

CHAPTER II

MATHEMATICAL PRELIMINARIES

II.1. INTERACTIONS PRESENT IN A PARAMAGNETIC  
ION EMBEDDED IN A CRYSTAL

When a paramagnetic ion is embedded in a magnetically dilute crystal the Hamiltonian in presence of an externally applied magnetic field can be written as

$$H = H_F + H_{SO} + H_C + H_{\mathcal{H}} \quad (\text{II.1.1})$$

where,  $H_F$  = nonrelativistic Hamiltonian for a free ion excluding magnetic interactions of electron orbits and spins.

$H_{SO}$  = spin-orbit interaction energy,

$H_C$  = crystal field interaction,

$H_{\mathcal{H}}$  = interaction energy due to the application of the external magnetic field  $\mathcal{H}$ . The spin-spin interaction, the exchange interaction of electrons, nuclear interaction and other possible interactions are usually small and have been neglected in our calculation. The non relativistic free atom Hamiltonian  $H_F$  is

$$H_F = \sum_i \left( T_i - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{r_{ij}} \quad (\text{II.1.2})$$

where  $T_i$  = K.E. of the  $i$ -th electron and  $\frac{-Ze^2}{r_i}$  = P.E. of the  $i$ -th electron in the attractive coulomb field of the nucleus.  $\frac{e^2}{r_{ij}}$  = electron electron repulsion term. If we neglect the inter-electronic repulsion term then the method of separation

of variables can be applicable and the Schrödinger equation corresponding to (II.1.2) can be solved. But this term is too large to be dropped and treated later by perturbation theory. So the general procedure for solving the eigenvalue problem of  $H_F$  is then to use the central field approximation. This means actually that it is fairly good approximation first to replace  $H_F$  by a central field Hamiltonian  $H_0$  which takes into account of the fact that each electron moves independently of the others in an effective central potential  $V(r)$  representing the combined effects of the attraction by the nuclear charge and a suitably averaged repulsion by the other electrons. Now we define  $(H_F - H_0)$  as the residual interaction  $H_r$ , which is treated as the perturbation potential. Thus we can write

$$H_F - H_0 = H_r \quad (\text{II.1.3})$$

where  $H_0$  = central field Hamiltonian and is given by

$$H_0 = \sum_i \left[ T_i + V_{\text{eff}}(r_i) \right] \quad (\text{II.1.4})$$

$V_{\text{eff}}(r_i)$  = P.E. energy of the  $i$ -th electron in the effective central field. The residual interaction  $H_r$  is given by<sup>71</sup>

$$H_r = H_F - H_0 = \sum_i \left( -V_{\text{eff}}(r_i) - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{r_{ij}} \quad (\text{II.1.5})$$

$H_r$  thus consists of one and two electron terms represented by

$$H_r^{ii} = \sum_i \left( -V_{\text{eff}}(r_i) - \frac{Ze^2}{r_i} \right) \quad (\text{II.1.6})$$

and

$$H_r^{ij} = \sum_{i < j} \frac{e^2}{r_{ij}} \quad (\text{II.1.7})$$

Now when one is interested entirely within the structure of a single configuration, the one electron term  $H_r^{ii}$  may be omitted in  $H_r$  since its effect is simply to shift a configuration as a whole. So we drop this term as calculations involving different electronic configurations will not be dealt with in the present thesis.

Thus we can write finally the total effective Hamiltonian (II.1.1) of a paramagnetic ion embedded in a crystalline lattice in presence of external field  $\mathcal{A}$  using the central field approximation for free ion as follows :

$$H = H_0 + H_r^{ij} + H_C + H_{SO} + H_{\mathcal{A}} \quad (\text{II.1.8})$$

The eigen value problem of the total Hamiltonian  $H$  given in (II.1.8) is tackled by treating  $H_0$  as the unperturbed Hamiltonian and  $(H-H_0)$  as the perturbation Hamiltonian. Further the perturbation  $(H-H_0)$  consists of a number of parts in order of decreasing strength, and the perturbation problem is tackled by applying these parts in stages in order of decreasing strength on the low lying states resulting from the previous perturbation part. The calculation of the matrix elements of the perturbation Hamiltonian is facilitated by defining a complete set of basis states in some well defined coupling schemes which are discussed in the next section.

## II.2. COUPLING SCHEME

We consider the following three coupling schemes that are used in the theory of atomic spectra

### (a) L-S coupling scheme

The free atom Hamiltonian  $H_F$ ,  $L^2$ ,  $S^2$ ,  $L_z$ ,  $S_z$  are mutually commuting dynamical variables where  $L$  and  $S$  are the resultants of individual electronic orbital angular momenta,  $l$ 's and spin angular momenta,  $s$ 's respectively. That means  $H_F$ ,  $L^2$ ,  $S^2$ ,  $L_z$  and  $S_z$  have simultaneous eigenstates and  $L$ ,  $S$ ,  $M_L$ ,  $M_S$  are good quantum numbers or in other words  $L^2$ ,  $S^2$ ,  $L_z$  and  $S_z$  are constants of motion. From the same argument we can have simultaneous eigen states of  $H_F$ ,  $L^2$ ,  $S^2$ ,  $J^2$  and  $J_z$  where  $J$ , the total angular momentum, is the resultant of  $L$  and  $S$  and also  $L^2$ ,  $S^2$ ,  $J^2$  and  $J_z$  are constants of motion. We can then classify the energy eigen states of the atom by the eigen value of the constants of motion i.e., by specifying the definite values of  $L$ ,  $S$ ,  $M_L$ ,  $M_S$  or  $L$ ,  $S$ ,  $J$ ,  $M_J$ . This description of the atom is valid only when  $H_{SO}$  is neglected in the free atom since otherwise  $L^2$  or  $S^2$  will not commute with the Hamiltonian. So in case of lighter atoms for which atomic number is small and  $H_{SO}$  is weak it is a good approximation to take  $H_{SO}$  as a small perturbation on the states represented by  $|SLM_S M_L\rangle$  or  $|SLJM_J\rangle$  in the basis of which  $L^2$  and  $S^2$  are diagonal. Any set

of states in which  $L^2$  and  $S^2$  are diagonal is referred to as Russel-Saunders' s coupling scheme.

(b) *jj* coupling scheme

For heavy atoms (large atomic number),  $H_{SO}$  can no longer be treated as a perturbation on L-S coupling states  $|SLM_S M_L\rangle$  or  $|SLJM_J\rangle$  but must be taken into account at the very beginning in the original single particle orbitals from which the resultant atomic states are built. This actually means that electronic wave functions are no longer simultaneous eigenstates of  $n, l, m_s, m_l$  but the simultaneous eigen states of  $n, l, j, m$  where  $j$  is the total angular momentum (resultant of  $l$  and  $s$ ) of a single electron. The individual electronic  $j$ 's then combine to produce the total  $J$  and its component  $M_J$  of the atom as constants of motion. The scheme characterised by the set of quantum numbers  $n, l, j$  for each electron and  $JM_J$  for the whole atom is known as the *jj* coupling scheme. In this scheme  $H_{SO}$  is diagonal and coulomb repulsion term is then taken as perturbation.

(c) Intermediate coupling scheme

When the coulomb repulsion and the spin-orbit interaction terms are comparable, neither L-S nor *j-j* coupling gives a good approximation, since the Hamiltonian of a free atom (which

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includes  $H_{SO}$ ) is not diagonal in either case. In this case we have to diagonalize the Hamiltonian matrix which includes both coulomb repulsion and SO interaction exactly and its diagonalization gives a representation in which both  $H_r^{ij}$  and  $H_{SO}$  are diagonal. This is known as the intermediate coupling. The wave function in this scheme is a linear combination of states represented by  $|SLJM_J\rangle$ .

### II.3. SCHEMES OF PERTURBATION CALCULATION DEPENDING ON THE MAGNITUDE OF CRYSTAL FIELD RELATIVE TO OTHER INTERACTIONS

The coupling scheme indicates the basis states necessary for starting perturbation calculation. The coupling schemes already stated are for the case of a free atom. The above description has to be modified in the case of paramagnetic ion occupying a site in the crystalline lattice i.e. if  $H_c$  is included in the perturbation ( $H-H_0$ ), the different parts of which are applied in stages as mentioned earlier. So we have to know how  $H_c$  compares in order of magnitude with the other perturbing quantities of equation (II.1.8) particularly  $H_{SO}$  and  $H_r^{ij}$  part of  $H_r$ . We shall confine our discussion to the rare-earth groups only with which the present thesis is concerned.

Now in case of rare-earth complexes,  $H_r^{ij} \approx H_{SO} \gg H_c$ . Evidently the intermediate coupling scheme described earlier

in the case of free atom is the most suitable one in this case and it is the most realistic approach for the perturbation procedure in rare-earth complexes.  $H_C$  is to be applied then on the Intermediate coupling states.

#### II.4. TENSOR OPERATORS AND THEIR USES IN THE PRESENT THESIS

For the calculation of the matrix elements of  $H_r$ ,  $H_{SO}$ ,  $H_C$  ( $H_C$  = crystal field interaction) etc between the atomic states we can expand the atomic states in terms of antisymmetrized product of one electron wave functions following the method of Slater<sup>72</sup> and the matrix elements of the operators are then evaluated in the manner as described by Slater<sup>72</sup> and Condon and Shortley<sup>54</sup>. But this method, though in principle applicable to most of the cases, is very cumbersome and extremely tedious in complex configurations. An alternative and much simpler but most powerful and elegant method known as tensor operator method has been developed in conjunction with group theory and concept of fractional parentage by Racah<sup>73</sup> and Wigner<sup>74</sup>.

