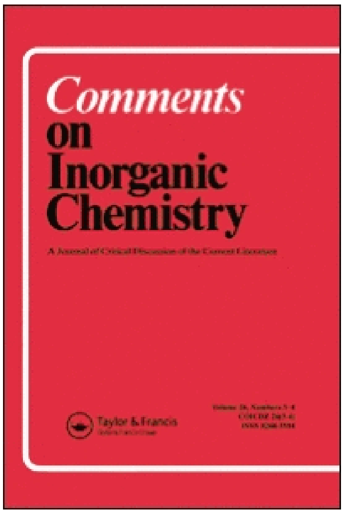

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Calculating EPR Spin Hamiltonian Parameters of Transition Metal Complexes

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INTRODUCTION

EPR spectra have been, and still are, a powerful tool for obtaining indirect information on the nature of the electronic ground state of transition metal complexes.[1-3] With relatively little effort it is generally possible to identify the nature of the orbitals which contribute to the ground state, the symmetry of the complex, the extent of delocalization of the unpaired electron(s) onto the ligands, the extent of coupling among neighboring paramagnetic centers, *etc.*

The quantitative interpretation of EPR spectra relies heavily on the spin Hamiltonian formalism.[4] This formalism allows one to obtain a set of parameters, the spin Hamiltonian parameters, SHP, which can be compared with values calculated through some more fundamental theory which in turn permits their correlation with the geometrical and electronic structure of the complex. The ligand field approach is widely used to calculate the **g**, **A**, **D** tensors of transition metal complexes, while with molecular orbital models it is possible to calculate the ligand hyperfine tensors as well. The two models have been employed from the very beginning of the chemical applications of EPR spectroscopy, but until recently the theoretical treatment was essentially limited to high-symmetry species, and low-symmetry effects were included using only perturbative approaches. The revolution brought about by the new generations of computers has made it relatively easy to perform lengthy calculations: this has

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changed our attitude towards the interpretation of the SHP of transition metal complexes.

It appeared of interest to us to offer some comments on these topics, since future developments of our understanding of the electronic structure of transition metal complexes will have to rely also on the picture offered by EPR spectroscopy. We will divide this Comment into two main sections, one devoted to the perspectives of ligand field models, and the other to those of molecular orbital models. A final section will summarize the main conclusions that can be drawn from the use of the two models.

LIGAND FIELD MODELS

The angular overlap model,[5] AOM, a ligand field model with parameters that are expected to describe the extent of σ and π metal–ligand interactions, has been an extremely useful tool for the interpretation of the magnetic properties[6–8] and the EPR spectra[9–10] of low-symmetry transition metal complexes. π back-bonding interactions are also considered allowing the e_π parameters to be negative.

The AOM does not assume cylindrical symmetry in the M–L interaction. This gives the AOM a greater intrinsic flexibility than the standard classical ligand field models. In fact, by using the AOM many examples of low-symmetry spectra, which were not easily understood using crystal field formalisms, have been satisfactorily explained. One classic example is given by hexakis pyridine–N–oxide metal complexes, which have almost strict octahedral symmetry if the MO_6^{2+} chromophores are considered, with six identical M–O distances and O–M–O angles of 89.3° and 90.7°, respectively.[11,12] In spite of this, the EPR spectra show large deviations from octahedral symmetry: $Co(pyO)_6^{2+}$ yields[13] $g_\parallel = 2.26$ and $g_\perp = 4.77$ while $Mn(pyO)_6^{2+}$ and $Ni(pyO)_6^{2+}$ show large zero-field splittings.[14,15] These low-symmetry effects are easily understood[16,17] using the AOM if the pyO ligands are assumed to be not linearly ligating, i.e., if the π interactions with the metal ions are assumed not to be isotropic, as a consequence of the inequivalence of the lone pairs on the oxygen donors.

