Chapter 1
INTRODUCTION

Electron Paramagnetic Resonance (EPR), Electron Spin Resonance (ESR) and Electron Magnetic Resonance (EMR) are synonymous terms, which describe the resonance absorption of microwave radiation by paramagnetic ions or the molecules having net spin (i.e., unpaired electron) and orbital angular momentum in a static magnetic field. Until the mid of 1950s, EPR has been the preserve of physicists, since its discovery by a Russian physicist Zavoisky [1], but routine applications to a variety of problems in chemistry and biology gradually become established. EPR is unusual in that the spectrum is normally obtained by sweeping the external magnetic field rather than the frequency, and is most usually carried out at a fixed microwave frequency in the range 9-10 GHz (X-band). EPR spectra are routinely obtained for paramagnetic transition ions in crystals, chemical complexes and bio-molecules. Samples may be in the form of crystal, powder, solution or frozen solution. Most commonly, these systems should have electron spin (S) and S can be any value from 1/2 to 7/2 in increments of 1/2. When the spin is odd, i.e., for example, S = 1/2, 3/2, 5/2 or 7/2, spectra are easily obtained at room temperature. However if the spin is even, i.e., for example, S = 1, 2 or 3, then the possibility of obtaining spectra depend upon a number of circumstances that are usually not met, thus the EPR of even spin systems is a very specialized one. EPR spectroscopy is capable of providing molecular structural details inaccessible by other analytical tools. EPR has been successfully applied in such diverse disciplines as biology, physics, geology, chemistry, medical science, material science, anthropology, to name a few. By utilizing a variety of specialized techniques, such as spin trapping, spin labeling, ESEEM and ENDOR, in conjunction with EPR,
Researchers are capable of obtaining detailed information about many topics of scientific interest. For example, chemical kinetics, electron exchange, electrochemical processes, crystalline structure, fundamental quantum theory, catalysis and polymerization reactions have all been studied with great success. Some of the paramagnetic transition metal ions that can be studied by EPR spectroscopy are given in the Table 11. Out of these metal ions, V, Fe, Mn, Co, Cu, Mo, and Ni are biologically important elements also.

The detection of EPR signals from metal ions in proteins can provide the following information:

a) Identification of the presence of a metal ion: Confirmation that the EPR signal belongs to a particular metal ion can sometimes be done by measurement of nuclear hyperfine signals (see below)

b) Following the changes in the oxidation state of the metal ion.

c) Identification of the surrounding ligands around the metal ion

d) Quantifying the concentration of paramagnetic centres

One of the major advantages of this spectroscopy is that a small percentage of paramagnetic impurity present in a bulk host can be studied in detail. The application and theory of this spectroscopy is discussed in detail in a number of books [2-8]. Nowadays, EPR has become an important tool in imaging [9-18], in estimating the ages of fossils [19] etc.

Electrons in molecular systems, by virtue of their spin and orbital motion, have spin magnetic moment \( \mu_s \) and orbital magnetic moment \( \mu_l \), given by

\[ \mu_s = -(2.0023 \frac{|e|}{4\pi m_e}) S \]
Table 1.1  Some of the paramagnetic transition metal ions that can be observable by EPR spectroscopy.

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<tr>
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<th>No of d-electrons</th>
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<tr>
<td>2nd</td>
<td>Mo(V)</td>
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<td>series</td>
<td>Nb(IV)</td>
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<td>3rd</td>
<td>La(II)</td>
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<td>series</td>
<td>Re(VI)</td>
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\[ \mu_i = - \left( \frac{|e|h}{4\pi m_e} \right) L \]  

where \( S \) and \( L \) are the spin and orbital angular momenta in units of \( h/2\pi \), \(|e|\) is the magnitude of the electronic charge and \( m_e \) is the mass of the electron. The factor 2.0023, known as the free-electron gyromagnetic ratio, arises out of the 'anomalous' Zeeman effect and can be derived from Dirac's relativistic wave mechanics and includes a correction of +0.0023 due to relativistic mass variation [20,21]. The total effective magnetic moment \( \mu \), which is the vector sum of the spin magnetic moment and orbital magnetic moment, therefore, can be expressed as

\[ \mu = \mu_s + \mu_i = -\beta_e \left( 2.0023 S + L \right) \]  

where \( \beta_e = |e|h/4\pi m_e \), is known as the Bohr magneton. For a free electron (rarely found in practical systems, except in cases such as conduction electrons or the system with ground state symbol \( S \)), the orbital contribution becomes zero. Hence, the interaction energy, in an applied magnetic field \( B \) is given by

\[ E = -2\beta B.S \]  

