

CHAPTER III

In this section we will discuss the type of informations one can obtain from the study of optical and magnetic properties of complexes.

A. OPTICAL PROPERTIES

The transition metal complexes which have great range of visual colours enable us to determine from their spectral studies a number of electronic interaction parameters appropriate to crystal state, such as Condon-Shortly parameters F_2 and F_4 or Racah parameters B and C, the spin-orbit coupling constant ζ (in crystals), the cubic ligand field strength Dq and the axial field strength Δ . The study of the polarization of the electronic spectral lines or bands helps us to identify the corresponding transitions definitely. From the study of the vibrational structures one can get some idea of the coupling of electronic and nuclear motions. The study of electronic spectra is also a powerful method for distinguishing the stereochemistry of the transition metal compounds. For example, examination of the electronic spectra of nickel (II) compounds readily distinguishes between octahedral, square-planar, tetrahedral and five co-ordinated structures, especially if supplemented with paramagnetic susceptibility measurement. Spectral studies are of greatest help to uniquely assess the paramagnetic behaviours of the complexes under the relevant ligand fields.

1. d-d Band, C-T Band and Ligand-Ligand Band

(a) Transition among the split components of d^n configuration of the central metal ion is known as ligand field bands. The general theory of relatively weak d-d transitions is given by Ballhausen⁴², Griffith⁴¹ and others. In order to understand the spectrum, the ion site symmetry should be accurately known. The frequencies of the bands obviously depend on the strength and symmetry of the crystal or ligand field. The intensities depend upon the small perturbations on the wavefunctions, the nature of which depend upon the ion site symmetry. In a centrosymmetric environment, d-d pure electronic transitions can take place only by magnetic dipole or electric quadrupole mechanism, both of which obey the parity conservation rule $g \leftrightarrow g$. A d-d transition in such environment can also gain intensity through excitation to or from a state containing one quantum of a non-totally symmetric vibration. When the inversion symmetry is absent at the ion site, ungerade character can be acquired by the electronic wavefunctions by direct mixing e.g. with p functions, often resulting in relatively high intensities.

(b) Nearly all complexes, even those possessing an inversion centre, have in addition to their "ligand field bands" some very intense absorption bands placed in the near ultraviolet region of the spectrum. These are termed as "charge-transfer" or "redox" spectra, due to the fact that the c.g. of the charge cloud moves through a large distance as a result of the transition

i.e. the transition involves transfer of an electron (either wholly or partly) from ligand to ion or vice versa. The charge transfer bands can be considered as transitions between two molecular orbitals of the complex ion which have widely different percent of an atomic orbital in it. Thus, for ligand-metal bands low-energy transitions may take place from the least tightly bound non-bonding ligand orbitals to the antibonding d-orbitals. In octahedral complexes, if the transitions take place from the g-type of level to u-characterised levels (it may be both spin and symmetry allowed) it will produce a strong absorption band.

(c) In addition to the above two types of transitions, there may be internal excitation of the ligands, i.e. ligand-ligand bands. We omit discussion on ligand-ligand bands and its perturbation in complex, since the present thesis does not deal with it.

In the next section we will discuss the selection rules which govern the probability of a transition and thereby help one to know the nature and origin of the transition.

2. Selection Rules

The necessary condition for transition to take place by electric dipole mechanism is that the transition moment

$$Q = \langle \Psi | \vec{r} | \Psi' \rangle \quad (46)$$

be non-zero, where \vec{r} is the radius vector having the symmetry of an electric dipole. Expanding Ψ into component product functions :

$$\Psi = \Psi_{orb} \cdot \Psi_{sp} \cdot \Psi_{vib} \cdot \Psi_{rot} \cdot \Psi_{trans} \quad (47)$$

It can be deduced that Q is zero unless $\Psi_{sp} = \Psi'_{sp}$ (i.e. when spin-orbit coupling is neglected) and in that case, expression for Q becomes $\langle \Psi_{orb} \cdot \Psi_{vib} | \vec{r} | \Psi'_{orb} \cdot \Psi'_{vib} \rangle$ for solid and liquid medium. For O-O band, the vibration is absent and the expression for Q becomes $\langle \Psi_{orb} | \vec{r} | \Psi'_{orb} \rangle$. If the direct product of the representations of Ψ_{orb} and Ψ'_{orb} does not contain the representation of the transition moment operator, the expression becomes zero, and the transition becomes orbitally forbidden.