π anisotropy effects are particularly important for those metal ions which have relevant contributions to the ground state from π antibonding orbitals, such as octahedral high-spin cobalt(II), low-spin iron(III), chromium(III), oxovanadium(IV), etc. Low-symmetry components for these metal ions are determined by the relative importance of the π interactions of the different ligands. For instance, in octahedral high-spin cobalt(II) complexes a tetragonal distortion can yield either $g_{\parallel} > g_{\perp}$ or $g_{\parallel} < g_{\perp}$: in fact if the ground ${}^4T_{1g}$ state of octahedral symmetry is split by a tetragonal perturbation in such a way that an orbital doublet becomes the ground level, then $g_{\parallel} > g_{\perp}$, while if an orbital singlet lies lowest, then $g_{\parallel} < g_{\perp}$. To a good approximation the extent of the splitting is given[18] by:

$$D = 4e^{\mathrm{eq}}_{\pi\perp} - 2e^{\mathrm{eq}}_{\pi\parallel} - 2e^{\mathrm{ax}}_{\pi} \qquad (1)$$

where D is the energy difference between the orbital singlet and doublet states, e^{eq}_{π} and e^{ax}_{π} are the AOM parameters relative to the π interaction of the equatorial and axial ligands, respectively, $\pi\parallel$ and $\pi\perp$ refer to the interaction parallel and perpendicular to the tetragonal axis. From (1) it is apparent that in this case it is not possible to immediately draw a conclusion regarding the type of tetragonal distortion from the pattern of g values.[3] In fact, the sign of D is determined by three terms, each of which may be positive, negative, or zero. It is this ambiguity which makes these systems different from those in which the nature of the ground state is largely determined by σ interactions. In fact, if we consider pseudo-octahedral copper(II) complexes, the ground orbital will be $x^2 - y^2$ or z^2, the energy splitting between the two being

$$D_1 = 2e^{\mathrm{eq}}_{\sigma} - 2e^{\mathrm{ax}}_{\sigma} \qquad (2)$$

Since the e_{σ} parameters must both be positive, D_1 is positive if $e^{\mathrm{eq}}_{\sigma} > e^{\mathrm{ax}}_{\sigma}$. Therefore the pattern of g values immediately reflects the sign of the tetragonal distortion.

The situation becomes even more complicated when the symmetry is lower than axial. In these cases it is necessary to record single crystal spectra: knowing both the principal values and directions of the spin Hamiltonian tensors it can be reasonably hoped to have available all the information needed to describe the electronic structure of the complex. This approach has recently been used for low-spin octahedral d^5 systems,[19] which have a ${}^2T_{2g}$ ground state. The splitting of the three orbital components is determined by low-symmetry effects, which depend on the relative π contributions of the six ligands bound to the central metal atom. For instance, in low-spin iron(III) porphyrins it has long been known that the principal directions of **g** are influenced by the nature and the orientation of the axial ligands.[20] If, for instance, one such ligand is a histidine molecule, it can be reasonably assumed that the π interaction with the iron(III) is anisotropic, being zero parallel to the aromatic ring, and different from zero orthogonal to it. In the general case of two axial ligands with different π anisotropies and orientations, the orbital containing the unpaired electron must be a linear combination of $|xz)$ and $|yz)$ orbitals of the type[10]:

$$|y'z') = \cos\alpha|yz) + \sin\alpha\,|xz) \tag{3}$$

with

$$\alpha = \frac{1}{2}\tan^{-1}\,[\Sigma_i \sin 2\psi_i(e^i_{\pi y} - e^i_{\pi x})]/[\Sigma_i \cos 2\psi_i(e^i_{\pi y} - e^i_{\pi x})] \tag{4}$$

where $e_{\pi y}$ and $e_{\pi x}$ are the π interactions parallel to the corresponding ligand axes, and ψ is the angle the x ligand axis makes with the x axis of the metal frame. In the case of two identical ligands Eq. (4) reduces to $\alpha = \psi$, which means that the trace of the $y'z'$ orbital in the xy plane is rotated by an angle ψ. Concurrently the principal directions of **g** in the xy plane rotate from the axes by an angle $-\psi$ so that experimental determination can yield indirect information on the orientation of the axial histidine ligand. Of course some caution must be exercised when two inequivalent axial ligands are present. A more detailed discussion on this is available elsewhere.[10]

Another example of the important role of anisotropic π interactions is given by the well-known Creutz–Taube[21] cation $[(NH_3)_{10}Ru_2pyr]^{5+}$, pyr = pyrazine. The single crystal EPR spectra[22,23] showed that the smallest g value, $g_3 = 1.334$, is orthogonal to the pyrazine plane, while the g_1 and g_2 values, $g_1 = 2.779$ and $g_2 = 2.489$, are close enough to each other to be considered the split components of $g_\perp$. Apparently in this case also the symmetry of the electronic structure of the complex is determined by the anisotropic π interaction with the axial pyrazine.