##### II.4(a). DEFINITION OF A TENSOR OPERATOR

An irreducible tensor operator of rank  $k$  is defined by Racah<sup>75</sup> as an operator  $T^{(k)}$  whose  $(2k+1)$  components satisfy

the same commutation rule with respect to the total angular momentum  $J$  as the spherical harmonic operators  $Y_k^q$  i.e.

$$\left[ (J_x \pm iJ_y), T_q^{(k)} \right] = \left[ (k \mp q)(k \pm q + 1) \right]^{1/2} T_{q \pm 1}^{(k)} \quad (\text{II.4.1})$$

$$\left[ J_z, T_q^{(k)} \right] = q T_q^{(k)} \quad (\text{II.4.2})$$

Evidently, the spherical harmonics are themselves tensor operators. One can easily show from the above definition that suitable linear combinations of the components of the orbital angular momentum or the spin or the cartesian  $(x, y, z)$  operator are the components of tensor operators with  $k = 1$ . The tensor operator form of  $x, y, z$  may also be easily obtained by expressing them in terms of the components of the first order spherical harmonics.<sup>76</sup>

## II.5. COEFFICIENT OF FRACTIONAL PARENTAGE

Calculation with the help of Racah formalism needs frequent use of the concept of fractional parentage. The idea is as follows :

Any state  $\Psi(\ell^n \alpha S L M_S M_L)$  of the configuration  $\ell^n$  may be expanded in terms of the products of states  $\Psi(\ell^{n-1} \alpha_1 S_1 L_1 M_{S_1} M_{L_1})$  of the first  $(n-1)$  electrons with those of the  $n$ -th electron having the same  $\ell$  value as follows :

$$\Psi(\ell^n \alpha S L M_S M_L) = \sum_{\alpha_1 S_1 L_1} \langle \ell^{n-1}(\alpha_1 S_1 L_1) \ell; S L | \rangle \ell^n \alpha S L \rangle \sum_{\substack{M_{S_1} M_{L_1} m_s m_\ell}} \langle S_1 \frac{1}{2} M_S | S_1 \frac{1}{2} M_{S_1} m_s \rangle \langle L_1 \ell M_L | L_1 \ell M_{L_1} m_\ell \rangle \Psi(\ell^{n-1}(\alpha_1 S_1 L_1 M_{S_1} M_{L_1})) \Phi(\ell, m_\ell, m_s) \quad (\text{II.5.1})$$

where  $\Phi(\ell, m_\ell, m_s)$  represents the state of the  $n$ -th electron having quantum numbers  $\ell, m_\ell, m_s$ . The first summation extends over all the terms  $\Psi(\ell^{n-1}(\alpha_1 S_1 L_1))$  of the complete set for the  $\ell^{n-1}$  configuration and the second sum merely performs the vector coupling of the total  $S$  and  $L$  values. In other words the state  $\Psi(\ell^n \alpha S L)$  representing a term of the  $\ell^n$  configuration may be written as the following linear combination

$$\Psi(\ell^n \alpha S L) = \sum_{\alpha_1 S_1 L_1} \Psi(\ell^{n-1}(\alpha_1 S_1 L_1) \ell; S L) \langle \ell^{n-1}(\alpha_1 S_1 L_1) \ell; S L | \ell^n \alpha S L \rangle \quad (\text{II.5.2})$$

The term  $\alpha_1 S_1 L_1$  of the  $\ell^{n-1}$  configuration is known as the parent of the term  $\alpha S L$  of the  $\ell^n$  configuration and the coefficient  $\langle \ell^{n-1}(\alpha_1 S_1 L_1) \ell; S L | \ell^n \alpha S L \rangle$  commonly abbreviated as  $\langle \bar{\Psi} | \Psi \rangle$  is known as the coefficient of fractional parentage (c.f.p.). The c.f.p. describes how the resultant state  $\Psi$  is built up from its possible parents  $\bar{\Psi}$  when another electron with the same  $\ell$  quantum number is added to the parent and can be looked upon as defining the state. They are chosen to yield the properly antisymmetrized eigenfunctions of the  $\ell^n$  configuration and are zero for all the forbidden states of the configuration.

Due to the equivalence of the electrons the matrix element of the sum of a single particle operator  $F = \sum_i f_i$  between two states of the configuration  $l^n$  is  $n$  times the corresponding matrix element for  $f_i$  where  $f_i$  is a single particle operator for the  $i$ -th particle, that is

$$\langle l^n \alpha SL | F | l^n \alpha' S' L' \rangle = n \langle l^n \alpha SL | f_i | l^n \alpha' S' L' \rangle \quad (\text{II.5.3})$$

Making use of (II.5.2) we get

$$\begin{aligned} \langle l^n \alpha SL M_S M_L | F | l^n \alpha' S' L' M'_S M'_L \rangle &= n \sum_{\alpha_1 S_1 L_1} \langle l^n \alpha SL \{ | l^{n-1}(\alpha_1 S_1 L_1) l SL \rangle \\ &\langle S_1 L_1 l_n^{SL} M_S M_L | f_i | S_1 L_1 l_n S' L' M'_S M'_L \rangle \langle l^{n-1}(\alpha_1 S_1 L_1) l S' L' \} | l^n \alpha' S' L' \rangle \end{aligned} \quad (\text{II.5.4})$$

The matrix element of  $f_i$  can be evaluated by expressing  $f_i$  in terms of the appropriate tensor operator and then using the tensor operator technique. The problem then reduces to finding the coefficients  $\langle l^n \alpha SL \{ | l^{n-1}(\alpha_1 S_1 L_1) l SL \rangle$  and  $\langle l^{n-1}(\alpha_1 S_1 L_1) l S' L' \} | l^n \alpha' S' L' \rangle$ . We shall assume that the phases of the states of the configurations  $l^n$ ,  $l^{n-1}$  and  $l$  have been chosen to ensure that the coefficients are real, hence

$$\langle l^n \alpha SL \{ | l^{n-1}(\alpha_1 S_1 L_1) l SL \rangle = \langle l^{n-1}(\alpha_1 S_1 L_1) l SL \} | l^n \alpha SL \rangle \quad (\text{II.5.5})$$

For matrix element of a single-particle operator  $F$  between two states of different configurations we can write following

Racah<sup>73</sup>

$$\begin{aligned} &\langle l^n \alpha SL M_S M_L | F | l^{n-1}(\alpha_1 S_1 L_1) l' S' L' M'_S M'_L \rangle \\ &= n^{1/2} \langle l^n \alpha SL \{ | l^{n-1}(\alpha_1 S_1 L_1) l SL \rangle \langle S_1 L_1 l_n^{SL} M_S M_L | f_n | S_1 L_1 l' S' L' M'_S M'_L \rangle \end{aligned} \quad (\text{II.5.6})$$

The coefficients of fractional parentages for  $d^n$  and  $f^n$  configurations have been tabulated in a convenient form by Nielson and Koster<sup>77</sup>. These tables are available for configurations upto half-filled shell. For configurations more than the half-filled shell, the c.f.p may be easily calculated from the recursion formula given by Racah<sup>73</sup>

$$\begin{aligned} & \langle l^{4l+1-n}(\alpha' S' L') l S L \rangle \{ l^{4l+2-n} \alpha S L \rangle \\ &= (-1)^{S+S'+L+L'-l} \frac{1}{2} \left[ \frac{(n+1)(2S'+1)(2L'+1)}{(4l+2-n)(2S+1)(2L+1)} \right]^{1/2} \\ & \quad \langle l^n(\alpha S L) l S' L' \rangle \{ l^{n+1} \alpha' S' L' \rangle \end{aligned} \quad (\text{II.5.7})$$

## II.6. REPRESENTATION OF A WAVE FUNCTION BY RACAH'S CONVENTION IN THE CASE OF $f^n$ CONFIGURATION

In the particular case of the f shell, Racah<sup>78</sup> introduced two groups providing two sets of quantum numbers W and U. The first is a set of three integral numbers  $W = (w_1 w_2 w_3)$  with  $w_1 \gg w_2 \gg w_3 \gg 0$  and all  $w \leq 2$ , while the second is a set of two integral numbers  $U \equiv (u_1 u_2)$ . With a few exceptions these labels distinguish all states of the f shell and using the symbol  $\alpha$  to separate these exceptions, the wave functions are denoted by

$$\Psi(f^n \alpha W U S L M_S M_L) . \quad (\text{II.6.1})$$

The states of any rare-earth ion having a configuration repre-

ted in general by  $4f^n$  are listed by Nielson and Koster<sup>77</sup> using this representation. In earlier work Racah used a 'seniority number'  $v$ , which is essentially equivalent to  $W$ , to label the states. The corresponding notation alternative to (II.6.1) is

$$\psi(f^n \alpha U v SL M_S M_L) \quad . \quad (\text{II.6.2})$$

## II.7. ELECTROSTATIC ENERGY FOR $f^n$ CONFIGURATION

By expanding the electrostatic interaction between electrons in Legendre polynomials of the cosine of the angle between them, the electrostatic energy  $E$  may be written as a linear combination of Slater radial integrals<sup>54</sup>,  $F_K$

$$E = \sum_{k=0}^{2l} f^k F_k, \quad k \text{ is even} \quad (\text{II.7.1})$$

For the two electron configuration the coefficients  $f^k$  are simply angular integrals over spherical harmonics. Using the calculated c.f.p. together with equation (1) of Racah<sup>78</sup> to derive the coefficients of the  $F_k$  in the configuration  $l^n$  from those in the configuration  $l^{n-1}$ , we may build up a chain process from the known  $l^2$  coefficients; but in the  $f$  shell such a process is tedious.