In centrosymmetric complexes, all the d-orbitals arising from a d^n configuration have the g-character and the direct product of two g-functions can never span any u-representation (to which \vec{r} belongs). So, for configurations in perfect octahedral environments one would expect no O-O band for electric dipole allowed $d \rightarrow d$ transitions. Whereas, in tetrahedral complexes, lacking centre of symmetry, these may be partially

allowed due to d-p mixing, for then the classification of wavefunctions either as g or u loses its meaning.

In transition metal complexes the spin and orbital selection rules are not strictly followed. As it is not possible to separate accurately the spin part and orbital part from total wavefunctions, the spin-forbidden bands with weaker intensity do occur in the spectra of transition metal ions. In explaining d-d transitions in octahedral complexes Van Vleck⁶¹ considered the mechanism of vibronic coupling - that is, a coupling of vibrational and electronic wavefunctions. The vibration of ligand atoms of the complex distorts the octahedron in such way that the centre of the symmetry is destroyed. Then the g-character of the states do not strictly hold and the transitions become allowed to a small extent. In order to couple the electronic wavefunction with vibrational wavefunctions one is to decide whether there are any vibrational wavefunction belonging to representations such that although the direct product representation of $\Psi_{elec} \times \bar{r} \times \Psi'_{elec}$ does not contain the totally symmetric representation A_1 , the direct product representation of $\Psi_{elec} \times \Psi_{vib} \times \bar{r} \times \Psi'_{elec} \times \Psi'_{vib}$, does. Whenever this is so the transition will be vibronically allowed. The orbital selection rule are further relaxed due to the presence of a small departure from cubic symmetry.

3. Polarization of Electronically Allowed Transitions

In non-cubic symmetry groups all the Cartesian axes are not equivalent, and it is found that, in general transitions will be allowed only for certain orientations of the electric vector of the incident light.

For illustration let us consider the case of M^{2+} in $CsCdCl_3$. In this complex the six Cl-ligand atoms form an approximately octahedral array but the true molecular symmetry is C_{3v} . Table 4a shows that the correlation of the O_h and C_{3v} ^{the} C_{3v} .

Table 4a.

O_h	\rightarrow	C_{3v}
$T_{1(g,u)}$	\rightarrow	$A_2 + E$
$T_{2(g,u)}$	\rightarrow	$A_1 + E$
$A_{2(g,u)}$	\rightarrow	A_2
$A_{1(g,u)}$	\rightarrow	A_1

As shown in the character table for C_{3v} (Table 5), Z belongs to A_1 representation and (x,y) to the E representation. From the irreducible representations spanned by the integrals $\langle \Psi | z | \Psi' \rangle$ and $\langle \Psi | x, y | \Psi' \rangle$, selection rules can be easily obtained. These are given in Table 6.

Table 5 : The character table for the group C_{3v}

C_{3v}	E	$2C_3$	3		
A_1	1	1	1	Z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y) (R_x, R_y)$	$(x^2 - y^2), xy, (xz, yz)$

Table 6 : Selection and polarization rules for the electric dipole transitions (point group C_{3v}) \parallel^l (polarized along C_3 axis) and \perp^r (polarized with plane perpendicular to C_3 axis)

	A_1	A_2	E
A_1	\parallel^l		\perp^r
A_2		\parallel^l	\perp
E	\perp^r	\perp^r	$\parallel^l + \perp^r$

Besides the electric dipole transition, the transition could also be allowed through the magnetic dipole vector. The transition probabilities depend upon the existence of non-zero matrix element

$$\langle \Psi | L + 2s | \Psi' \rangle \quad (48)$$

However, the relative probability of a magnetic-dipole transition to that for an electric-dipole transition is very small ($\approx 10^{-6}$), if the inversion symmetry is lost in some way.

