CHAPTER 2

THEORETICAL CONSIDERATIONS
2-1 PRELIMINARIES

The foundation of the modern theory of paramagnetism rests on the work of Pierre Curie. In 1895, Pierre Curie while measuring the magnetic properties of different substances over a wide range of temperature found that the susceptibility of paramagnetic materials obeys the law $\chi = C/T$, now well known as Curie law, where $C$ is the molar Curie constant, $T$ is the absolute temperature and $\chi$ is the molar susceptibility. The credit of the deduction of this law goes to Langevin. In 1905, Langevin was able to give a quantitative explanation of the law using Maxwell-Boltzmann Statistics considering a gas composed of molecules having permanent magnetic moment due to circulating electrons in an applied magnetic field; he obtained an expression $\chi = \frac{\sigma_0^2}{3RT}$; $\sigma_0 = N A \mu_0$, being the gram molecular magnetic moment, where $N_A$ is the Avogadro number and $\mu_0$, the molecular magnetic moment. Here the Curie constant is $\frac{\sigma_0^2}{3R}$. The inclusion of the temperature independent part $\alpha$ arising from the induced moments responsible for diamagnetism yields the Langevin-Debye relation $\chi = \frac{\sigma_0^2}{3RT} + N_A \alpha$.

Langevin’s classical derivation of the Curie law is open to a serious criticism which was pointed out by Ms Van Leeuwen. Ms Van Leeuwen said that if the permanent magnetic moment is associated with and proportional to the angular momentum of the moving electric charges, then the magnetic moment can not have a fixed magnitude $\mu_0$; also when the Maxwell-Boltzmann statistics is applied rigorously to such a system, the
diamagnetic and paramagnetic contributions to the magnetization annul each other. In fact, Langevin applied classical statistics to the external degrees of freedom only while invoking quantum ideas in requiring the moment of the particles to have a fixed value \( \mu \).

In case of solids, however, when measurements are extended well below the room temperature, considerable deviation from the Curie law is observed. It was felt that the mutual interactions among the magnetic dipoles were responsible for these deviations, and this led to a modification of the Curie law into the form \( \chi = C/ (T-\theta) \) known as Curie-Weiss law, where \( \theta \) is called paramagnetic Curie temperature.

The occurrence of the magnetic moment is due mainly to the electronic orbital and spin moments of an ion or atom. The nuclear magnetic moment arising from the nuclear spin being very small, contributes negligibly towards the magnetic susceptibility but they play a very important role in magnetic resonance studies. Permanent magnetic dipoles occur wherever an atom or an ion contains a partly filled electron shell. Such systems have a resultant angular momentum due partly to the orbital motion and partly to the intrinsic spin of the electrons with each of which is associated a magnetic dipole moment. The requirement of partly filled electron shell restricts the occurrence of paramagnetism in compounds to certain well-defined regions of the periodic table known as the transition groups such as iron group (incomplete 3d shell), rare earth group (incomplete 4f shell) etc.

For most of the rare earth elements except heavy ones the coupling is of Russell Saunders type i.e., spin orbit interaction is small compared to Coulomb interaction. In this approximation a configuration gives rise to different terms each of which is
characterized by a total orbital angular momentum $L$ and a total spin angular momentum $S$.

2-2 FREE ION

The calculation of the energy levels and the wave functions of the triply ionized rare earth ions is usually carried out by considering interactions only among the 4f electrons themselves, since the remaining 54 electrons in xenon like structure are in spherical shells and therefore do not contribute significantly to the relative positions of the 4f energy levels. Here we neglect the small effect which arises from the interaction between the aspherical 4f shell (because it is not closed and can distort the a closed spherical shell) and a closed spherical shell. The Hamiltonian that determines the 4f energy levels can be written as

$$\mathcal{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Z^* e^2}{r_i} + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \zeta(r_i) \hat{l}_i \cdot \vec{s}_i$$

Where $N = 1, 2, 3, \ldots, 14$ is the number of 4f electrons, $Z^* e$, the screened charge of the nucleus, because we have neglected the closed electronic shells; $\zeta(r_i)$ is the spin orbit coupling function.

$$\zeta(r_i) = \left( \frac{\hbar^2}{2m^2 c^2 r_i} \right) \left( \frac{dU(r_i)}{dr_i} \right)$$
This gives rise to stationary states \( |4f^n, L, S, J, J_z\rangle \) of the paramagnetic rare earths where the four quantum numbers in the ket provide the magnetic characteristics of the state.

