt{2}S_2 + (\beta_0 / \alpha_0) \Gamma(\mu)\} \quad (16)$$

$$K_1' = 1 - (\beta_0 / \alpha_0) S_0 + (\beta_1' / 2\alpha_1') \{2S_1 + (\beta_0 / \alpha_0) \Gamma(\mu)\} \quad (17)$$

$$K_2' = 1 - (\beta_0 / \alpha_0) S_0 - (\beta_2' / \sqrt{2}\alpha_2') \{\sqrt{2}S_2 + (\beta_0 / \alpha_0) \Gamma(\mu)\} \quad (18)$$

$$K(1,2) = 1 + (\beta_1 \beta_2) / \sqrt{2}\alpha_1 \alpha_2 - (\beta_1 / \alpha_1) S_1 - (\beta_2 / \alpha_2) S_2 \quad (19)$$

$$q_1 = 1 - (\beta_0 \beta_1 \mu \xi_L) / 2 \alpha_0 \alpha_1 \xi_M \quad (20)$$

$$q_2 = 1 - (\beta_0 \beta_2 \mu \xi_L) / \sqrt{2} \alpha_0 \alpha_2 \xi_M \quad (21)$$

$$q_1' = 1 + (\beta_0 \beta_1' \mu \xi_L) / 2 \alpha_0 \alpha_1' \xi_M \quad (22)$$

$$q_2' = 1 + (\beta_0 \beta_2' \mu \xi_L) / \sqrt{2} \alpha_0 \alpha_2' \xi_M \quad (23)$$

$$q(1,2) = 1 + (\beta_1 \beta_2 \xi_L) / \sqrt{2} \alpha_1 \alpha_2 \xi_M \quad (24)$$

$$\Gamma(\mu) = \mu - (1 - \mu^2)^{1/2} R < s(1) | \partial / \partial \gamma(1) | p_{\gamma}(1) > \quad (25)$$

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

$$S_0 = \mu S_{p\sigma} + (1 - \mu^2)^{1/2} S_s \quad (26)$$

$$S_{p\sigma} = < d_x 2 - \sqrt{2} | \chi_{p\sigma} (b_{1g}) > \quad (27)$$

$$S_s = < d_x 2 - \sqrt{2} | \chi_s (b_{1g}) > \quad (28)$$

$$S_1 = < d_{xy} | \chi_{p\pi} (b_{2g}) > \quad (29)$$

$$S_2 = < d_{xz} | \chi_{p\pi} (e_{g1}) > \quad (30)$$

$$A_{\parallel}^1 = -4/7 \alpha_0^2 P \quad (31)$$

$$A_{\perp}^1 = 2/7 \alpha_0^2 P \quad (32)$$

$$A_{\parallel}^2 (CF) = \{8 \alpha_0^2 \alpha_1^2 q_1 \xi_M / \Delta_1 + 6/7 \alpha_0^2 \alpha_2^2 q_2 \xi_M / \Delta_2\} P \quad (33)$$

$$A_{\perp}^2 (CF) = 11/7 \alpha_0^2 \alpha_2^2 q_2 \xi_M / \Delta_2 P \quad (34)$$

$$A_{\parallel}^2 (CT) = \{8 \alpha_0^2 \alpha_1^2 q_1' \xi_M / \Delta_1' + 6/7 \alpha_0^2 \alpha_2^2 q_2' \xi_M / \Delta_2'\} P \quad (35)$$

$$A_{\perp}^2 (CT) = 11/7 \alpha_0^2 \alpha_2^2 q_2' \xi_M / \Delta_2' P \quad (36)$$

$$A_{\parallel}^3 (CF) = \alpha_0^2 \{ 4/7 (\alpha_0^2 \alpha_1^2 - \alpha_1^4) q_1^2 \xi_M^2 / \Delta_1^2 + 2/7 (3/2 \alpha_2^4 + \alpha_0^2 \alpha_2^2 q_2 - 4 \alpha_2^4 q_2) q_2 \xi_M^2 / \Delta_2^2 - 2 [2q(1,2) q_2 + 3/7 q_1 q_2 + 3/7 q_1 q(1,2)] \alpha_1^2 \alpha_2^2 \xi_M^2 / \Delta_1 \Delta_2 \} P \quad (37)$$

$$A_{\perp}^3 (CF) = \alpha_0^2 \{ -2/7 (\alpha_0^2 \alpha_1^2 + \alpha_1^4) q_1^2 \xi_M^2 / \Delta_1^2 - 1/14 (2 \alpha_0^2 \alpha_2^2 q_2 - 11 \alpha_2^4) q_2 \xi_M^2 / \Delta_2^2 + 11/7 [q_2 - q(1,2)] \alpha_0^2 \alpha_1^2 \alpha_2^2 q_1 \xi_M^2 / \Delta_1 \Delta_2 \} P \quad (38)$$