B. MAGNETIC PROPERTIES

Though the gross magnetic properties of the halides and halide complexes of the first-row transition metals are fairly simple and the determination of oxidation state and stereochemistry from the closeness of their magnetic moment to their spin-only value is often safe, the variation of the magnetic properties of single crystals, particularly their anisotropies, at different temperatures is rather complicated. The mean magnetic moment of complexes with A and E ground terms usually differ from the spin-only value by a small amount, which depends upon the relationship between the spin-orbit coupling and the magnitude of the cubic ligand field. The mean magnetic moment of the complexes having 6A_1 (S) ground term is very near to their spin-only value and the variation of temperature has very little effect on the moment (Curie Law). The magnetic moment of complexes possessing T ground terms depart appreciably from the spin-only value because of the orbital degeneracy left over by the cubic field. The presence of low-symmetry ligand field components and t_{2g} electron delocalization causes further splittings and reorganization of the energy levels and are mainly responsible for further modifications of the magnetic moment and departure from Curie Law. In these circumstances

observed magnetic behaviours of the complexes can be very conveniently described by the spin Hamiltonian technique, which will be discussed in the following section.

The Spin Hamiltonian

In determining the behaviour of a paramagnetic ion of iron group in a crystalline electric medium, the cubic part of the crystal field plays the dominant role in splitting the orbital levels and then comes the smaller asymmetric fields - trigonal, tetragonal or orthorhombic, giving the finer shades of magnetic, microwave and optical behaviours. The energy levels will, in general, still remain degenerate in spins until one considers further the spin-orbit interaction and the external magnetic field. In the study of magnetic susceptibility and paramagnetic resonance, interest lies mainly in the lowest few levels and the levels removed from these by not more than few hundred cm^{-1} , as it is assumed that the upper levels are not populated at the temperatures of the experiment. Pryce⁸³ and Abragam and Pryce⁹ have developed a very useful method of calculating the energy of the lowest spin levels in which the electronic and nuclear interactions of the ground level with the excited levels are taken into consideration. This spin Hamiltonian formalism has also been developed in a more general way by Koster and Statz⁸⁴ from group theoretical considerations. Experimentally the spin Hamiltonian and its constants are determined from the E.S.R. spectra, which often misses the finer points in physical interpretation, whereas, theoretically, the spin

Hamiltonian and its constants are computable from the wavefunctions of the ion, which though clearing the physical background is most often wrapped in great computation difficulties for the want of proper wavefunctions for the complexes.

Abragam and Pryce divided the spin Hamiltonian problem in two cases : 1) non-degenerate in which an orbitally non-degenerate level lying lowest under a cubic field gives only a small splitting under the joint action of axial crystalline field and spin-orbit coupling. 2) Degenerate, where the degenerate orbital level under cubic field undergoes further splitting due to small axial field and the levels of split component are not large in comparison with the spin orbit coupling and the case is considered as that of near degeneracy. The two cases will be discussed separately.

(a) Non-Degenerate Ground Level

Collecting the various terms from the general Hamiltonian Eqn. (2) and replacing them by their operators involving \bar{L} and \bar{S} i.e., H_{LS} is replaced by $\xi \bar{L} \bar{S}$, H_z by $\beta H (\bar{L} + 2\bar{S})$ and considering the spin-spin interaction H_{SS} and replacing it by $-P [(\bar{L} \cdot \bar{S})^2 + \frac{1}{2} (\bar{L} \cdot \bar{S}) - \frac{1}{3} L(L+1) S(S+1)]$ the total perturbing potential takes the form

$$H_s = \xi \bar{L} \bar{S} - P [(\bar{L} \cdot \bar{S})^2 + \frac{1}{2} (\bar{L} \cdot \bar{S})] + \beta H (\bar{L} + 2\bar{S}) \quad (49)$$

in which the term $\frac{1}{3} [L(L+1) S(S+1)]$ is excluded as it gives a constant shifting of the levels and where P is a

factor of proportionality. Usual perturbation method with the above Hamiltonian continued upto second order and the derived expression which do not contain L but contains S , is known as the spin Hamiltonian. Operation of this new Hamiltonian on $(2S + 1)$ spin states of the ground level then yields the energy states of the system.