Quantum mechanical derivation of the Langevin-Debye formula by Van Vleck [1] yields the basic expression for the molar magnetic susceptibility as follows:

\[
\chi = N_A \frac{\sum_{nm} \left[ \frac{W_{nm}^{(1)^2}}{kT} - 2 W_{nm}^{(2)} \right] e^{-\frac{W_{nm}^{(0)}}{kT}}}{\sum_{nm} e^{-\frac{W_{nm}^{(0)}}{kT}}}
\]

where \( W_{nm} \) is the energy associated with the atom or molecule in the stationary state \( |nm\rangle \) and in the applied magnetic field it is given by

\[
w_{nm} = w_{nm}^{(0)} + w_{nm}^{(1)} H + w_{nm}^{(2)} H^2 + \ldots
\]

\( w_{nm}^{(1)}, w_{nm}^{(2)}, \ldots \) etc. are the first, second etc. order corrections to the free ion energy \( w_{nm}^{(0)} \) due to Zeeman interaction and \( N_A \) is the Avogadro number.

In establishing the above expression for \( \chi \) it is assumed that every atom or ion is in the same \( L, S, J \) state. Depending on the strength of the \( L-S \) coupling the above expression for the magnetic susceptibility reduces to the special cases viz., wide multiplet, narrow multiplet, and multiplet separations comparable to \( kT \).
(i)  **Wide Multiplet**

When the L-S coupling is very strong and the energy separation between the ground and first excited J multiplet is very large comparable to kT i.e. $h\nu (J J') >> kT$ then almost all the ions are in their lowest J multiplet. This is the most familiar case among the rare earth ions. The Van Vleck expression for susceptibility then becomes

$$\chi = \frac{\chi_{LV} B^2 J(J+1)}{3kT} + N_a \alpha$$

where $J$ is the total angular momentum quantum number and $\alpha = \alpha_d + \alpha_v$, $\alpha_d$ is the diamagnetic contribution and $\alpha_v$ is the well-known Van Vleck temperature independent term arising from second order contribution from excited J- multiplets.

(ii)  **Narrow Multiplet**

In this case $h\nu (J J') << kT$; the L-S coupling is very weak and in the presence of an external field the L and S are quantized almost separately about the field axis. The paramagnetic part of the susceptibility expression becomes

$$\chi = N_A \frac{\beta^2}{3kT} [L(L+1) + 4S(S+1)]$$

The magnetic properties of the iron group elements fall in this category.
(iii) **Multiplet separation comparable to kT**

In the intermediate case \( h \nu (J^J) \) is comparable to \( kT \) so that upper \( J \) levels are also occupied appreciably by the electrons at ordinary temperatures. Hence their contribution to the susceptibility should also be considered. The distribution of the ions in the upper multiplets can be determined by using the M.B. distribution and the modified expression for \( \chi \) will be

\[
\chi = N_A \sum_J \left[ \frac{g_J^2 \beta J(J+1)}{3kT} + \alpha_J \right] (2J+1) e^{-\frac{W_J^J}{kT}} / \sum_J (2J+1) e^{-\frac{W_J^J}{kT}}
\]

The dependence of \( g_J \) on \( J \) is shown explicitly by the subscript \( J \). In the case of Sm\(^{3+}\) and Eu\(^{3+}\) (where the first excited multiplet situated at 900 cm\(^{-1}\) and 300 cm\(^{-1}\), respectively) in the rare earth series this modified expression is necessary to account for the susceptibility. For the remaining rare earths ions, the wide multiplet case holds in general unless the temperature is too high i.e., as long as \((W_{nj}^0 - W_{nj}^0) >> kT\).

**2-3 CRYSTAL FIELD INTERACTION**

Over the decades interest in paramagnetism has been sustained by the fascinating variety of behavior observed in the transition group salts. This is due mainly to the interaction of the magnetic electrons of the paramagnetic ion with the charges on the
surrounding (usually diamagnetic) ligands, which gives rise to complex splitting of the energy levels of the free ion. In the case of, say, a free rare earth ion, where the environment about the ion is of spherical symmetry, each level is \((2J+1)\) fold degenerate. When the rare earth ion is embedded in a crystal, it behaves quite differently from that in its free state as the spherical symmetry is destroyed due to the crystalline electric field (CEF) i.e., the electric field produced by its surrounding neighbors. The \((2J+1)\) fold degeneracy of the \(J\)-multiplet is partly or fully lifted depending on the site symmetry about the rare earth (RE) ion. Most of the \(\text{RE}^{3+}\) ions (except \(\text{Gd}^{3+}\) ion) in a crystal exhibit considerable magnetic anisotropy; this, and other deviations from the Curie law are well accounted for by the crystalline electric field interaction.