Apart from these examples, which are particularly well suited for a discussion in qualitative terms, it must be understood that it is possible to compute the energy levels of transition metal complexes, together with the magnetic properties and the SHP, using appropriate computer programs, without making any assumption regarding the symmetry of the complex, by fixing the ligands to the coordinates determined in the crystal structures. The results of these calculations yield values which can be directly compared to the experimental ones, providing estimates of the e_σ and e_π parameters.[3]

In this Comment a question that needs to be answered is: what are the prospects in the area? The feeling of the authors is that not many innovations can be expected. The ligand field models, which were so important in favoring the renaissance of inorganic chemistry in the 1950's, have apparently been fully exploited. The only desirable development is that they become more widely used, with the existing computer routines (which calculate spectral and magnetic properties without any approximation regarding the geometrical structure) being made available to potential users who may as yet not be familiar with them. In particular, it can be expected that more attention will be devoted to metallo-enzymes and metallo-proteins, since several crystal structures and many spectral data are now available. Indeed, some interesting applications have already appeared in the literature.[10,24]

MOLECULAR ORBITAL MODELS

Several different MO methods, ranging from extended Hückel to *ab initio*, have been traditionally used to calculate the SHP.[25–28] A model which is currently under intensive examination is the self-consistent-field multiple-scattering Xα method (SCF–MS–Xα).[29] With this model it is possible to handle systems containing heavy metal ions without many difficulties, using radial functions which have great flexibility, since they are numerically calculated, as well as to easily perform relativistic calculations. In the MS–Xα model the muffin-tin approximation of the molecular potential together with Slater's statistical exchange-potential functional[30] drastically reduce the computer time needed for the SCF calculations.

In the framework of the Slater statistical approximation to the exchange-correlation potential other methods have been developed which do not use the muffin-tin approximation, namely the discrete variational Xα and the LCAO–Xα methods.[31,32] The computer time needed for the calculation of the SHP with these methods is, however, expected to be much greater than that required for the MS–Zα method and up to now their applications have been quite limited.[33]

At the present time the SCF–MS–Xα method has been used to calculate the SHP of a few different metal complexes[34–41] ranging from $CuCl_4^{2-}$ to $IrCl_6^{3-}$. The latter[40] is one of the few examples where a relativistic approach has been used, allowing the authors to calculate the g tensor in a rather straightforward manner.

In a nonrelativistic approach the SHP can be calculated only through a perturbation treatment, which, although not totally satisfactory, usually provides results in good agreement with the experimental data. Considering, for the sake of simplicity, only the case of one unpaired electron the spin-orbit coupling and electron Zeeman perturbation Hamiltonian may be assumed to have the form[34,39]:

$$\hat{H} = \Sigma_k \, \xi_k(r_k) \, \hat{l}^k \cdot \hat{s}^k + \mathbf{B} \cdot (\hat{l}^k + 2.0023 \, \hat{s}^k)\mu_B \qquad (5)$$

where the k summation extends over all atoms, $\hat{l}^k$ and $\hat{s}^k$ are the angular and spin momentum operators on the k atom, and ξ_k has the form:

$$\xi_k(r_k) = (\alpha^2/2r_k) \, dU(r_k)/dr_k \qquad (6)$$

where α is the fine structure constant. In the proximity of the nucleus the potential $U(r_k)$ is usually approximated by $-Z_k/r_k$, so that