As the ground state is an orbital singlet denoted by $|0\rangle$ the expectation value of L is zero, i.e.

$$\langle 0 | L_x | 0 \rangle = \langle 0 | L_y | 0 \rangle = \langle 0 | L_z | 0 \rangle = 0$$

and the combination $L_i L_j$ gives symmetric tensors, i.e.,

$$\frac{1}{2} \langle 0 | L_i L_j + L_j L_i | 0 \rangle = \frac{1}{3} L(L+1) \delta_{ij} + l_{ij}$$

with $l_{ij} = 0$

Hence, for the first order perturbation the energy of the ground state is given by

$$\begin{aligned} \delta_1 E_0 &= \langle 0 | \bar{S} \bar{L} \bar{S} - P [(\bar{L} \cdot \bar{S})^2 + \frac{1}{2} (\bar{L} \cdot \bar{S})] + \beta \bar{H} (\bar{L} + 2\bar{S}) | 0 \rangle \\ &= 2\beta \bar{H} \cdot \bar{S} - P l_{ij} S_i S_j \end{aligned} \quad (50)$$

In the second order in which spin-orbit coupling contributes appreciably to the ground manifold, we proceed as

$$\delta_1 E_1 = - \sum_{n \neq 0} \frac{\langle 0 | H' | n \rangle \langle n | H' | 0 \rangle}{E(n) - E(0)} \quad (51)$$

where $(n = 1, 2, \dots)$ refers to the orbital excited states with energies $E(n)$

Hence

$$\begin{aligned} \delta_1 E_1 &= - \sum_{n \neq 0} \frac{\langle 0 | \bar{S} \bar{L} \bar{S} + \beta \bar{H} \cdot \bar{L} | n \rangle \langle n | \bar{S} \bar{L} \bar{S} + \beta \bar{H} \bar{L} | 0 \rangle}{E(n) - E(0)} \\ &= - \sum_{n \neq 0} \frac{\langle 0 | \bar{L}_i | n \rangle \langle n | \bar{L}_j | 0 \rangle}{E(n) - E(0)} \left[(\beta \bar{H}_i + \bar{S} \bar{S}_i) (\beta \bar{H}_j + \bar{S} \bar{S}_j) \right] \\ &= - \Delta_{ij} \left[\beta^2 \bar{H}_i \bar{H}_j + 2 \bar{S} \beta \bar{S}_i \bar{H}_j + \bar{S}^2 \bar{S}_i \bar{S}_j \right] \quad (52) \end{aligned}$$

Collecting the contributions from first and second order, the total Hamiltonian is given by

$$H_3 = D_{ij} S_i S_j + \beta g_{ij} \bar{H}_i \bar{S}_j - \beta^2 \Delta_{ij} H_i H_j \quad (53)$$

where the symmetrical positive tensor Δ_{ij} is given by

$$\Delta_{ij} = \sum_{n \neq 0} \frac{\langle 0 | \bar{L}_i | n \rangle \langle n | \bar{L}_j | 0 \rangle}{E(n) - E(0)} \quad (54)$$

and

$$\begin{aligned} D_{ij} &= -P_{lij} - \bar{S}^2 \Delta_{ij} \\ g_{ij} &= 2(\delta_{ij} - \bar{S} \Delta_{ij}) \end{aligned}$$

In Eqn. (53), the first term is responsible for the splitting of the spin levels in zero magnetic field, and the last term which does not contain spin variables, is not of importance in resonance studies. It gives a uniform shifting of the energy levels and is responsible for an induced magnetic moment i.e. the 'high frequency term' in the susceptibility.

When there is reduction in symmetry, the spin Hamiltonian (Eqn. 53) is further modified as it must partake of the point group symmetry of the ligand complex. For the case of orthorhombic symmetry, the spin Hamiltonian reduces to

$$H_s = D \left[S_z^2 - \frac{1}{3} s(s+1) \right] + \beta (g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) + E (S_x^2 - S_y^2) - \beta^2 \Delta_{ij} H_i H_j \quad (55)$$

and for trigonal and tetragonal cases the E-term is zero and

g_z is replaced by $g_{||}$, g_x and g_y by g_{\perp}

The advantage of the spin Hamiltonian lies in the description of the resonance spectrum of an ion in terms of a relatively small number of parameters g , D and E . With these constants one can build up suitable theoretical framework on electronic configuration of an ion which will in turn give the knowledge of local field symmetry and bonds besides giving information on various interactions. The spin Hamiltonian helps one to calculate susceptibilities of the lowest group of levels and thereby there remains a co-relation between susceptibility and e.s.r. results.