In the crystal field theory we consider the effective field to be static; dynamic interactions with the lattice or among individual ions are not considered explicitly. All RE ions in a crystal are considered to have exactly identical surrounding. The theoretical investigations of Van Vleck [1], Bethe [2], Schlapp and Penney [3], Abragam and Pryce [4], Elliot and Stevens [5], Judd [6] and the extensive experimental work on RE single crystals by the Leiden group [7] and by Krishnan and his coworkers [8] led to the formulation for the understanding of the paramagnetic behavior of the RE ions in solids. In this model the CF parameters obtained from experimental observations are the effective parameters which takes into account not only the field produced by the point charges around the magnetic ions but the aggregate effects of all possible phenomena (effect of the induced moments of both the ligands and other ions, effects of distortion in the closed shell, effects of overlap and covalency etc.) that may occur in the crystalline lattice.
The typical orders of magnitude of different types of interactions experienced by the RE ion in crystals are

i) crystal field interaction $\sim 10^2 \text{ cm}^{-1}$

ii) electronic Zeeman interaction $\sim 10^0 \text{ cm}^{-1}$, H $\sim 1 \text{ KG}$

iii) magnetic hyperfine interaction $\sim 10^{-1} \text{ cm}^{-1}$

iv) nuclear quadrupole interaction $\sim 10^{-2} \text{ cm}^{-1}$ and

v) nuclear Zeeman interaction $\sim 10^{-3} \text{ cm}^{-1}$

In the case of RE ions in crystals, the CF interactions play a dominant role. For most RE ions the CF interaction is weak compared to the spin orbit interaction ($10^3 \text{ cm}^{-1}$) and hence the total angular quantum number $J$ remains a good quantum number. However, when the first excited multiplet is very close to the ground multiplet, $J$-mixing through the CF must be taken into account. This gives rise to the stationary $J$-mixed CF states for the lanthanides which determine the magnetic characteristics of the ion. Also, in rare earths there is considerable mixing of the states with the same $J$-value belonging to different terms, the so-called intermediate (IC) coupling or term mixing, arising from different terms through the spin orbit coupling term $\sum_\sigma \zeta(r_i)\vec{l}_i \cdot \vec{s}_i$. Therefore, it is necessary to include the IC effects for precise determination of the energy level structure and the corresponding wave functions of the RE ions in crystals.

The Hamiltonian $\mathcal{H}$ for an ion placed in a crystal matrix may be expressed as $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{CF}}$ where $\mathcal{H}_0$ is the Hamiltonian of the free ion and $\mathcal{H}_{\text{CF}}$ is the crystal field Hamiltonian. In this model we do not consider the overlap of the ligand wave functions with that of the paramagnetic ion and, therefore, the CF potential obeys Laplace's
equation $\nabla^2 V_c = 0$. The solution of this equation is expressed in terms of the normalised spherical harmonics as

$$V_c = \sum_k \sum_{n=0}^{\infty} \sum_{m=-n}^{n} A_{nm}(r^n) \phi_{4f} Y_{nm}(\theta, \phi)$$

where the summation over $k$ is over all the $4f$ electrons, $A_{nm}$'s are constants and $Y_{nm}$'s can be defined in terms of the associated Legendre polynomials $P_{nm}(\cos \theta_k)$ by the expression

$$Y_{nm}(\theta, \phi) = (-1)^n \left[ \frac{1}{4\pi} \frac{(2n+1)(n-|m|)!}{(n+|m|)!} \right]^{1/2} P_{nm}(\cos \theta_k) e^{im\phi_k}$$

In Racah's tensor operator formalism [9] the CF interaction term $H_{CF}$ can be expressed as

$$H_{CF} = - \sum_i eV(r_i, \theta_i, \phi_i) = \sum_{nm} B_{nm} C_{nm};$$

here $|m| \leq n$ and $B_{nm} = \pm B_{n,-m}$; + sign is for even m and - sign is for odd m.