$$\langle \xi_k(r_k) \rangle \propto \langle r_k^{-3} \rangle \qquad (7)$$

The value of $\langle \xi_k(r_k) \rangle$ is different for different orbitals, but the usual procedure is that of assuming one value for it, with the justification that the experimental spin-orbit coupling constant is often little affected by the charge on the atom.[36] When this is not the case, as in chromium, attempts have been made to evaluate the average value for the Xα functions.[42] The calculated values for Cr^{n+}, with the integer n ranging from 0 to 5, are always larger than the experimental values, the discrepancy decreasing smoothly from 34% for Cr^0 to 20% for Cr^{5+}. In only one case was $\xi_k(r_k)$ calculated through a relativistic Xα approach, although not at the self-consistent level, but in a perturbative scheme.[40] The values obtained for the different orbitals of Ir and Cl yielded satisfactory agreement with the experiment.

The **g** tensor for the case of one unpaired electron can be evaluated through the relation[25]:

$$g_{tv} = g_e \delta_{tv} + g_e \Sigma_{m = n} \Sigma_{k,k'} \langle f_n^k | \xi_k(r_k) l_t^k | f_m^k \rangle \langle f_m^{k'} | l_v^{k'} | f_n^{k'} \rangle / (E_n - E_m) \quad (8)$$

where *n* indicates the ground state, the summation over *m* runs over all excited states, and *t* and *v* are cartesian components.

Although Eq. (8) has been successfully employed within the extended Hückel model,[25,26] to our knowledge it has never been used in the Xα method. The usual procedure employed to compute the *g* values has generally been that of expressing the molecular orbitals according to a minimal basis set of atomic orbitals, and to use Eq. (8), often neglecting the ligand orbital contributions, and not always including multiple center contributions when evaluating matrix elements involving the spin-orbit coupling operator. So, for instance, for an unpaired electron which is in a MO mainly corresponding to metal *xy* in tetragonal symmetry[43]:

$$g_{\parallel} = g_e - 8\zeta_d \alpha_1^2 \beta_1^2 / E_{x^2-y^2} \quad (9)$$

$$g_{\perp} = g_e - 2\zeta_d \alpha_1^2 \gamma_1^2 / E_{xz(yz)} \quad (10)$$

where α_1, β_1, and γ_1 are the metal orbital coefficients in the LCAO expansion of the predominantly *xy*, $x^2 - y^2$, and *xz* MO's.

The calculation of the above coefficients in the Xα formalism is not immediately clear. Often it has been assumed that they are given by the fractional charge associated with the corresponding partial wave of the SCF–MS–Xα orbital. This is not entirely correct, and in fact, during the calculation of the electronic structure of pseudotetrahedral and square-planar copper(II) complexes, we found,[39] by projecting the highest occupied Xα MO's on the LCAO MO's, that some differences between the two sets of values do exist as shown in Table IV of Ref. 39.

The agreement which has been found between observed and calculated g values has been often reasonably good, despite the many approximations which are inherent to the method. The test, however, should be that of using Eq. (8) rigorously, as the first goal, with the final goal being to compute correctly the g values in a completely relativistic approach.

The problem of how important it is to expend so much effort to calculate g tensors, which are generally well understood in the frame of simple ligand field models, remains open. It is our opinion that this kind of calculations is more relevant to testing the validity of the wave functions which are obtained through some quantum-mechanical model, than to the interpretation of the EPR spectra. It will be interesting, however, to check whether the "covalency" effects which have been invoked through the use of orbital reduction factors[44] will be confirmed by the calculations.

This is a general feature in chemistry: simple models are developed to interpret sets of experimental data using some quantum-mechanical technique and an essentially phenomenological approach. With these models many properties are rationalized, but their calculation from first principles is difficult. When the improvement of the theoretical models and of the computing techniques finally make the calculation of the molecular properties possible, it is difficult to reconcile the phenomenological and the purely theoretical approach. So, for instance, a chemist will for a long time still explain stability of molecules in terms of σ and π bond strengths, or of multiple bond character, even when these qualitative considerations are difficult to reconcile with the results of calculations, which necessarily use different points of view. Indeed, what is intuitively simple in a qualitative approach may be extremely difficult to explain in those same terms in a quantitative approach. An example is that of isotropic exchange interactions, where many pathways are accurately discussed in terms of overlaps of metal and ligand orbitals determining direct exchange and superexchange mechanisms. When *ab initio* calculations of the coupling constants of copper acetate hydrate have been made,[45] it was found that the above mechanisms yielded an exchange coupling constant $J = 0$, simply cancelling each other, and that double spin polarization terms were needed to account for the experimentally determined $J = 286\ \mathrm{cm}^{-1}$, due to the inherently different approach which was used.