To simplify the calculation, Racah observed that, in the two-electron problem, the coefficient  $f^k$  is essentially the expectation value of the scalar product operator  $(y_k(1) \cdot y_k(2))$  of two spherical harmonics. Although this operator is a scalar

with respect to rotations in three dimensions it is neither scalar nor has simple properties with respect to the more general groups of transformations used to classify the wave functions. However, by taking certain linear combinations of these operators one may construct new operators which have simple transformation properties under the groups employed. The energy becomes

$$\mathcal{E} = \sum_{k=0}^{\infty} e_k E^k, \quad (\text{II.7.2})$$

where the  $e_k$  are the expectation values of the new operators and the  $E^k$  are linear combinations of the  $F_k^s$ .

In the  $f$  shell we have

$$\begin{aligned} E^0 &= F_0 - 10F_2 - 33F_4 - 286F_6, \\ E^1 &= \frac{1}{9} (70F_2 + 231F_4 + 2002F_6), \\ E^2 &= \frac{1}{9} (F_2 - 3F_4 + 7F_6) \\ E^3 &= \frac{1}{3} (5F_2 + 6F_4 - 91F_6) \end{aligned} \quad (\text{II.7.3})$$

For configuration  $f^n$  Racah<sup>78</sup> has shown that both  $e_0$  and  $e_1$  are diagonal in the  $UvSL$  scheme with values,

$$\begin{aligned} e_0 &= \frac{1}{2} n(n-1), \\ e_1 &= \frac{9}{2} (n-v) + \frac{1}{4} v(v+2) - S(S+1) \end{aligned} \quad (\text{II.7.4})$$

The remaining co-efficients are more difficult to derive and necessitate the use of the c.f.p. discussed in II.5. Using these, Racah has prepared subsidiary tables from which the

values of  $e_2$  and  $e_3$  may be derived in any configuration  $f^n$ . One can calculate the electrostatic part of any  $f^n$  system by using the above mentioned procedure. However, Nielson and Koster<sup>77</sup> gave extensive tables where they gave the electrostatic part of any of  $f^n$  system in terms of  $E^0, E^1, E^2, E^3$  and we have used this table in dealing with the problems discussed in the present thesis.

## II.8. MATRIX ELEMENTS OF THE SPIN-ORBIT INTERACTION

Using the tensor operator methods of Racah<sup>75</sup> together with the fractional parentage coefficients, the matrix element of the spin-orbit operator  $\zeta \sum_i (\bar{s}_i \cdot \bar{l}_i)$  between two general states  $\Psi_{JM}, \Psi'_{JM}$  of the configuration  $l^n$  is given by

$$\begin{aligned} \langle \Psi_{JM} | \zeta \sum_i (\bar{s}_i \cdot \bar{l}_i) | \Psi'_{JM} \rangle &= -n \zeta \{ 3 l(l+1)(2l+1)(2L+1) \\ & (2L'+1)(2S+1)(2S'+1)/2 \}^{1/2} (-1)^{J+L+S'+1} \begin{Bmatrix} J & L & S \\ 1 & S' & L' \end{Bmatrix} \\ & \sum_{\bar{\Psi}} \langle \bar{\Psi} | \bar{\Psi} \rangle \langle \bar{\Psi}' | \bar{\Psi} \rangle (-1)^{S+\bar{S}+L+\bar{L}+l+\frac{1}{2}} \begin{Bmatrix} \bar{S} & S & \frac{1}{2} \\ 1 & \frac{1}{2} & S' \end{Bmatrix} \begin{Bmatrix} \bar{L} & L & l \\ 1 & l & L' \end{Bmatrix} \end{aligned} \quad (\text{II.8.1})$$

where  $\langle \bar{\Psi} | \bar{\Psi} \rangle$  stands for the coefficient of fractional parentage. The SO matrix element in terms of  $\zeta$  has been calculated by several workers. Spedding<sup>79</sup> calculated the SO matrix elements for  $f^2$  system and Judd and Loudon<sup>80</sup> calculated the matrix elements for  $f^3$  system. Later Nielson and Koster<sup>77</sup> has given

the values of the matrix elements of SO interaction in a tabular form for all  $f^n$  systems.

## II.9. THE CRYSTAL FIELD

Assuming that the crystal field potential  $V$  satisfies Laplace's equation over the space not occupied by charges, it can be expanded as a sum of spherical harmonics as follows :

$$V(r, \theta, \phi) = \sum_{k=0}^{\infty} \sum_{q=-k}^k a_{kq} r^k Y_k^q(\theta, \phi) \quad (\text{II.9.1})$$

with the sign convention  $(Y_k^q)^* = (-1)^q Y_k^{-q}$ . It is to be noted that  $V$  is real which imposes the condition  $a_{kq} = (-1)^q a_{k-q}^*$ . The quantities  $a_{kq}$ 's are known as crystal field coefficients.

The number of terms in the potential expression may be considerably limited following the three rules.

i) If there is a centre of inversion there will be no harmonics of odd  $k$  in the potential expression.

ii) Odd harmonics may also be omitted for non-centro-symmetric ion site provided we confine ourselves within a given configuration. To show this we consider the state of an ion written in terms of product of one-electron wave functions  $\phi_i(n^a \ell^a m_\ell^a m_s^a)$  ( $i$  refers to the  $i$ -th electron). The matrix element of crystal field interaction between two such states reduces to sum of one electron integrals  $\int \phi_i^*(n \ell m_\ell^a m_s^a) V \phi_i(n \ell m_\ell^b m_s^b) d\tau$ .

The parity of two  $\phi$  functions are the same for a given configuration. When  $V$  is odd the integral becomes an odd function and therefore the integral vanishes. However, such odd order potentials may admix different configurations and will have to be considered in the case of configuration mixing.

iii) For the integral  $\int \phi_i^*(n l m_l^a m_s^a) V \phi_i(n l m_l^b m_s^b) d\tau$  to be non-vanishing it has to fulfil the triangular condition (the triangle formed by the values representing order of the three spherical harmonics i.e.  $l$  for both wave functions and  $k$  for the potential) which gives  $k \leq 2l$ . Hence, all terms in (II.9.1) having  $k > 2l$  may be omitted.

It may be shown that when we confine ourselves to a single configuration  $l^n$  the matrix element of the  $k$ -th harmonics of the crystal field interaction between two states of the ion contains the reduced matrix element  $\langle l \| C^{(k)} \| l \rangle$  as a factor where  $C^{(k)}$  is an irreducible tensor operator corresponding to the  $k$ -th harmonic of the potential. The reduced matrix element is non-vanishing only when,

(a)  $l+k+l$  is even i.e.  $k$  is even.

(b)  $l, k, l$  satisfies the triangular condition i.e.  $k \leq 2l$ .

The above two rules thus immediately follow.

Again the number of terms will also be reduced by the symmetry of the surroundings of the ion and that the terms occurring depend very much on the co-ordinate axes chosen and are in their simplest form when the axes coincide with the

symmetry axes of the point group. The present thesis deals with 4f electrons of rare-earth group so we shall retain the terms upto  $k = 6$  . .

If we take a common example, the  $D_{3h}$  symmetry, which means there is a threefold axis, a twofold axis perpendicular to it, and a reflection plane perpendicular to the threefold axis which makes  $a_{66}$  real (a crystal symmetry that is found approximately in the RE ethyl sulphates), the development can be written

$$V_{D_{3h}} = a_{20}r^2Y_2^0 + a_{40}r^4Y_4^0 + a_{60}r^6Y_6^0 + a_{66}r^6(Y_6^6 + Y_6^{-6}) \quad (\text{II.9.2})$$

where for convenience the summation over  $i$ , the number of 4f electrons has been dropped out.

This can be again rewritten as,

$$V_{D_{3h}} = a_{20}U_0^{(2)} + a_{40}U_0^{(4)} + a_{60}U_0^{(6)} + a_{66}(U_6^{(6)} + U_{-6}^{(6)}) \quad (\text{II.9.3})$$

where  $U_q^{(k)} = r^k Y_k^q$ , which is called as the tensor operator of rank  $k$  and having  $q$ -th component. The quantities  $a_{kq}$ 's are called the crystal field coefficients. The crystal field interaction of an ion having  $n$  electrons in the unfilled shell is

$$H_c = - \sum |e| V \quad (\text{II.9.4})$$

$$= - \sum_{k, q} \sum |e| a_{kq} r^k Y_k^q = - \sum_{k, q} \sum |e| a_{kq} U_q^{(k)} \quad (\text{II.9.5})$$

where the summation in (II.9.4) and first summation in (II.9.5) extend over all the  $n$  electrons. The quantities  $-|e| a_{kq} \langle r^k \rangle_n$

which occur in crystal field calculations are known as crystal field parameters where  $\langle r^k \rangle_{nl}$  is the radial integral given by  $\langle r^k \rangle_{nl} = \int \Psi_{nl}^* \Psi_{nl} r^k r^2 dr$  and  $\Psi_{nl}$  is the radial part of the wave function of the electron corresponding to the  $nl$  subshell.