$C_{nm}$'s are the tensor operators related to spherical harmonics $Y_{nm}$ by the equation

$$C_{nm} = \left( \frac{4\pi}{2n+1} \right)^{1/2} Y_{nm} \quad \text{and} \quad B_{nm}$'s are constants that parametrize the crystal field can be written as

$$B_{nm} = -e \left[ \frac{2n+1}{4\pi} \right]^{1/2} A_{nm}(r^n) \phi_{4f}$$

The following considerations greatly reduced the number of terms in the expression

i) For $4f$ electrons ($l=3$), $n \leq 2l$ and hence the terms up to $n = 6$ need to be considered because it can be shown from group theory that the matrix elements are zero for all potentials for which $n > 2l$. 
ii) Matrix elements of all terms with odd $n$ vanish due to parity considerations since we do not include any configuration interaction.

iii) The term with $n = 0$, in the expansion is a spherically symmetric and simply shifts all the electronic energy levels by a constant factor. Since we are concerned with the relative energies, the constant term may be ignored.

iv) Finally, the number of terms in the above expansion are further restricted by the crystal field symmetry about the RE ion.

For energy level structure of the 4f electrons in the free ion, the mutual coulomb interaction terms ($\mathcal{H}_{\text{col}}$) and the spin orbit interaction ($\mathcal{H}_{\text{so}}$) are mainly responsible. In order to obtain the CF energies and the corresponding wave functions, it is preferable to diagonalize the Hamiltonian $\mathcal{H} = (\mathcal{H}_{\text{col}} + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{CF}})$ for the complete 4f configuration. However, if one is interested primarily in the ground term energies and eigenvectors, for example, to determine the physical properties of the ion, it would be more appropriate to work on a truncated basis of $(2L+1)(2S+1)$ eigenkets, $|4f^n; \alpha, L, S, J, J_z\rangle$, spanning the ground term and diagonalize the Hamiltonian $\mathcal{H} = \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{CF}}$. Here $\mathcal{H}_{\text{so}} = \sum_{\alpha'} \lambda_{\alpha'} (\vec{L} \cdot \vec{S})^{\alpha'}$ is not merely a phenomenological contrivance to produce the baricentres of the J-multiplets but is an effective operator based on some sound scientific foundation which takes into account precisely the effects of spin orbit coupling as would be obtained if one use the complete 4f$^n$ configuration.

The matrix elements of $C_{nm}$ are closely related to the Wigner coefficient through the reduced matrix elements and those can be obtained by using the Wigner-Eckart
theorem; if one is within a pure Russell-Saunders basis, the reduced matrix elements may easily be derived from the available doubly reduced matrix elements \([10]\) using the tensor operator techniques of Racah \([9]\). The general matrix elements of \(C_{nm}\) is given by

\[
\langle 4f''\alpha\alpha'\alpha''\alpha''', J, J', J', J'_z \mid C_{nm} \mid 4f''\alpha\alpha'\alpha''\alpha''', J, J', J', J'_z \rangle = (-1)^{J-J'} (- J_z \pm m \pm J'_z)^n \langle 4f''\alpha\alpha'\alpha''\alpha''', J, J', J', J'_z \rangle
\]

where the last factor, the reduced matrix elements is given by

\[
\delta(SS') (-1)^{S+L'+J'+J}(2J+1)(2J'+1)^{1/2} \langle J, J' \mid L, L \mid n \rangle \langle 4f''\alpha\alpha'\alpha''\alpha''', J, J', J', J'_z \rangle
\]

where the last factor in the expression is doubly reduced matrix elements independent of \(J\), which differs from that of the unit tensor \(U_{nm}\) \([11]\), by the constant factor \(N_n; 3j, 6j\) and other symbols have their usual connotation \([12]\). The advantage of using the representation \(\mid 4f^n; L, S, J, J_z \rangle\) is that an IC state may be represented as \(\sum \eta_a \mid 4f^n; L, S, J, J_z \rangle\) (\(\eta\)'s being the mixing IC coefficients) and its effects may be included in evaluating the CF matrix elements through the introduction of the IC factors computed from \(\eta\)'s, which modify the reduced matrix elements corresponding to the term under consideration, \(\eta\)'s depend mainly on the free ion parameters and on \(\xi\), in particular.