The other important SHP which can be obtained through MO calculations are the hyperfine tensors **A**, which are given by the sum of three contributions:

$$\mathbf{A} = \mathbf{A}_{\mathrm{F}} + \mathbf{A}_{\mathrm{D}} + \mathbf{A}_{\mathrm{L}} \tag{11}$$

where $\mathbf{A}_{\mathrm{F}}$ is the Fermi contact contribution, $\mathbf{A}_{\mathrm{D}}$ is the spin dipolar contribution, and $\mathbf{A}_{\mathrm{L}}$ is the orbit dipolar contribution. $\mathbf{A}_{\mathrm{F}}$ in turn is given by the sum of two terms, one relevant to the unpaired spin density determined by the unpaired electron in a *s* orbital, and the second relevant to the spin polarization of the inner *s* orbitals by the unpaired electron in a different orbital.[46] The former can be obtained through both a nonspin polarized, NSP, and a spin polarized, SP, treatment, and is given by

$$\mathbf{A}_{\mathrm{F},1} = (8\pi/3)\, P|\psi(0)|^2_{\mathrm{ns}} \tag{12}$$

where $P = g_e g_N \mu_B \mu_N$, and the second, which can be obtained only through a SP treatment, is given by

$$\mathbf{A}_{\mathrm{F},2} = (8\pi/3)\, P|\rho^{\uparrow}(0) - \rho^{\downarrow}(0)| \tag{13}$$

where $\rho^{\uparrow}(0)$ and $\rho^{\downarrow}(0)$ are the spin-up and the spin-down densities on the nucleus, respectively. According to the formalism which is used in the ligand field treatment of metal hyperfine interactions, one obtains:

$$\mathbf{A}_{\mathrm{F},1} = -P_0 \tag{14}$$

where $P_0 = P\langle r^{-3}\rangle$, the average of r^{-3} being calculated in the orbital containing the unpaired spin.

The other two terms are given by the expectation values of appropriate operators over the Slater determinant defining the ground state. In particular, the orbit dipolar operator is of the form:

$$\hat{\mathbf{O}}_{\mathrm{L}} = (P/r^3)\, \hat{\mathbf{I}}_{\mathrm{M}} \cdot \hat{\mathbf{L}}^{\mathrm{M}} \tag{15}$$

i.e., it contains the same orbital momentum operator which is responsible of the deviation of the *g* values from the free-electron value. Therefore it can be conveniently reexpressed in terms of the deviation of the principal *g* values from the spin-only value. The operator representing spin dipolar interaction, on the other hand, depends only on the spin coordinates and takes the form:

$$\hat{O}_S = (P/r^3)\{[3(\hat{r}\cdot\hat{s})(\hat{r}\cdot\hat{I}_M)/r^2] - \hat{I}_M\cdot S\} \qquad (16)$$

The three terms, A_F, A_L, A_D have in common the P_0 value which is used as a parameter in the ligand field and in the qualitative MO approach to the metal hyperfine splitting. It is now important to compare the P_0 value calculated for some complexes with the Xα formalism with the values which are generally used for metal complexes, and those which are calculated for the isolated ions. In Table I we report some values for different free ions and complexes.