## II.10. MATRIX ELEMENTS OF CRYSTAL FIELD INTERACTION IN THE CASE OF RARE-EARTH IONS

The fundamental problem is to calculate the matrix elements of the form

$$\langle f^n \alpha U V S L J M_J | U_q^{(k)} | f^n \alpha' U' V' S' L' J' M_J' \rangle$$

Since  $U_q^{(k)}$  does not contain any spin variables so we have  $S = S'$ . By applying Wigner Eckart<sup>81,82</sup> theorem we have

$$\begin{aligned} & \langle f^n \alpha U V S L J M_J | U_q^{(k)} | f^n \alpha' U' V' S' L' J' M_J' \rangle \\ &= (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \langle f^n \alpha U V S L J | U^{(k)} | f^n \alpha' U' V' S' L' J' \rangle \quad (\text{II.10.1}) \end{aligned}$$

Again

$$\begin{aligned} & \langle f^n \alpha U V S L J | U^{(k)} | f^n \alpha' U' V' S' L' J' \rangle \\ &= (-1)^{S+k+J+L'} \begin{Bmatrix} J & J' & S \\ L & L' & k \end{Bmatrix} [(2J+1)(2J'+1)]^{1/2} \\ & \quad \langle f^n \alpha U V S L || U^{(k)} || f^n \alpha' U' V' S' L' \rangle \quad (\text{II.10.2}) \end{aligned}$$

Therefore (II.10.1) becomes

$$\begin{aligned} & (-1)^{2J+S+k+L'-M_J} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \begin{Bmatrix} J & J' & S \\ L & L' & k \end{Bmatrix} \\ & \quad \langle f^n \alpha U V S L || U^{(k)} || f^n \alpha' U' V' S' L' \rangle \quad (\text{II.10.3}) \end{aligned}$$

where,

$$(f^n \alpha_{UVSL} || U^{(k)} || f^n \alpha' U' v' SL')$$

is called the reduced matrix element which is tabulated by Nielson and Koster<sup>77</sup>. The same thing can be further reduced by using the fractional parentage as follows :

$$\begin{aligned} & (f^n \alpha_{UVSL} || U^{(k)} || f^n \alpha' U' v' SL') \\ &= n \sum_{\bar{\Psi}} (\Psi \{ | \bar{\Psi} \}) (\Psi' \{ | \bar{\Psi} \}) (-1)^{L+k+3-L'+L+L'+3+3} \\ & \quad \left\{ \begin{matrix} L & L & \bar{L} \\ 3 & 3 & k \end{matrix} \right\} [(2L+1)(2L'+1)]^{1/2} (f || U^{(k)} || f) \\ &= n \sum_{\bar{\Psi}} (\Psi \{ | \bar{\Psi} \}) (\Psi' \{ | \bar{\Psi} \}) (-1)^{\bar{L}+k+3+L} \left\{ \begin{matrix} L & L' & \bar{L} \\ 3 & 3 & k \end{matrix} \right\} [(2L+1)(2L'+1)]^{1/2} \\ & \quad (f || U^{(k)} || f) \end{aligned} \quad (II.10.4)$$

Therefore

$$\begin{aligned} & (f^n \alpha_{UVSLJM_J} | U_q^{(k)} | f^n \alpha' U' v' SL' J' M'_J) \\ &= n \sum_{\bar{\Psi}} (-1)^{2J+S+2k+L'-M_J+\bar{L}+3+L} (\Psi \{ | \bar{\Psi} \}) (\Psi' \{ | \bar{\Psi} \}) \begin{pmatrix} J & k & J' \\ -M_J & q & M'_J \end{pmatrix} \\ & \quad \left\{ \begin{matrix} L & L' & \bar{L} \\ 3 & 3 & k \end{matrix} \right\} \left\{ \begin{matrix} J & J' & S \\ L & L' & k \end{matrix} \right\} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} (f || U^{(k)} || f) \\ & \quad (II.10.5) \end{aligned}$$

$$\begin{aligned} &= n \sum_{\bar{\Psi}} (-1)^{2J+S+L'+L-M_J+3+\bar{L}} (\Psi \{ | \bar{\Psi} \}) (\Psi' \{ | \bar{\Psi} \}) \begin{pmatrix} J & k & J' \\ -M_J & q & M'_J \end{pmatrix} \\ & \quad \left\{ \begin{matrix} L & L' & \bar{L} \\ 3 & 3 & k \end{matrix} \right\} \left\{ \begin{matrix} J & J' & S \\ L & L' & k \end{matrix} \right\} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} (f || U^{(k)} || f) \\ & \quad (II.10.6) \end{aligned}$$

where  $(\Psi \{ | \bar{\Psi} \})$  are the coefficient of fractional parentages (c. f. p)

and

$$\begin{aligned}
 \langle f || U^{(k)} || f \rangle &= \left[ \frac{2k+1}{4\pi} \right]^{1/2} {}_{4f} \langle r^k \rangle_{4f} \langle f || C^k || f \rangle \\
 &= \left[ \frac{2k+1}{4\pi} \right]^{1/2} {}_{4f} \langle r^k \rangle_{4f} (-1)^3 \left[ (2 \cdot 3 + 1) (2 \cdot 3 + 1) \right]^{1/2} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \\
 &= -7 \left[ \frac{2k+1}{4\pi} \right]^{1/2} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} {}_{4f} \langle r^k \rangle_{4f} \quad (\text{II.10.7})
 \end{aligned}$$

The quantities like  $-|e| a_{kq} {}_{4f} \langle r^k \rangle_{4f}$  have been treated as crystal field parameters and a simple symbol  $A_{kq}$  has been used for  $-|e| a_{kq} {}_{4f} \langle r^k \rangle_{4f}$ .

The similar type of calculation can be done by using operator equivalent method which has been discussed by Stevens<sup>83</sup>.

When Steven's operator equivalent method is used the CF potential is expressed in cartesian form and the CF parameters are obtained in Steven's form and they are denoted by  $B_k^q$ 's instead of  $A_{kq}$ 's. In our subsequent calculation we shall use  $A_{kq}$ 's which are the CF parameters in tensor operator form.  $B_k^q$ 's are related with  $A_{kq}$ 's by simple constant factors given below

$$\begin{aligned}
 A_{20} &= 4 \sqrt{\frac{\pi}{5}} B_2^0 ; & A_{40} &= \frac{16}{3} \sqrt{\pi} B_4^0 ; & A_{60} &= 32 \sqrt{\frac{\pi}{13}} B_6^0 \\
 A_{66} &= 32 \sqrt{\frac{\pi}{3003}} B_6^6 ; & A_{63} &= 16 \sqrt{\frac{\pi}{1365}} B_6^3 ; & A_{43} &= \frac{4}{3} \sqrt{\frac{\pi}{35}} B_4^3
 \end{aligned}$$

Since the operator equivalent technique was not used in the subsequent CF calculation, so the details of that is not discussed here.

## II.11. CALCULATION OF MAGNETIC SUSCEPTIBILITY

A free paramagnetic ion in the absence of an external magnetic field, will in general have a number of degenerate and non-degenerate states. These states are classified according to their energy values into different groups labelled by the index  $m$ ; degenerate states having the same energy form a group, each non-degenerate state is a group by itself. Suppose a correct zeroth order state  $\Psi_{ml,i}$  assumes an energy  $W_{ml,i}$  in the magnetic field  $\mathcal{H}$  which is applied in the direction  $i$  ( $i \equiv x, y, z$ ). The additional suffix  $l$  is used to specify a particular component state when it belongs to a degenerate group i.e.  $\Psi_{ml,i}$  is the correct zeroth order  $l$ -th state belonging to the  $m$ -th group, the correct zeroth order states of a degenerate group being decided by the fact that the Zeeman perturbation  $\beta \mathcal{H}(L_i + 2S_i)$  is diagonal in a basis of these states. The general expression for the ionic paramagnetic susceptibility of a system of free ions<sup>1</sup> is given by

$$K_i = \lim_{\mathcal{H} \rightarrow 0} \frac{N}{\mathcal{H}} \frac{\sum_{ml} \frac{\partial W_{ml,i}}{\partial \mathcal{H}} \exp\left(-\frac{W_{ml,i}}{kT}\right)}{\sum_{ml} \exp\left(-\frac{W_{ml,i}}{kT}\right)} \quad (\text{II.11.1})$$

$$= \lim_{\mathcal{H} \rightarrow 0} \frac{NkT}{\mathcal{H}} \frac{\partial}{\partial \mathcal{H}} \ln Z_i \quad (\text{II.11.2})$$

where

$$Z_i = \sum \exp\left(-\frac{W_{ml,i}}{kT}\right) \quad (\text{II.11.3})$$

where the summation extends over all indices  $m, l$  corresponding to all states.