These free ion parameters are responsible mainly for fixing the baricentres of the different \(J\) multiplets and exerts a little influence on the CF splitting by \(H_{CF}\) through the IC factors. Thus for the energies and wave functions within the ground term, diagonalization of the Hamiltonian \(H = H_{so} + H_{CF}\) should be quite adequate with the correct IC factors and appropriate \(\lambda^{\times}\) or centres of gravity (CG) of the \(J\)-multiplets. For Stark levels within the \(J\)-manifolds separately, small errors in the \(\lambda^{\times}\) or CG's of the \(J\)-
multiplets would hardly make any difference. This approach gives excellent results to compute the complete energy level structure of the $^4I$ term for Nd: Laci$_3$. The energies agree exactly with those computed by Crosswhite et al [13] by diagonalizing the full $4f^3$ configuration. It is to be mentioned that the simultaneous diagonalization of $\mathcal{H}_{so} + \mathcal{H}_{cf}$ inherently takes care of the crystal field $J$-mixing; the eigenkets are $J$-mixed eigenfunctions and can be written as $\sum_{J, J_z} a_{\alpha SLJ_z} |\alpha LSJJ_z\rangle$ where $J$ runs over all the $J$-values associated with the ground term.

2-3 ZEEMAN INTERACTION

In an external magnetic field the degeneracy of the CF levels are lifted. In RE ions with an odd number of electrons, every CF stark level must be at least twofold degenerate (Kramers degeneracy); there is no such restriction on the ions with even number of electrons. When the crystal is placed in a magnetic field the remaining degeneracies of the crystal field stark levels are removed. In the first order theory the Zeeman interaction (i.e., the interaction between $N$ electrons and the external magnetic field $H$) term in the Hamiltonian can be written as $\mathcal{H} = \beta \sum (L + 2S) \cdot H = \beta (L + 2S) \cdot H$ and hence the total Hamiltonian is given by $\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{so} + \mathcal{H}_{cf} + \beta (L + 2S) \cdot H$, where $\beta$ is the Bohr magneton. The Zeeman interaction term reduces to $\beta g_J^J \cdot J \cdot H$ for a $J$ manifold when the $\mathcal{H}_{so}$ term is strong (as in
the case of rare earths). $g_L'$ is effective Lande splitting factor which differs appreciably from that of the pure L-S case when admixture of the ground state with the higher Russell-Saunders state is appreciable.

In Russell-Saunders coupling, the matrix elements according to Wigner-Eckart theorem can be written as

$$\langle \alpha \Lambda S J_z \mid L + 2S \mid \alpha \Lambda S J_z' \rangle = (-1)^{J-J'} \begin{pmatrix} J & 1 & J' \\ -J_z & 0 & J_z' \end{pmatrix} \langle \alpha \Lambda S J \mid L + 2S \mid \alpha \Lambda S J' \rangle$$

which involves 3j and 6j symbols \[ [6] \]. For the diagonal elements we have

$$\langle \alpha \Lambda S J_z \mid L + 2S \mid \alpha \Lambda S J_z \rangle = \langle J \mid \Lambda \mid J \rangle \langle \alpha \Lambda S J_z \mid J \rangle \langle \alpha \Lambda S J_z \rangle$$

where

$$\langle J \mid \Lambda \mid J \rangle = g_L' = 1 + \left[ \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right]$$

The matrix element for the off diagonal elements of $(L+2S)$ between the states of different $J$ occurs only for $J$ values differing in $\pm 1$ and are given by

$$\langle J + 1, J_z \mid L_z + 2S_z \mid J, J_z \rangle = \langle J + 1 \mid \Lambda \mid J \rangle \left[ (J+1)^2 - J_z^2 \right]^{1/2}$$

for the parallel Zeeman effect and

$$\langle J + 1, J_z \pm 1 \mid L_z + 2S_z \mid J, J_z \rangle = \mp \langle J + 1 \mid \Lambda \mid J \rangle \left[ \frac{(J+J_z+1)(J+J_z+2)}{2} \right]^{1/2}$$

for the perpendicular Zeeman effect, where

$$\langle J + 1 \mid \Lambda \mid J \rangle = \left[ \frac{(J+L+S+2)(-J+S+L)(J+S-L+1)(J+L-S+1)}{4(J+1)^2(2J+1)(2J+3)} \right]^{1/2}$$
The \( \Lambda \) - factors between the same \( J \)-levels and those between the different \( J \)-levels are computed and the Zeeman energies for the magnetic field parallel and perpendicular to the symmetry axis (for uniaxial systems) are obtained from the above expressions.