To find the eigenvalues of a spin Hamiltonian, say,

$$H_s = g_{||} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + D \left\{ S_z^2 - \frac{1}{3} s(s+1) \right\}$$

Let us consider the example of Ni^{2+} ($3d^8$) with $S = 1$ when H is parallel to the z-axis. The perturbation matrix in the spin-states $\langle 1|$, $\langle 0|$ and $\langle -1|$ is then

	⟨1	⟨0	⟨-1	
⟨1	$D + g_z \beta H$	0	0	(56)
⟨0	0	0	0	
⟨-1	0	0	$D - g_z \beta H$	

which given the eigen value

$$\begin{aligned}
 E_1 &= D + g_z \beta H_z \\
 E_2 &= 0 \\
 E_3 &= D - g_z \beta H_z
 \end{aligned}
 \tag{57}$$

when the applied magnetic field is zero ($H = 0$), we get only two levels one non-degenerate and the other with two-fold degeneracy, and the separation between them is D , the "zero field splitting".

The expression for susceptibility K_i ($i = x, y$ or z according as H is \parallel to x, y or z -axis) is given by

$$K_i = -\frac{N}{H} \frac{\sum_s \frac{\partial W_s(i)}{\partial H} \exp\left(-\frac{W_s(i)}{kT}\right)}{\sum_s \exp\left(-\frac{W_s(i)}{kT}\right)}
 \tag{58}$$

where summation is carried over $(2S + 1)$ eigenvalues of the Hamiltonian (55) operating upon the $(2S + 1)$ spin states.

The expression (58) can be written as

$$K_i = \frac{NkT}{H} \frac{\partial}{\partial H} \ln Z(i) \quad (59)$$

where

$$\begin{aligned} \ln Z(i) &= \ln \sum_s \exp \left(- \frac{W_s(i)}{kT} \right) \\ &= \frac{\bar{W}}{kT} + \ln(2S + 1) + \frac{\langle (W_s(i) - \bar{W})^2 \rangle}{2k^2 T^2} \\ &\quad - \frac{\langle (W_s(i) - \bar{W})^3 \rangle}{6k^3 T^3} \end{aligned} \quad (60)$$

where \bar{W} , $\langle (W_s(i) - \bar{W})^2 \rangle$ and $\langle (W_s(i) - \bar{W})^3 \rangle$ are the averages of $W_s(i)$, $(W_s(i) - \bar{W})^2$ and $(W_s(i) - \bar{W})^3$ respectively averaged over all the $(2S + 1)$ levels.

(b) Degenerate Ground Level

In iron group of elements, the ground state in an octahedral field, when not an orbital singlet, can be either an orbital doublet or triplet. The doubly degenerate E is 'non-magnetic' which is not split by either spin-orbit coupling or a trigonal field, but breaks up into two orbital singlets by a tetragonal or rhombic fields and so the method of calculation is similar to the case (a). Where an orbital triplet (T_1 or T_2) lies lowest, low symmetric field will cause it to break into a singlet and a doublet. As this splitting is comparable to that of spin-orbit interaction, the two perturbations are, therefore, simultaneously applied on the ground manifold.

If z-axis is chosen as the axis of quantization, the component of L in the ground manifold can be defined by the matrices

$$\begin{aligned}
 L_x &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i\alpha' \\ 0 & -i\alpha' & 0 \end{pmatrix} \\
 L_y &= \begin{pmatrix} 0 & 0 & -i\alpha'' \\ 0 & 0 & 0 \\ i\alpha'' & 0 & 0 \end{pmatrix} \\
 L_z &= \begin{pmatrix} 0 & i\alpha & 0 \\ -i\alpha & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
 \end{aligned} \tag{61}$$