Van Vleck has also given a more convenient expression e.g.

$$K_i = \frac{\sum_m \left[ \frac{(W_{ml,i}^{(1)})^2}{kT} - 2W_{ml,i}^{(2)} \right] \exp\left(-\frac{W_m^{(0)}}{kT}\right)}{\sum_{ml} \exp\left(-\frac{W_m^{(0)}}{kT}\right)} \quad (\text{II.11.4})$$

where  $W_m^{(0)}$ ,  $W_{ml,i}^{(1)}$  and  $W_{ml,i}^{(2)}$  are defined by the expansion of energy  $W_{ml,i}$  in a power series in the applied field  $\mathcal{H}$  as follows :

$$W_{ml,i} = W_m^{(0)} + W_{ml,i}^{(1)} \mathcal{H} + W_{ml,i}^{(2)} \mathcal{H}^2 + \dots \quad (\text{II.11.5})$$

Thus  $W_m^{(0)}$  is the unperturbed energy in the zero magnetic field (the indices  $l$  and  $i$  are superfluous in the zeroth order energy and hence are omitted in  $W_m^{(0)}$ ).  $W_{ml,i}^{(1)} \mathcal{H}$  and  $W_{ml,i}^{(2)} \mathcal{H}^2$  are the first and second order Zeeman perturbation when a magnetic field  $\mathcal{H}$  is applied along the direction  $i$ . The quantities  $W_{ml,i}^{(1)}$  and  $W_{ml,i}^{(2)}$  are explicitly given as follows,

$$W_{ml,i}^{(1)} = \langle \psi_{ml,i} | \beta(L_i + 2S_i) | \psi_{ml,i} \rangle \quad (\text{II.11.6})$$

$$W_{ml,i}^{(2)} = - \sum_{np} \frac{|\langle \psi_{ml,i} | \beta(L_i + 2S_i) | \psi_{np,i} \rangle|^2}{W_n^{(0)} - W_m^{(0)}} \quad (\text{II.11.7})$$

The expression (II.11.4) can be obtained from (II.11.1) using the expansion (II.11.5) and assuming that (i) the Zeeman terms are very much smaller than  $kT$  so that exponentials when expanded can be approximated by neglecting higher terms in their

expansion and (ii) there is no permanent polarization in zero magnetic field i.e.

$$\sum_{m\ell} W_{m\ell, i}^{(1)} \exp\left(-\frac{W_{m\ell}^{(0)}}{kT}\right) = 0$$

The above derivation of susceptibility is quite general and holds good so far as any magnetic degeneracy is left over even in the process of molecules or solid state formations.

## II.12. CALCULATION OF g-VALUES

Electron paramagnetic resonance spectrum corresponds to transition between the two components into which the lowest doublet ( $\phi_1, \phi_1'$ ) splits when an external magnetic field is applied. We shall assume uniaxial symmetry of the ion so that e.p.r spectrum for the two cases, magnetic field parallel and perpendicular to the symmetry axis will be considered. Diagonalisation of the Zeeman perturbation  $\beta \mathcal{A}(L_Z + 2S_Z)$  constructed in a basis of two component states  $\phi_1$  and  $\phi_1'$  of the lowest doublet gives the energies of the two components into which the doublet ( $\phi_1, \phi_1'$ ) splits when  $\mathcal{A} \parallel Z$  and the energy separation  $\Delta W^Z$  between the two components when  $\mathcal{A} \parallel Z$  is given by

$$\Delta W^Z = \beta \mathcal{A} \left| \langle \phi_1 | L_Z + 2S_Z | \phi_1 \rangle - \langle \phi_1' | L_Z + 2S_Z | \phi_1' \rangle \right|$$

Thus

$$g_{\parallel} = g_Z = \frac{\Delta W^Z}{\beta \mathcal{A}} \left| \langle \phi_1 | L_Z + 2S_Z | \phi_1 \rangle - \langle \phi_1' | L_Z + 2S_Z | \phi_1' \rangle \right| \quad (\text{II.12.1})$$

Similarly diagonalisation of the matrix of Zeeman perturbation  $\beta \mathcal{A}(L_\alpha + 2S_\alpha)$  constructed in a basis of the states  $\phi_1$  and  $\phi_1'$  when  $\mathcal{A} \parallel \alpha$  ( $\alpha = x$  or  $y$ ) gives the value of the splitting as

$$\Delta W^\alpha = 2\beta \mathcal{A} \left| \langle \phi_1 | L_\alpha + 2S_\alpha | \phi_1 \rangle \right|$$

where  $\alpha = x$  or  $y$  and

$$\begin{aligned} g_\perp = g_x = g_y &= \frac{\Delta W^\alpha}{\beta \mathcal{A}} \\ &= 2 \left| \langle \phi_1 | L_x + 2S_x | \phi_1 \rangle \right| = 2 \left| \langle \phi_1 | L_y + 2S_y | \phi_1 \rangle \right| \quad (\text{II.12.2}) \end{aligned}$$

### II.13. CALCULATION OF THE MATRIX ELEMENT

#### OF THE TYPE $\langle SLJM | (L_i + 2S_i) | SL'JM' \rangle$

To calculate the matrix element of  $\langle SLJM | (L_i + 2S_i) | SL'JM' \rangle$  we have to express  $L_i$  and  $S_i$  in tensor operator form as follows:

For  $i = z$

$L_z$  and  $S_z$  can be treated as  $T_0^{(1)}$  tensor operator. For  $i = x$ ,  $L_x$  or  $S_x$  can be written as,

$$\sqrt{\frac{1}{2}} (T_{-1}^{(1)} - T_1^{(1)})$$

And for  $i = y$ ,  $L_y$  or  $S_y$  can be written as,

$$i \sqrt{\frac{1}{2}} (T_1^{(1)} + T_{-1}^{(1)})$$

And if the tensor operator form be applied here we shall obtain the following results :

$$\langle SLJM_J | L_z | SLJM_J \rangle = M_J \frac{L(L+1) + J(J+1) - S(S+1)}{2J(J+1)}$$

$$\langle SLJM_J | S_Z | SLJM_J \rangle = M_J \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$$

$$\langle SLJM_J | L_Z | SLJ + 1, M_J \rangle = - \langle SLJM_J | S_Z | SLJ + 1, M_J \rangle$$

$$= - \left[ \frac{(J+M_J+1)(J-M_J+1)(S+L+J+2)(S+L-J)(S-L+J+1)(-S+L+J+1)}{(2J+3)(2J+2)^2(2J+1)} \right]^{1/2}$$

$$\langle SLJM_J | L_X | SLJM_J + 1 \rangle = \frac{[(J-M_J)(J+M_J+1)]^{1/2}}{4J(J+1)} [J(J+1) + S(S+1) + L(L+1)]$$

$$\langle SLJM_J | S_X | SLJM_J + 1 \rangle = \frac{[(J-M_J)(J+M_J+1)]^{1/2}}{4J(J+1)} [J(J+1) + S(S+1) - L(L+1)]$$

$$\langle SLJM_J | L_X | SLJM_J - 1 \rangle = \frac{[(J+M_J)(J-M_J+1)]^{1/2}}{4J(J+1)} [J(J+1) + L(L+1) - S(S+1)]$$

$$\langle SLJM_J | S_X | SLJM_J - 1 \rangle = \frac{[(J+M_J)(J-M_J+1)]^{1/2}}{4J(J+1)} [J(J+1) + S(S+1) - L(L+1)]$$

$$\langle SLJM_J | L_X | SLJ + 1, M_J + 1 \rangle = - \langle SLJM_J | S_X | SLJ + 1, M_J + 1 \rangle$$

$$= \frac{1}{4(J+1)} \left[ \frac{(J+M_J+1)(J+M_J+2)(J+L+S+2)(-J+L+S)(J-L+S+1)(J+L-S+1)}{(2J+1)(2J+3)} \right]^{1/2}$$

$$\langle SLJM_J | L_X | SLJ + 1, M_J - 1 \rangle = - \langle SLJM_J | S_X | SLJ + 1, M_J - 1 \rangle$$

$$= - \frac{1}{4(J+1)} \left[ \frac{(J-M_J+1)(J-M_J+2)(J+L+S+2)(-J+L+S)(J-L+S+1)(J+L-S+1)}{(2J+1)(2J+3)} \right]^{1/2}$$

#### II.14. COVALENCY REDUCTION OF ORBITAL ANGULAR MOMENTUM

Since the magnetic properties and optical absorption are connected with the orbitals of the unfilled shell of the central metal atoms, such aspects of them as are determined by the behaviour of electrons close to the nucleus of the central

metal ion will be reduced if the orbitals overspill on the ligands. Particularly the orbital angular momentum and the spin-orbit coupling co-efficient will be effectively reduced by such covalency effect from their respective free ion values. Now the covalency effect in the case of rare-earth ion, although small has been felt necessary for the past few years. We also find during our calculations that unless a reduction of the orbital moment matrices presumably due to the covalency effect is assumed, it becomes impossible to achieve a good fit to the g-values and magnetic susceptibilities in some of the rare-earth complexes. The covalency effect implies that the electrons in the unfilled shell of the rare-earth ion do not move in pure f-orbitals, they move in modified orbitals, the so called molecular orbitals, in which the f-orbitals of the metal atom are admixed slightly with the orbitals of the ligand electrons as required by the symmetry of the complex. Denoting the molecular orbital corresponding to a pure f-orbital by  $f^{\text{mol}}$  we define the covalency reduction factor for the orbital angular momentum operator by the ratios:

$$\frac{\langle f_a^{\text{mol}} | l_i | f_b^{\text{mol}} \rangle}{\langle f_a | l_i | f_b \rangle} = k_i^{\text{ab}} \quad (i \equiv x, y, z) \quad (\text{II.14.1})$$