The perturbation produced by the external magnetic field on the ion is very small compared to that produced by the crystal field. Therefore we can safely diagonalize the crystal field Hamiltonian and treat the effect of magnetic field as a perturbation. The first order Zeeman energies for the two cases viz., \( H \parallel Z \) and \( H \perp Z \) (where \( Z \) is the symmetry axis of the paramagnetic cluster) are obtained by diagonalization of the Zeeman matrix in the degenerate manifold of Stark states for each Stark level. The resulting eigenfunctions are used for computing the second order energies. The perturbation theory for the degenerate system should be used when the degeneracies are not lifted by the first order calculations. Although, the latter is of purely theoretical interest as far as the calculation of magnetic susceptibilities are concerned using Van Vleck formula (the Boltzmann factors for the magnetically split levels are the same in the Van Vleck's susceptibility expression) since the trace remains invariant under a similarity transformation.

2-5 ELECTRONIC HEAT CAPACITY

The effect of the CF on the electronic heat capacity \( (C_e) \) of the RE crystal is profound. This is reflected in the characteristic thermal variation of \( C_e \) in the form of Schottky
anomalies given rise to by the low lying CF Stark levels. The usual relation is

$$C_s = \frac{d}{dT} \langle E \rangle_T$$

where \( \langle E \rangle_T = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \) is the thermal average of the Stark energies.

\( C_s \) is computed using the expression

$$C_s = N_A \frac{d}{dT} \left[ \frac{\text{Tr}(H\rho)}{\text{Tr}\rho} \right]$$

where \( H \) is the Hamiltonian matrix, \( \rho \) is the statistical density matrix and \( N_A \), the Avogadro’s number. When \( H \) is in the diagonal form

$$C_s = \frac{N_A k}{Z^2} \left[ Z \sum_i \left( \frac{E_i}{kT} \right) e^{-E_i/kT} - \left\{ \sum_i \left( \frac{E_i}{kT} \right) e^{-E_i/kT} \right\}^2 \right]$$

\( Z \) being the partition function, \( E_i \)'s being the Stark energies obtained by diagonalizing the total Hamiltonian matrix. Normally for most of the ions (except Eu and Sm) it is sufficient to consider the energy levels of the ground multiplet only for calculation of \( C_s \) upto room temperature. Here the nuclear contribution arising out of nuclear hyperfine coupling, which would be of any consequence only at very low temperatures, has been neglected.

2-6 NUCLEAR ELECTRIC QUADRUPOLE INTERACTION

Nuclei with spin \( I \geq 1 \) may possess, in addition to the nuclear magnetic moment, an electric quadrupole moment. Now the nuclear level splitting is caused by the hyperfine
magnetic field and an electric field gradient (EFG) produced by the CF at the nuclear site. The magnetic field and the EFG depend on the population of the electronic states and the electronic relaxation times. In the absence of any magnetic field the hyperfine splitting is due to the interaction of the nuclear quadrupole moment with the EFG produced by the 4f electrons and the ligand charges. Considering the nucleus to be of finite dimension the electrostatic interaction energy between the nucleus and an electron is given by

\[ \mathcal{H}_Q = -e^2 \iint \frac{\rho_e(r_e) \rho_n(r_n) dr_e dr_n}{|r_n - r_e|} \]

where \( \rho_e(r_e) \) and \( \rho_n(r_n) \) are the electron and nuclear charge densities, \( r_e \) and \( r_n \) are measured relative to the center of the nucleus.

This expression can be expanded in terms of spherical harmonics,

\[ \mathcal{H}_Q = \sum_{l,m} A_{lm} B_{lm}^* \]

where \( A_{lm} \) is related to the nuclear properties and \( B_{lm}^* \) is the complex conjugate of \( B_{lm} \), which is related to the electronic properties. Invariance under parity operation excludes terms with odd \( l \), and the series converges rapidly because successive terms with even values of \( l \) decrease as \( (r_n/r_e)^2 \). The first term \((l=0)\) is just the coulomb interaction between the electron and a point charge \( Ze \) and results in shifts in energy revealed by isotope and chemical shift etc. The terms with \( l = 2 \) arise from the interaction of nuclear quadrupole moment with the electric field gradient (EFG) tensor and this splits the nuclear energy levels. In the case of rare earth ions in crystals the EFG consists of two parts viz., the EFG produced by the crystalline electric field, \( q_c \), and due to the aspherical 4f electrons \( q_v \). The EFG actually seen by a nucleus is the sum of the \( q_c \) and \( q_v \) and EFG's associated
with distortion induced in the closed electrons shells produced by the perturbing electrostatic fields. This distortion is also of two kinds.

a) The distortion of the closed electron shell in the Xenon structure by the CF which is proportional to \( q_C \) and the proportionality constant, \( \gamma_\infty \) called the lattice sternheimer factor.

b) Due to the induced quadrupole moment in the closed electron shells resulting from the interaction of the spherical shell with the partially filled 4f shells and is proportional to \( q_V \) with the proportionality constant \( R_q \) called the atomic sternheimer factor.