Here,  $\alpha_i$ ,  $\beta_i$  and  $\mu$  are MO coefficients,  $K$  is the core polarization contribution,  $P$  is hyperfine interaction parameter,  $\Delta_1$  and  $\Delta_2$  are the excitation energies &  $\xi_M$  and  $\xi_L$  are given by the spin-orbit coupling operators,

$H_{SO}^M = \xi_M (r) \mathbf{l} \cdot \mathbf{s}$  and  $H_{SO}^L = \xi_L (r - r_k) \mathbf{l}_k \cdot \mathbf{s}$  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.

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

Crystal system	g-tensor		A-tensor		Optical absorption data (in $\text{cm}^{-1}$ )	
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	crystal field transitions	charge transfer transitions
L-Threonine:Cu <sup>2+</sup>	2.260	2.056	180.0	19.35	$\Delta_1 = 11722$ $\Delta_2 = 14165$	$\Delta_1' = 18199$ $\Delta_2' = 18199$
Rubidium cadmium sulphate:Cu <sup>2+</sup>	2.423	2.071	105	61	$\Delta_1 = 7690$ $\Delta_2 = 8966$	$\Delta_1' = 12118$ $\Delta_2' = 12118$
Calcium malonate:Cu <sup>2+</sup>	2.236	2.0152	54	36	$\Delta_1 = 14858$ $\Delta_2 = 17273$	$\Delta_1' = 17951$ $\Delta_2' = 20582$
Sodium citrate:Cu <sup>2+</sup>	2.445	2.118	78	51	$\Delta_1 = 15576$ $\Delta_2 = 16807$	$\Delta_1' = 19685$ $\Delta_2' = 20576$
Calcium cadmium acetate:Cu <sup>2+</sup>	2.36	2.06	119	13	$\Delta_1 = 12800$ $\Delta_2 = 14000$	$\Delta_1' = 12000$ $\Delta_2' = 13500$
Ammonium tartrate:Cu <sup>2+</sup>	2.449	2.099	73	50	$\Delta_1 = 14388$ $\Delta_2 = 15361$	$\Delta_1' = 18904$ $\Delta_2' = 20619$
L-asparaginato zinc(II) :Cu <sup>2+</sup>	2.239	2.0495	169	63	$\Delta_1 = 14727$ $\Delta_2 = 17114$	$\Delta_1' = 17800$ $\Delta_2' = 20790$

### 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,  $\text{Cu}^{2+}$  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  $[g-g_0]$  and  $A$  tensor are calculated using formulae (9-26) and (31-38), respectively. The value of metal-ligand distance  $R$  has been taken as  $2.265 \text{ \AA}$ . The corresponding values of overlap integrals given by (27-30) are  $S_s = 0.095$ ,  $S_{p\sigma} = 0.116$ ,  $S_1 = 0.090$  and  $S_2 = 0.063$ . The values of MO coefficients used are taken from Table 2 of Aramburu and Moreno's work [13] as  $\alpha_0 = 0.827$ ,  $\beta_0 = 0.686$ ,  $\alpha_1 = 0.934$ ,  $\beta_1 = 0.451$ ,  $\alpha_2 = 0.937$ ,  $\beta_2 = 0.412$ ,  $\alpha'_1 = 0.368$ ,  $\beta'_1 = 0.897$ ,  $\alpha'_2 = 0.354$ ,  $\beta'_2 = 0.913$ . Atomic parameters included in the theoretical expressions  $\xi_M = 790 \text{ cm}^{-1}$  and  $\xi_L = 515 \text{ cm}^{-1}$ . Also,  $\mu = 0.966$  and  $P = 0.036 \text{ cm}^{-1}$ .

Different contributions to  $[g-g_0]$  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  $[g-g_0]$  tensor arising from charge transfer levels  $\Delta^2g(\text{CT})$  is not negligible. However, second order contribution from

crystal field levels  $\Delta^2g(\text{CF})$  is dominant. Also, the term  $\Delta^3g(\text{CF})$  is negative.