For rare-earth ions  $k_i^{\text{ab}}$  will be very near to but slightly less than unity. The matrix elements of  $L_i$  ( $i \equiv x, y, z$ ) that occur in the calculation of g-values and magnetic susceptibilities

are of the type

$$\langle SLJM | L_i | S' L' J' M' \rangle \quad (\text{II.14.2})$$

In (II.14.2) the states between which the matrix element of the resultant orbital angular momentum  $L_i$  is considered refer to the whole atom built up from the individual electron states. Now if the electrons are of pure f-type, the matrix element in (II.14.2) will be denoted by  $Q_i$ . If they are not of pure f-type its value will be modified from the value that one would obtain when the resultant atomic states are built up from pure f-electrons and will be denoted by  $Q_i^m$ . This modified value  $Q_i^m$  has to be used in place of  $Q_i$ . To find the relation between  $Q_i$  and  $Q_i^m$  one should express the states  $|SLJM\rangle$  and  $|S'L'J'M'\rangle$  in terms of determinantal product states and then replace the individual pure f-states of electrons by their corresponding molecular orbital states  $f^{\text{mol}}$ . We now make a simplifying approximation that  $k_i^{ab}$  is the same for all pairs of orbitals and further consider that the reduction factor partakes of the symmetry of the complex. In the case of uniaxial symmetry of the complex (e.g.  $D_{3h}$ ) we will have only two covalency reduction factors  $k_{\parallel}$  ( $=k_z$ ) and  $k_{\perp}$  ( $=k_x$  or  $k_y$ ). In the case of rare-earth ions these reduction factors are all very near to unity and the above approximation may be considered as quite reasonable. With the above approximation we shall have  $Q_i^m = k_i Q_i$  ( $i \equiv x, y, z$ ). In the case of uniaxial

symmetry when  $i$  refers to the  $z$  direction we shall denote  $k_i$  by  $k_{\parallel}$  and when  $i = x$  or  $y$ ,  $k_i$  will be denoted by  $k_{\perp}$ . This means that in order to take the effect of covalency into account we have to replace the operator  $L_i$  by the effective operator  $k_i L_i$  in the matrix element between two resultant atomic states. In the present thesis  $k_{\parallel}$  and  $k_{\perp}$  will be treated as two additional parameters to be evaluated from experiment.

## II.15. ELECTRIC DIPOLE TRANSITION MOMENTS

The crystal field of  $\text{Ln}^{3+}$  ion in either a crystalline or molecular environment, is pictured as arising from the electrostatic potential due to the net charges of the surrounding ligands<sup>84</sup>. This electrostatic potential then acts to split the  $\text{Ln}^{3+}$  free ion electronic energy levels in the familiar weak field approximation. But this idea is not general while calculating the crystal field splittings from parameters based solely on the net charges and spatial distribution of the ligands because the predicted splittings are often much smaller in magnitude than the observed level spacings.

We take a lanthanide ion ~~surrounded by  $N$  ligands. We~~ also consider that the ligands are non-interacting and ~~partition~~ the total system into two. The  $\text{Ln}^{3+}$  ion subsystem is designated by  $A$  and the ligand subsystem by  $B$  and an individual ligand will be denoted by  $L$ .

So the complete hamiltonian of our system can be written as follows :

$$H = H_A^O + H_B^O + H_{AB} \quad (\text{II.15.1})$$

where

$$H_A^O = L_n^{3+} \text{ free ion hamiltonian .}$$

$$H_B^O = \sum_L h_L$$

$$h_L = \text{hamiltonian for the L-th ligand.}$$

$$H_{AB} = \text{A-B interaction hamiltonian.}$$

The interaction hamiltonian may be expanded in metal ion-ligand pairwise potentials :

$$H_{AB} = \sum_L \sum_{l_A} \sum_{l_L} V_L(l_A, l_L) \quad (\text{II.15.2})$$

where  $V_L(l_A, l_L)$  = electrostatic potential between the  $l_A$ -th multipole of the lanthanide ion charge distribution and  $l_L$ -th multipole of the charge distribution of the L-th ligand.

$V_L(l_A, l_L)$  may again be partitioned as follows :

$$H_{AB} = \sum_L \sum_{l_A} V_L(l_A, 0) + \sum_L \sum_{l_A} \sum_{l_L \geq 1} V_L(l_A, l_L) \quad (\text{II.15.3})$$

$$= \mathcal{V} + \mathcal{U} \quad (\text{II.15.4})$$

The operator  $\mathcal{V}$  represents the electrostatic interactions between the metal ion multipoles and the ligand monopoles (net charges) and as such represents the standard point charge

crystal field.  $\mathcal{U}$  is the interaction between the metal ion multipoles and the higher ( $l_L \gg 1$ ) multipoles of the ligands. In the present thesis we take  $l_L = 1$ .

$$\mathcal{U} = \sum_L \sum_{l_A} V_L(l_A, 1)$$

Richardson termed  $\mathcal{V}$  as the 'static-coupling' operator and  $\mathcal{U}$  as the 'dynamic coupling operator'.

## II.15(a). POINT CHARGE PART

Now let us try to find out the expression for the crystal field parameter for static coupling operator (which is actually called the point charge part). In absence of any external radiation the central metal ion and the ligand charges may be treated as point charges. i.e. the charge distribution of the central metal ion and the ligands are assumed to be centred to two points. This is the basic consideration of the point charge model. The theory disregards the metal-ligand electron exchange. In case of point charge model it is generally considered that a particular charge distribution of the ligands taken to be that of the ground state, perturbs all the electronic states of the metal-ion. On expansion of the potential provided by the point charges around the central metal ion we have the form of the potential as

$$\mathcal{V} = \sum_l \sum_{l_A} V_L(l_A, 0)$$

by expanding the CF potential the following form of the CF parameters will come as

$$A_{kq}(\text{chg}) = (-1)^q 7e \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \sum_L q_L R_L^{-(k+1)} \left[ \frac{4\pi}{2k+1} \right]^{1/2} Y_{\ell}^{-m}(\Theta_L, \Phi_L) \langle r^k \rangle_{4f} \quad (\text{II.15(a).1})$$

where

$(R_L, \Theta_L, \Phi_L)$  = spherical polar co-ordinates of the ligand group L .

#### II.15(b). POLARIZABILITY CONTRIBUTION

From the dynamic contribution on the crystal field potential we have the crystal field parameters due to the polarizability contribution. An approximation to the CF potential is afforded by a multipole expansion of each of the charge distributions of metal ion and the ligand, centred upon their respective co-ordinate origins, and the truncation of each series is done after the leading term. The term retained for the ligand group charge distributions is up to the electric dipole. The allowed electric charge distributions of an  $\ell \rightarrow \ell$  metal ion transition are the even multipole moments,  $2^n$ -poles, with  $n = 2, 4, \dots, 2\ell$ , each having  $(2n+1)$  components. In the ligand polarization model the electron exchange between the

ligands and the metal ions is also neglected as in the case of point charge model.

The polarizability contribution thus comes from the interaction of the dipole moment of the ligand with the quadrupole, hexadecapole etc. moment of the central metal ion. And this comes out as second order effect and should be included in the crystal field parameter. This contribution in the crystal field was extensively used by Mason<sup>85</sup>. Later Richardson and Faulkner<sup>68</sup> introduced this polarizability contribution in the CF level calculations.

The polarizability contribution to the crystal field parameter is given by<sup>68</sup>

$$A_{kq}(\text{pol}) = 14e(k+1)(-1)^q \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} q_A \sum_L \bar{\alpha}_L R_L^{-(k+4)} \left[ \frac{4\pi}{2k+1} \right]^{1/2} Y_{\ell}^{-m}(\Theta_L, \Phi_L)_{4f} \langle r^k \rangle_{4f} \quad (\text{II.15(b).1})$$

where

$$q_A = \text{net charge on } \text{Ln}^{3+} = 3,$$

$$\bar{\alpha}_L = \text{'mean' isotropic polarizability of ligand L.}$$

This is a constant for a particular ligand group. Saxe et al.<sup>86</sup> gave the values of  $\bar{\alpha}_L$  in a tabular form for different ligand groups.