Therefore the total EFG can be written as 
\[ q = q_C (1-\gamma_\infty) + q_V (1-R_q) \]

When the electronic relaxation is fast compared to the nuclear precession times the nucleus sees a time-averaged EFG. Thus the quadrupole splitting \( \langle \Delta E_Q \rangle_T \) between any two adjacent nuclear states \( |I, I_z\rangle \text{ and } |I, I_z+1\rangle \) due to the 4f contribution to the EFG would be highly temperature dependent, whereas that due to lattice is more or less constant. The quadrupole splitting between any two adjacent nuclear states \( |I, I_z\rangle \text{ and } |I, I_z+1\rangle \) is expressed as 

\[
\left( \langle \Delta E_Q \rangle_T \right) = \left( 2I_z + 1 \right) [PN \cdot \langle PJZ \rangle_T + P_{\text{LAT}} \cdot \left( \frac{B_{20}}{2} \right)]
\]

\[
PN = -\frac{3e^2Q(1-R_Q)(r^{-3})_{4f}}{4I(2I-1)}, \quad \langle PJZ \rangle_T = \left( \frac{\sum (3z_i^2 - r_i^2)}{r_i^2} \right)_T
\]

\[
P_{\text{LAT}} = -\frac{3Q(1-\gamma_\infty)}{I(2I-1)(r^{-3})_{4f}(1-\sigma_z)}
\]
Here, $\sigma_2$ is the shielding factor, $Q$, the quadrupole moment, $B_{20}$, the CF parameter in the tensor operator formalism, and other symbols have their usual connotation. The first term within the square bracket is the 4f contribution and the second term is the lattice contribution towards the splitting. The 4f contribution is temperature dependent as the electron population varies with temperature among the different Stark states and the lattice contribution is more or less temperature independent which arises due to the interaction of the nuclear quadrupole moment with the lattice part of the EFG. We thus compute the variable part in the temperature dependent component in order to obtain the thermal variation of $\langle \Delta E_Q \rangle_T$. In many cases they are of opposite sign so that the nuclear level scheme may get inverted with the variation of temperature. An experimental study of the variation of the nuclear electric quadrupole splitting with temperature carries a strong signature of the CF energies and wave functions.

### 2-7 MAGNETIC HYPERFINE INTERACTION

The magnetic hyperfine interaction arises from the interaction of the magnetic field at the nucleus generated by the magnetic moment of the electron cloud and the nuclear magnetic moment. The hyperfine interaction Hamiltonian can be written as $\mathcal{H}_{\text{hf}} = -\mu_N \cdot H_e$ where $\mu_N$ is the nuclear magnetic moment and $H_e$ is the effective hyperfine magnetic field at the nucleus which is expressed as $H_e = -2\beta \langle r^3 \rangle_{4f} \langle N_z \rangle$; where $N_z$ is the component of the hyperfine vector operator [19]
\[ N = \sum_i \left[ \vec{I}_i - \vec{s}_i + \frac{3r_i^2(r_i \cdot \vec{s}_i)}{r^3} \right] \] which behaves very much like \((\vec{L} + 2\vec{S})\). Since we are considering \(J\)-mixed CF states the expectation value \(\langle N_z \rangle\) would involve the evaluation of the off diagonal elements in \(J\). In the presence of a magnetic field at very low temperatures, when only the lowest electronic Zeeman state is occupied, it would be sufficient to find the expectation value in this state. The effective hyperfine magnetic field \(H_e\) can also be written as \([15]\) \(H_e = A/\beta_{N\|N}\), where \(A = 2\beta \beta_{N\|N}\langle r^3 \rangle_{4f} \langle J\|N\|J \rangle\) and is called hyperfine structure constant, and \(\beta_{N\|N} = \mu_N/\chi\); other symbols have their usual connotations \([15]\).