Where α , α' and α'' are constants which are nearly equal to one another and have values near to 1 for D-state ions (ground state T_2) and for F-state ions (ground state T_1) these are equal to $3/2$ in the weak cubic field approach⁹ and 1 in a strong field approach⁴¹. The departure from these values is related to the ratio of the lower symmetric field to the cubic field. In a cubic field $\alpha = \alpha' = \alpha''$ are exactly equal, for an axial field $\alpha = \alpha'' \neq \alpha'$ and in orthorhombic field $\alpha \neq \alpha' \neq \alpha''$. Considering the case in an axial field, the anisotropic field operator can be written as

$$V_T = \begin{pmatrix} (-1/3)\Delta & 0 & 0 \\ 0 & (-1/3)\Delta & 0 \\ 0 & 0 & (2/3)\Delta \end{pmatrix} \quad (62)$$

where the axial field separation between a singlet and a doublet of the ground manifold T_1 or T_2 is Δ . Following Abragam and Pryce⁹ one may introduce a fictitious angular momentum \bar{l} , with the total value $l' = 1$ operating in the ground manifold having matrices given by

$$l'_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad l'_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad l'_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (63)$$

The quantities $-\alpha$ and $-\alpha'$ may be considered to be effective orbital Lande g-factors for directions $\parallel \bar{l}$ and $\perp \bar{l}$ to the symmetry axis. So we can write for the spin-orbit interaction :

$$H_{LS} = -\alpha S_{\parallel} l_z S_z - \alpha' S_{\perp} (l_x S_x + l_y S_y) \quad (64)$$

and the calculation is carried on the 'pseudo' atomic P-state with spin multiplicity equal to that of the ground state. The great advantage of introducing a fictitious angular momentum l' is that $(l'_z + S_z)$ is a constant of the motion and its eigen values of $m = m_l - m_s$ are used to classify the various possible states.

Two cases may arise depending upon the values of
 1) the lowest level being non-degenerate corresponding to $m = 0$ (even electron case) and 2) the lowest level degenerate corresponding to $m = \pm M$ (odd electron case). In the former case, if the separation between the lowest level and next higher one is large, one must consider higher groups of levels lying close together, as there is no contribution to paramagnetic resonance from the lowest level. On the other hand, if the lowest level is close to other levels, they should be considered as one group⁵⁷. In the latter case one must consider only the lowest Kramer's doublet¹³. To describe the paramagnetic resonance of the ion, therefore, one should introduce a fictitious spin S' and apply spin Hamiltonian method on the ground levels.

Following Van Vleck¹, expression for magnetic susceptibility K_i ($i = x, y$ or z (according as H is \parallel^l to x, y or z -axis) can be written as

$$K_i = N \frac{\sum_{m_k} \left[W_{m_k}^{(1)2}(i)/kT - 2 W_{m_k}^{(2)}(i) \right] \exp\left(-\frac{W_{m_k}^0}{kT}\right)}{\sum \exp\left(-\frac{W_{m_k}^0}{kT}\right)} \quad (65)$$

where $W_{m_k}^0$ is the unperturbed energy and $W_m^{(1)}(i)$ and $W_m^{(2)}(i)$ are given by

$$\begin{aligned} W_m^{(1)}(i) &= \langle \Psi_{m_k} | \mu_i | \Psi_{m_k} \rangle \\ W_m^{(2)}(i) &= - \sum_{m_k'} \frac{|\langle \Psi_{m_k} | \mu_i | \Psi_{m_k'} \rangle|^2}{W_{m_k'} - W_{m_k}^0} \end{aligned} \quad (66)$$

where $\mu_{||} = \beta(-\alpha L_z + 2\hat{S}_z)$, $\mu_{\perp} = \beta[-\frac{\alpha'}{2}(L_+ + L_-) + \hat{S}_+ \hat{S}_-]$

$$L_{\pm} = L_x \pm iL_y, \quad \hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$$

where Ψ_{m_k} and $\Psi_{m'_k}$ are two wavefunctions having the same unperturbed energy $W_{m_k}^0$; the eigenvalues of the operator $(L'_z + S_z)$ associated with these wavefunctions differ by 0 for $i = Z$ and by ± 1 for $i = x$ or y . Ψ_{m_k} and $\Psi_{m'_k}$, however, are two wavefunctions belonging to two different unperturbed energies $W_{m_k}^0$ and $W_{m'_k}^0$ respectively; the eigenvalues of $(L'_z + S_z)$ associated with these wavefunctions again differ by 0 for $i = Z$ and by ± 1 for $i = x$ or y .