So the resultant crystal field parameter is obtained from both the charge and the polarizability contribution :

$$A_{kq} = A_{kq}(\text{chg}) + A_{kq}(\text{pol})$$

II.15(c). STATIC-COUPLING MECHANISM IN THE  
ELECTRIC DIPOLE TRANSITION MOMENT

The static-coupling contribution to the electric dipole transition moment is defined as that arising from  $\mathcal{V}$  part of  $H_{AB}$ . This operator operates only on metal ion (A) wave functions and it connects metal ion states of opposite parity. That means the matrix element (or the electric dipole moment) of this operator only exists between one state in  $4f^n$  configuration and the other in  $4f^{n-1}n'd$  or  $4f^{n-1}n'g$ . Following Judd-Ofelt<sup>52-53</sup> mechanism Richardson and Faulkner<sup>68</sup> obtained the static contribution to the electric dipole transition moment from a state  $|A_0\rangle$  to an excited state  $|A_a\rangle$  as follows :

$P_{0a}^{(S)}$  = Static contribution of the electric dipole moment.

$$= e^2 \sum_q \sum_{l_A(\text{odd})} \sum_{m_A} \sum_L q_{L'} \frac{(-1)^{l_A+m_A}}{R_L} \sum_{\lambda} (-1)^{m_A+q+J-M_J} \\ (2\lambda+1) \begin{pmatrix} 1 & \lambda & l_A \\ q & -m_A-q & m_A \end{pmatrix} \begin{pmatrix} J & \lambda & J' \\ -M_J & m_A+q & M_J' \end{pmatrix} (-1)^{S+L'+J+\lambda} \\ \left[ (2J+1)(2J'+1) \right]^{1/2} \left\{ \begin{matrix} L & \lambda & L' \\ J' & S & J \end{matrix} \right\} (SL \parallel U^{(\lambda)} \parallel SL') \begin{matrix} \square \\ \square \\ \square \end{matrix} (l_A, \lambda) \quad \text{(II.15(c).1)}$$

where

$$\begin{aligned} \overline{H}_1(l_A, \lambda) &= 2 \sum_{n'' l''} (2l+1)(2l''+1)(-1)^{l+l''} \begin{pmatrix} 1 & \lambda & l_A \\ l & l'' & l \end{pmatrix} \\ &\begin{pmatrix} l & 1 & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'' & l_A & l \\ 0 & 0 & 0 \end{pmatrix} (4f \parallel r \parallel n'' l'') (n'' l'' \parallel r^{l_A} \parallel 4f) / \Delta(n'' l'') \end{aligned}$$

The summation  $\sum_{n'' l''}$  is taken over  $n'' d$  and  $n'' g$  and for  $f$  system  $l = 3$ . The calculation of  $\overline{H}_1(l_A, \lambda)$  has been discussed by Krupke<sup>87</sup>.  $\Delta(n'' l'')$  is defined as an 'average energy' parameter.  $(SL \parallel U^{(\lambda)} \parallel SL')$  is called the reduced matrix element which can be obtained from, Nielson and Koster's table.

## II.15(d). DYNAMIC COUPLING MECHANISM IN THE ELECTRIC DIPOLE TRANSITION MOMENT

In the Judd-Ofelt<sup>52,53</sup> theory the ligands surrounding the lanthanide ion are considered only in as much as their ground state field produces the perturbation required to mix excited configuration into the  $4f$  configurations. But the ligand wave functions are also perturbed by the metal ion. Now we try to explain what is meant by Dynamic Coupling mechanism. Let us call the metal ground and excited functions as  $|M_o\rangle$  and  $|M_a\rangle$  and those of the ligand as  $|L_o\rangle$  and  $|L_b\rangle$ . The combined wave function of the total system will be simply the product functions i.e.  $|M_o L_o\rangle$ .

The first order perturbed ground and excited states  $|A\rangle$  and  $|B\rangle$  as

$$|A\rangle = |M_o L_o\rangle - \sum_b \frac{\langle M_a L_b | \underline{V} | M_o L_o \rangle}{E_a + E_b} |M_a L_b\rangle$$

$$|B\rangle = |M_a L_o\rangle - \sum_b \frac{\langle M_a L_b | \underline{V} | M_a L_o \rangle}{E_a - E_b} |M_o L_b\rangle$$

where

$$E_a = |M_a\rangle \leftarrow |M_o\rangle \text{ transitional energy.}$$

$$E_b = |L_b\rangle \leftarrow |L_o\rangle \text{ transitional energy.}$$

The summation on the right hand side of  $|A\rangle$  and  $|B\rangle$  runs over all transitions of the ligand which are electric dipole allowed.

$\underline{V}$  represents the coulombic interaction of the charge distributions on metal and ligand.

The  $f \leftrightarrow f$  transition thus acquires a first order electric dipole transition moment which is given by :

$$e \langle A | D_q^{(1)} | B \rangle = e \sum_b 2E_b (E_b^2 - E_a^2)^{-1} \langle M_o M_a | \underline{V} | L_o L_b \rangle \langle L_o | D_q^{(1)} | L_b \rangle$$

$D_q^{(1)}$  = induced dipole operator. The electric dipole moments  $\langle L_o | D_q^{(1)} | L_b \rangle$  located on the ligand are correlated coulombically with the charge distribution at the lanthanide ion caused by the  $f \leftrightarrow f$  transition. The correlation is given by the matrix element  $\langle M_o M_a | \underline{V} | L_o L_b \rangle$ .

Now applying the Judd-Ofelt mechanism and by expressing the wave function in  $|4f\alpha [SL] JM\rangle$  form we ultimately have the contribution of the electric dipole moment due to dynamic coupling as<sup>68</sup>

$P_{oa}^{(d)}$  = Dynamic contribution of the electric dipole moment from a state  $|A_o\rangle$  to an excited state  $|A_a\rangle$

$$\begin{aligned}
 &= e \langle A_o | D_q^{(1)} | A_a \rangle \\
 &= \sum_q \sum_{l_A} \sum_{m_A} \sum_L (-1)^q \bar{\alpha}_L(qq) T_{m_A - q}^{(l_A, 1)} {}^{(L)} Z_{oa}^{(d)}(l_A, m_A)
 \end{aligned}
 \tag{II.15(d).1}$$

where

$$T_{m_A - q}^{(l_A, 1)}(L) = \frac{(-1)^{1+m_A+q}}{R_L^{l_A+2}} \left[ \frac{(l_A+1+m_A-q)! (l_A+1-m_A+q)!}{(l_A+m_A)! (l_A-m_A)! (1-q)! (1+q)!} \right]^{1/2} C_{-m_A+q}^{l_A+1}(\Theta_L, \Phi_L)$$

$${}^{(L)} Z_{oa}^{(d)}(l_A, m_A) = \langle A_o | D_{m_A}^{l_A} | A_a \rangle = -e \sum_{\alpha} r_{\alpha}^{l_A} \langle A_o | C_{m_A}^{l_A}(\Theta_{\alpha}, \Phi_{\alpha}) | A_a \rangle$$

$\bar{\alpha}_L(qq)$  =  $q$ -th diagonal component of the polarizability tensor for the  $L$ -th ligand group.

$$= \sum_b \frac{2E_b e^2 \langle L_o | D_q^{(1)} | L_b \rangle^2}{E_b^2 - E_a^2}$$

and

$$C_{m_A}^{l_A}(\Theta_{\alpha}, \Phi_{\alpha}) = \left[ \frac{4\pi}{2l_A+1} \right]^{1/2} Y_{l_A}^{m_A}(\Theta_{\alpha}, \Phi_{\alpha})$$

since the transition charge distribution, arises entirely from within the  $4f^n$  configuration of the metal ion, the only values of  $l_A$  leading to nonvanishing values of  $Z_{oa}^{(d)}$  are  $l_A = 2, 4$  and  $6$ . Other terms are already explained before. The computational model is followed from the procedures of Mason, Peacock and Stewart<sup>88</sup>, Richardson and Faulkner<sup>68</sup>.

## II.16. MAGNETIC DIPOLE TRANSITION MOMENT

The theory of magnetic dipole transitions is well known<sup>53</sup>, and therefore we are interested only in the application to the crystal field problem. Generally the magnetic dipole transitions are  $10^{-6}$  times less intense than the electric dipole transition. But in cases of parity-forbidden (i.e.  $g \rightarrow g$ ,  $u \rightarrow u$ ) transitions in complexes, having inversion symmetry, the electric dipole moment will vanish owing to symmetry reasons but magnetic dipole moment may play a significant role in making the purely electronic 0-0 band allowable.

The magnetic dipole moment operator is given by

$$M = - \frac{e}{2mc} \sum_i (\underline{L}_i + 2\underline{S}_i) \quad (\text{II.16.1})$$

Expressing  $\underline{L}_i$  and  $\underline{S}_i$  in tensor operator and utilizing the intermediate coupling notation for the metal ion ( $f \rightarrow f$ ) states, the magnetic dipole transition moment for the transition

$$|\Psi [SL] JM\rangle \rightarrow |\Psi' [S'L'] J'M'\rangle$$

is given by

$$\begin{aligned} M_{\Psi\Psi'} &= \langle \Psi [SL] JM | m_q | \Psi' [S'L'] J'M' \rangle \\ &= \delta(\Psi, \Psi') \delta(S, S') \delta(L, L') (-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix} \\ &\quad \langle [SL] J \| m \| [S'L'] J' \rangle \end{aligned} \quad (\text{II.16.2})$$

where  $\underline{m}_q$  is the  $q$ -th (spherical) component of the magnetic dipole moment operator. The reduced matrix elements of  $\underline{m}$  are given by

$$\langle [SL]J \parallel \underline{m} \parallel [SL]J \rangle = \frac{1}{2} \mu_B \left[ \frac{2J+1}{J(J+1)} \right]^{1/2} \left\{ (g_s - 1) [S(S+1) - L(L+1)] + (g_s + 1) J(J+1) \right\} \quad (\text{II.16.3})$$

$$\langle [SL]J \parallel \underline{m} \parallel [SL]J+1 \rangle = \frac{1}{2} \mu_B (g_s - 1) \left\{ [(S+L+1)^2 - (J+1)^2] [(J+1)^2 - (L-S)^2] (J+1)^{-1} \right\}^{1/2} \quad (\text{II.16.4})$$

and

$$\langle [SL]J \parallel \underline{m} \parallel [SL]J-1 \rangle = \frac{1}{2} \mu_B (g_s - 1) \left\{ [(S+L+1)^2 - J^2] [J^2 - (L-S)^2] (J)^{-1} \right\}^{1/2} \quad (\text{II.16.5})$$

In equations (II.16.3) - (II.16.5)

$$\mu_B = - \frac{e\hbar}{2mc}$$

$g_s$  = gyromagnetic ratio of the electron.