The values of Morton and Preston[47] (obtained by the Xα method) for the free ions tend to be larger, in absolute value, than those used for ligand-field-type analysis, obtained through SCF Hartree–Fock

TABLE I

P_0 Values for free metal ions and metal complexes[a]

Complex	Calculated Value	Free Ion Calculated Values Ligand Field[b]	Xα[c]
$CuCl_4^{2-}$	440[d]	360	399
Cp_2Co	208[e]	220, 98	
VOF_4^{2-}	129.4[f]		146
$VOCl_4^{2-}$	123[f]		
VOF_5^{3-}	130[f]		
$VOCl_5^{3-}$	123.7[f]		
$CrOF_4^-$	−36.1[g]		−34
$CrOCl_4^-$	−34.0[g]		
$CrOF_5^-$	−36.3[g]		
$CrOCl_5^-$	−34.3[g]		
$MoOF_4^-$	−56.2[h]	−44	−50.2
$MoOCl_4^-$	−52.5[h]		
$MoOBr_4^-$	−51.6[h]		
$MoOF_6^{3-}$	−56.7[h]		
$MoOCl_5^{3-}$	−53.0[h]		

[a] All values in 10^{-4} cm^{-1}.
[b] Ref. 46.
[c] Ref. 47.
[d] Ref. 39.
[e] Ref. 34. cp = cyclopentadienyl.
[f] Ref. 35.
[g] Ref. 42.
[h] Ref. 43.

calculations, while the Xα values calculated for metal complexes are sometimes larger and sometimes smaller. Although the Morton and Preston values were calculated with $\alpha = 1$, and the values for the complexes use α values around 0.7, it seems that there is no obvious trend to a decrease in P_0 in complexes as compared to free ions. Therefore it is apparent that the ligand field analysis, which always reduces P_0 in the complexes, suffers a great limitation. Generally this is not a major problem, because it only affects the values of the numerous other parameters which are required for the analysis of the data. Since, in general, it is difficult to judge the quality of the parameters, no clear indication emerges, but in some extreme examples great difficulties do arise.

One such case is that of pseudotetrahedral copper(II) complexes. Starting with $CuCl_4^{2-}$ systems, it was recognized that the EPR spectra of these complexes are characterized by: (i) large $g_\parallel$ and $g_\perp$ values; (ii) small $|A_\parallel|$ and relatively large $|A_\perp|$ values. In the original analysis of the spectra of Cs_2CuCl_4, Sharnoff[48] used a qualitative minimal basis set MO treatment, showing that the large *g* values are determined by the low energy of the *d–d* transitions. In order to justify the low $|A_\parallel|$ value, he had to assume that the A_D value is much smaller than usually found in square-planar or octahedral complexes, due to the admixture of metal *p* orbitals into the ground state, which was allowed by the noncentric symmetry. This assumption has been questioned[49] since the extent of *d–p* mixing should decrease on lowering the symmetry, as shown by the larger $|A_\parallel|$ values observed in CuO_2Cl_2 and CuN_2Cl_2 chromophores as compared to those of $CuCl_4^{2-}$. MS–Xα calculations have later shown[39] that indeed the low $A_\parallel$ value in $CuCl_4^{2-}$ is determined by a fairly large *P* value, higher than anticipated using simplified treatments, which makes the A_L contribution to A more important.

CONCLUSIONS

EPR spin Hamiltonian parameters provide a decisive test of the quality of the eigenfunctions of quantum-mechanical treatments which describe the ground state of transition metal complexes. Within the simple ligand field schemes they yield relevant information on the low-symmetry effects, which are present in all the complexes. A ligand field description of the ground state of a complex cannot be regarded as satisfactory unless the principal values and directions of the g, A, D tensors are correctly reproduced. On the other hand, it is rewarding that this simple approach allows one to calculate satisfactorily the SHP with the angular overlap parameters which can be transferred, with the limitations discussed in Ref. 10, from one complex to another.

On the MO side, the innocent hope of directly obtaining the "MO coefficients" from the EPR spectra is definitely abandoned, but we are now in the position to approach rather complicated systems with more and more rigorous procedures. It must be hoped that it will soon be possible to calculate the SHP of, at least, model complexes with great accuracy. In particular, great attention should be paid to the hyperfine tensors of the ligand atoms, because now many experimental data are available, due to the increasing application of ENDOR and ESEM techniques. The lack of suitable theoretical models made the interpretation of the data rather infrequent: it is to be hoped that in the near future this restriction will be overcome.

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