If the quadrupole interaction is also taken into account then the total hyperfine Hamiltonian becomes

\[ \mathcal{H}_{4f} = a_{\|} S_z I_z + \frac{A_\perp}{2} (S_z I_z + S_y I_y) + P \left[ J_z^2 - \frac{1}{3} I(I+1) \right] \]

where \(a_{\|} = 4\beta \beta_{N\|N}\langle r^3 \rangle_{4f} \langle J_z \| N_z \| - \rangle\) and \(A_\perp = 2\beta \beta_{N\|N}\langle r^3 \rangle_{4f} \langle J_z \| N_z \| - \rangle\) are the parallel and perpendicular components of \(A\). \(+\) and \(-\) are the two degenerate states of the ground doublet and \(S\), the effective spin vector. The quadrupole interaction parameter \(P\) is expressed as

\[ P = -\frac{9e^2Q}{4I(2I-1)} \left[ 1 - R_q \right] \langle r^{-3} \rangle_{4f} \left( \sum_i \frac{3z_i^2 - r_i^2}{r_i^3} \right) + \frac{2(1 - \gamma_m) B_{2e}}{3e^2 \langle r^2 \rangle_{4f} (1 - \sigma_2)} \]

The Hamiltonian for an axial symmetry in the presence of a magnetic field along the symmetry axis may be written as \(\mathcal{H}_n = a_{\|} I_z + P \left[ I_z^2 - \frac{1}{3} I(I+1) \right] \) where \(a_{\|} = A_{\|}/2\).
The expression for $H_{nf}$ is valid only for point nucleus and necessary correction is to be made for appreciable nuclear volume and for non-vanishing electron density at the nucleus. The correction is shown to be negligible [12] for triply ionized RE ions.

The electron nucleus interaction is stronger by an order of magnitude than the nuclear Zeeman effects in an external magnetic field of moderate strength (10KG) and hence the influence of the latter on the hyperfine energy may be ignored in the weak field approximation. At very low temperatures, only the lowest electronic Zeeman level which would be occupied contributes the magnetic field at the nucleus; at higher temperatures contributions from all the Zeeman levels of the ground and excited Stark states are to be considered. Thus in the presence of a magnetic field the variation of the hyperfine magnetic field with temperature at the nucleus would be similar to that of the magnetic susceptibility. This corresponds to a well defined variation of the NMR spectrum amenable to experimental study.

To determine the nuclear energy level the Hamiltonian $H_{nf}$ is diagonalized in the $|S I S_z I_z\rangle$ space. The expression for pairs of hyperfine energies for the spin $\frac{1}{2}$ system is given by [16]

$$E = \frac{1}{2} \left[ \frac{-A_{zz}}{2} + P \left( 2I_z^2 - 2I_z + 1 - \frac{2I(I + 1)}{3} \right) \right]$$

$$= \pm \left( A_{zz}^2 (I_z^2 - I_z^2 + \frac{1}{4}) + A_{zz}^2 (I^2 - I_z^2 + I + I_z) + P^2 (2I_z - 1)^2 - A_{zz}^2 P (2I_z - 1)^2 \right)^{\frac{1}{2}}$$

where $I_z$ takes on values I to -(I-1). The remaining two energies are identical and are given by

$$\frac{1}{2} A_{zz} I_z + P \left[ I(2I - 1) \right]$$.
The magnetic hyperfine interaction lifts the degeneracy of the nuclear energy level and splits it into \((2I+1)\) equally spaced levels each separated by \(A(J_z)\). However, in the presence of nuclear quadrupole interaction, the levels are further changed. This hyperfine splitting causes a redistribution of the spin orientations and Schottky type anomalies appear in the nuclear heat capacity \((C_N)\), usually, below 1K. The hyperfine heat capacity at different temperatures is computed using the relation similar to that of the electronic heat capacity and is given by

\[
C_N = \frac{R}{Z^2} \left[ \sum_i E_i^2 e^{-E_i/kT} \right] - \left[ \sum_i \frac{E_i e^{-E_i/kT}}{kT} \right]^2
\]

where \( Z = \sum_i e^{-E_i/kT} \), and \(E_i\)'s are the hyperfine energies. For the RE ions, above 1K the expression for \(C_N\) may be approximated as [17]

\[
C_N = \left( \frac{R}{kT} \right)^2 \frac{I(I+1)(A_i^2 + 2A_i^2)}{12} + \frac{P^2}{45} \left\{ I(I+1)(2I+3)(2I-1) \right\}
\]

since \(E_i \sim 0.1 \text{ cm}^{-1}\) or less and the terms of orders higher than \((1/T)^2\) are neglected. However, for precise calculations the exact expression should be used.
REFERENCES


[10] Racah G., Phys. Rev. 61, 186 (1942); 62, 438 (1942); 63, 367 (1942).