For the hyperfine A-tensor, the main contributions are  $-K$ ,  $A_1$ ,  $A^2(\text{CF})$ ,  $A^2(\text{CT})$ ;  $A^3(\text{CF})$  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  $K = 130 \times 10^{-4} \text{ cm}^{-1}$  obtained theoretically from free  $\text{Cu}^{2+}$  ion [22] and less than  $K = 68 \times 10^{-4} \text{ cm}^{-1}$  calculated by Bencini and Gatteschi [23]. The order of covalency in the complexes studied may thus be given as,  $\text{Cu}^{2+}$  /sodium citrate >  $\text{Cu}^{2+}$ /calcium malonate,  $\text{Cu}^{2+}$ /ammonium tartrate >  $\text{Cu}^{2+}$ /calcium cadmium acetate >  $\text{Cu}^{2+}$ /L-threonine >  $\text{Cu}^{2+}$ /L-asparaginato zinc (II) >  $\text{Cu}^{2+}$ /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  $\sigma$ -level  $3b_{1g}$  than in the  $\pi$ -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  $\text{CuCl}_4^{2-}$  [13].

Table 2. Different contributions to  $[g-g_0]$  tensor of various crystal systems

system		$\Delta^2g(\text{CF})$	$\Delta^2g(\text{CT})$	$\Delta^3g(\text{CF})$	Total		-K	$A_1$	$A_2(\text{CF})$	$A_2(\text{CT})$	$A_3(\text{CF})$	Total
L-Threonine	$g \parallel -g_0$	.197881	.097132	-.00881	<b>.286203</b>	$A \parallel$	-128	-140.694	109.854	21.19278	-3.88409	<b>-141.63</b>
	$g \perp -g_0$	.038023	.03127	-.01434	<b>.054953</b>	$A \perp$	-128	70.34698	15.86775	4.110061	-.16217	<b>-37.93738</b>
Rubidium cadmium sulphate	$g \parallel -g_0$	.301577	.145874	-.02153	<b>.425921</b>	$A \parallel$	-155	-140.694	167.933	31.82765	-9.36173	<b>-105.2951</b>
	$g \perp -g_0$	.06007	.046962	-.03386	<b>.073172</b>	$A \perp$	-155	70.34698	25.06878	6.172553	-.33245	<b>-53.74414</b>
Calcium malonate	$g \parallel -g_0$	.156086	.098474	-.00579	<b>.24877</b>	$A \parallel$	-40	-140.694	86.9371	21.19503	-2.51527	<b>-75.07714</b>
	$g \perp -g_0$	.031181	.02765	-.00908	<b>.049751</b>	$A \perp$	-40	70.34698	13.0126	3.634195	-.08804	<b>46.90574</b>
Sodium citrate	$g \parallel -g_0$	.148891	.0898	-.00587	<b>.232821</b>	$A \parallel$	-32	-140.694	83.45358	13.17893	-2.47097	<b>-78.53246</b>
	$g \perp -g_0$	.032046	.027658	-.00856	<b>.051144</b>	$A \perp$	-32	70.34698	13.3734	2.528189	-.05432	<b>54.19425</b>
Calcium cadmium acetate	$g \parallel -g_0$	.181182	.147309	-.00852	<b>.319971</b>	$A \parallel$	-108	-140.694	101.4331	31.76285	-3.60828	<b>-119.1063</b>
	$g \perp -g_0$	.038471	.042154	-.01259	<b>.068035</b>	$A \perp$	-108	70.34698	16.05476	5.540666	-.08788	<b>-16.14547</b>
Ammonium tartrate	$g \parallel -g_0$	.161185	.09351	-.00698	<b>.247715</b>	$A \parallel$	-40	-140.694	90.4286	20.22291	-2.92776	<b>-72.97025</b>
	$g \perp -g_0$	.035062	.0276	-.01008	<b>.052582</b>	$A \perp$	-40	70.34698	14.63229	3.627673	-.05892	<b>48.54802</b>

L-asparaginato zinc(II)	$g_{\parallel} - g_0$	.159029	.099309	-.00593	<b>.252408</b>	$A_{\parallel}$	-140	-140.694	88.50861	21.33819	-2.5859	<b>-173.4331</b>
	$g_{\perp} - g_0$	.031471	.027373	-.00939	<b>.049454</b>	$A_{\perp}$	-140	70.34698	13.1335	3.597835	-.09477	<b>-53.01646</b>

### 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.

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