To compute the magnetic dipole transition moment for a transition between crystal field levels, the spherical basis results of equation (II.16.2) can be converted into the crystal field basis using appropriate crystal field wave functions. It is important to emphasize, however, that a simple symmetry transformation of the spherical into the crystal field basis is inadequate in this case. In particular for  $J \rightarrow J+2$  transitions it is the inter-term crystal field mixings that

contribute to the magnetic dipole intensity. It is essential then, that crystal field induced J-mixing be included in the magnetic-dipole moment calculations.

## II.17. CALCULATION OF ROTATIONAL STRENGTH

The electric and magnetic field vector of a right/left circularly polarised light wave along the +Z direction is given by

$$E_x \cos\omega t \mp E_y \sin\omega t = \frac{1}{2}(E_x + iE_y)e^{-i\omega t} + \frac{1}{2}(E_x - iE_y)e^{i\omega t}$$

$$H_x \sin\omega t \mp H_y \cos\omega t = \frac{1}{2}(H_y + iH_x)e^{-i\omega t} + \frac{1}{2}(H_y - iH_x)e^{i\omega t}$$

When we are considering the case of an absorption, the term containing  $e^{-i\omega t}$  will only be important for bringing about transition (Rotating wave approximation). For circularly polarized light  $E_x = E_y = E$  (say) and  $H_x = H_y = \mathcal{H}$  (say).

So we can write

$$E(\cos\omega t \pm \sin\omega t) \rightarrow \frac{1}{2} E(1 \pm i)e^{-i\omega t} \quad (\text{II.17.1})$$

$$\mathcal{H}(\sin\omega t \pm \cos\omega t) \rightarrow \frac{1}{2} \mathcal{H}(1 \pm i)e^{-i\omega t} \quad (\text{II.17.2})$$

neglecting the term containing  $e^{i\omega t}$  for the problem under discussion. The time average of (II.17.1) and (II.17.2) gives  $E/2$  and  $\mathcal{H}/2$ . Now the Hamiltonian of interaction between the light wave and molecule is given by

$$\underline{E} \cdot e\underline{r} + \underline{H} \cdot \underline{\mu}$$

$$= e \frac{E}{2} (\underline{x} + iy) + \frac{e}{2mc} \frac{\mathcal{H}}{2} (\underline{L}_y + i\underline{L}_x)$$

$$= (e \frac{E}{2} \underline{x} + \frac{e}{2mc} \frac{\mathcal{H}}{2} \underline{L}_y) + i(e \frac{E}{2} \underline{y} + \frac{e}{2mc} \frac{\mathcal{H}}{2} \underline{L}_x)$$

Let

$$\hat{\alpha} = eE\underline{x} + \frac{e}{2mc} \mathcal{H} \underline{L}_y$$

$$\hat{\beta} = eE\underline{y} + \frac{e}{2mc} \mathcal{H} \underline{L}_x$$

$$\therefore H_{\text{int}} = \text{interaction hamiltonian} = \frac{1}{2} \hat{\alpha} + \frac{1}{2} i\hat{\beta} = \hat{\alpha}' + i\hat{\beta}' .$$

The probability of absorption of right and left circularly polarised light corresponding to transition between non-degenerate level  $a \rightarrow b$  is given by the well-known expression

$$P_R = \frac{2\pi}{\hbar} \langle a | \hat{\alpha}' + i\hat{\beta}' | b \rangle \langle a | \hat{\alpha}' + i\hat{\beta}' | b \rangle^* \delta_{a,b+\omega}$$

$$P_L = \frac{2\pi}{\hbar} \langle a | \hat{\alpha}' - i\hat{\beta}' | b \rangle \langle a | \hat{\alpha}' - i\hat{\beta}' | b \rangle^* \delta_{a,b+\omega}$$

The circular dichroism is the difference of absorption of right and left circularly polarised light. Therefore the difference in absorption

$$P_R - P_L = \frac{2\pi}{\hbar} \left[ \langle a | \hat{\alpha}' + i\hat{\beta}' | b \rangle \langle a | \hat{\alpha}' + i\hat{\beta}' | b \rangle^* - \langle a | \hat{\alpha}' - i\hat{\beta}' | b \rangle \langle a | \hat{\alpha}' - i\hat{\beta}' | b \rangle^* \right] \delta_{a,b+\omega}$$

where

$$\begin{aligned} & \langle a | \hat{\alpha}' + i\hat{\beta}' | b \rangle \langle a | \hat{\alpha}' + i\hat{\beta}' | b \rangle^* - \langle a | \hat{\alpha}' - i\hat{\beta}' | b \rangle \langle a | \hat{\alpha}' - i\hat{\beta}' | b \rangle^* \\ &= 2 \left[ -i \langle a | \hat{\alpha}' | b \rangle \langle a | \hat{\beta}' | b \rangle^* + i \langle a | \hat{\beta}' | b \rangle \langle a | \hat{\alpha}' | b \rangle^* \right] \end{aligned}$$

$$\begin{aligned}
&= -2i \langle a | \hat{\alpha}' | b \rangle \langle a | \hat{\beta}' | b \rangle^* + 2i \langle a | \hat{\beta}' | b \rangle \langle a | \hat{\alpha}' | b \rangle^* \\
&= -2i \left[ \langle a | \hat{\alpha}' | b \rangle \langle a | \hat{\beta}' | b \rangle^* - \left\{ \langle a | \hat{\alpha}' | b \rangle \langle a | \hat{\beta}' | b \rangle^* \right\}^* \right] \\
&= -2 \times 2 \times i \times i \times \text{Imaginary part of } \langle a | \hat{\alpha}' | b \rangle \langle a | \hat{\beta}' | b \rangle^* \\
&= 4 \times \text{Imaginary part of } \left[ \langle a | \hat{\alpha}' | b \rangle \langle a | \hat{\beta}' | b \rangle^* \right] \\
&= 4 \times \frac{1}{2} \times \frac{1}{2} \times \text{Imaginary part of } \left[ \langle a | \hat{\alpha} | b \rangle \langle a | \hat{\beta} | b \rangle^* \right] \\
&= \text{Im } \langle a | \hat{\alpha} | b \rangle \langle b | \hat{\beta} | a \rangle \\
&= \text{Im} \left\langle a \left| eE \underline{x} + \frac{e}{2mc} \mathcal{H} \underline{L}_y \right| b \right\rangle \left\langle b \left| eE \underline{y} + \frac{e}{2mc} \mathcal{H} \underline{L}_x \right| a \right\rangle \\
&= \text{Im} \left[ \left\{ eE \langle a | \underline{x} | b \rangle + \frac{e\mathcal{H}}{2mc} \langle a | \underline{L}_y | b \rangle \right\} \left\{ eE \langle b | \underline{y} | a \rangle + \frac{e\mathcal{H}}{2mc} \langle b | \underline{L}_x | a \rangle \right\} \right] \\
&= \text{Im} \left[ e^2 E^2 \langle a | \underline{x} | b \rangle \langle b | \underline{y} | a \rangle + \frac{e^2 E \mathcal{H}}{2mc} \langle a | \underline{x} | b \rangle \langle b | \underline{L}_x | a \rangle \right. \\
&\quad \left. + \frac{e^2 \mathcal{H} E}{2mc} \langle a | \underline{L}_y | b \rangle \langle b | \underline{y} | a \rangle + \frac{e^2 \mathcal{H}^2}{4m^2 c^2} \langle a | \underline{L}_y | b \rangle \langle b | \underline{L}_x | a \rangle \right]
\end{aligned}$$

In the above expression  $e^2 E^2 \langle a | \underline{x} | b \rangle \langle b | \underline{y} | a \rangle$  and  $\frac{e^2 \mathcal{H}^2}{4m^2 c^2} \langle a | \underline{L}_y | b \rangle \langle b | \underline{L}_x | a \rangle$  are real so we can omit these. So the above expression becomes

$$\begin{aligned}
&= \text{Im} \frac{e^2 E \mathcal{H}}{2mc} \left[ \langle a | \underline{x} | b \rangle \langle b | \underline{L}_x | a \rangle + \langle a | \underline{L}_y | b \rangle \langle b | \underline{y} | a \rangle \right] \\
&= \text{Im} \left[ \langle a | eE \underline{x} | b \rangle \langle b | \frac{e\mathcal{H}}{2mc} \underline{L}_x | a \rangle + \langle a | \frac{e\mathcal{H}}{2mc} \underline{L}_y | b \rangle \langle b | eE \underline{y} | a \rangle \right] \\
&= \text{Im} \left[ \langle a | eE (\underline{x} + i\underline{y}) | b \rangle \langle b | \frac{e\mathcal{H}}{2mc} (\underline{L}_y + i\underline{L}_x) | a \rangle \right]
\end{aligned}$$

This expression is for oriented set of molecules with light propagating along Z direction. For randomly oriented molecules, we have to take the average over all possible orientations and then the above expression turns to Imaginary part

of  $\langle a|\underline{r}|b\rangle\langle b|\underline{M}|a\rangle$  . Hence the Rotational strength in proper unit is given by

$$R_K = \text{Im} \langle a|\underline{r}|b\rangle \cdot \langle b|\underline{M}|a\rangle .$$

The above derivation seems to be the most straight forward and simplest way of deriving an expression for  $CD^{70}$  .