For free electron systems, the spin momenta are quantized along the applied field axis with \( z \) components \( S_z = |\pm 1/2> \). In other words, the time independent components of the precessing spin vectors lie either parallel or anti-parallel to the direction of the applied d.c. field \( B \). Thus only two energy states are possible for a free electron at \( \pm \beta B S_z \) about the unperturbed energy level, as shown in Figure 11. Transitions between these levels are possible when the system is subjected to an oscillating electromagnetic field. It can be easily shown that the net paramagnetic moment (present as a result of Boltzmann distribution) precesses about the external field axis with an angular velocity \( \omega \) given by \( \omega = -|e|B/2m_e \), termed as the Larmor
Figure 11  Schematic representation of the resonance condition in the frequency mode.
precession frequency. A small rotating magnetic field $B_1$ rotating in the same sense as the net magnetization vector causes exchange of energy between itself and the system of spins causing transitions to occur between the Zeeman states. i.e., at resonance $\omega_{B1} = - |e| B_1/2m_e$. Experimentally, microwave field replaces the rotating field $B_1$. The alternating field can be shown to be equivalent to the rotating field as far as EPR and NMR are concerned. The condition that the oscillating field should be applied perpendicular to the static external field has been obtained using quantum mechanics which also explains the selection rules for magnetic dipole transitions. According to the outcome of the time-dependent perturbation theory [22], the time-independent transition probability is proportional to the square of the absolute value of the transition moment ($P$). Hence, $P$ is given by

$$P = \langle \psi_j | V | \psi_i \rangle^2$$

where $\langle \psi_j |$ and $| \psi_i \rangle$ are the initial and final state vectors and $V$ is the time-independent part of the perturbation that connects these states. In EPR, $\psi_i$ and $\psi_j$ correspond to $M_s$ values and if $B_{1x} = 2B_1 \cos \omega t$ and $V = \beta B_1 S$, then

$$P = \langle \psi_j | V | \psi_i \rangle^2 = <\frac{1}{2}| \beta B_1 S + \frac{1}{2}>^2$$

$$= \beta^2 [<\frac{1}{2}| B_x S_x + \frac{1}{2}] + <\frac{1}{2}| B_y S_y + \frac{1}{2}]$$

The first term in square brackets is zero. Hence, $B_1$ parallel to the axis of quantization will be ineffective. Also when $B_1$ is perpendicular to the axis of quantization, the operators $S_x$ and $S_y$ lead to $\psi_j = \psi_i \pm 1$ and hence the selection rule $\Delta M_s = \pm 1$. However, in triplet spin ground states, the transitions can occur at low fields with $B_1$ parallel to the axis of quantization. On the other hand, unpaired electrons in transition metal complexes do possess orbital angular momentum. The spin momentum and the
orbital angular momentum vectors couple to give a resultant angular momentum, \( J \), with \((2J+1)\) degeneracy. The \( J \) values range from \( |L+S| \) to \( |L-S| \). The energy levels in a magnetic field \( B \) are given by

\[
E = g\beta B M_j
\]

The corresponding \( g \)-factors, known as the Lande \( g \)-factors are given by

\[
g = 1 + \frac{J(J+1) - L(L-1) + S(S+1)}{2J(J+1)}
\]

with \( J = |L-S| \) for less than half-filled d-shell and \( J = |L+S| \) for more than half-filled shell.

The effectiveness of the coupling of the spin and orbital motion, however, depends on the exact nature of the environment of the paramagnetic ion. Surrounding ionic charges, bonded ligands etc produce a strong electrostatic field and the spin-orbit coupling will breakdown due to the ‘quenching’ of the orbital angular momentum. Thus EPR systems can be divided into three main categories i.e., weak-field, intermediate field and strong field cases (discussed below).

EPR is sensitive to the changes in symmetry of the environment. Apart from this, a number of interactions modify and split the energy levels of the unpaired electron. The former causes a shift in the center of gravity of the spectrum, whereas the latter influences the fine structure. In favorable circumstances, a detailed analysis of the EPR spectrum leads to a very accurate determination of bonding parameters and the electronic structure of the ground state, not easily possible in many other types of spectroscopy. A general consideration of the interaction involved in the case of a paramagnetic species (with particular emphasis on transition metal ions) in a crystal.
field is formulated in terms of generalized Hamiltonian. A consequence of this, involving only spin-operators, is the spin-Hamiltonian (which is an artificial, though practical) concept is described subsequently.

The spin Hamiltonian consists of various terms, which have been arisen due to different types of interactions between electron spin with either the applied magnetic field or nuclear spin or another electron spin and the nuclear spin either with the applied magnetic field or another nuclear spin. The origin and importance of these interactions are mentioned below.

**Zeeman Interaction:** \( \mathcal{H}_{\text{Zee}} \)

This arises due to the interaction of the external magnetic field with the spin and orbital magnetic moment of the electrons and nuclear spin magnetic moment and is given by

\[
\mathcal{H}_{\text{Zee}} = \beta (L + 2S) B - g_a \beta_n B \sum_l l_i
\]

where \( \beta_n \) is the nuclear magneton, \( g_a \) is nuclear g value and \( l_i \) are the various magnetic nuclear spins. The first term is known as the electron Zeeman interaction. The second term, which is the nuclear Zeeman interaction, is of minor importance in EPR, except in cases where the hyperfine coupling is much smaller than the nuclear Zeeman Interaction.
Spin-Orbit Interaction: $\mathcal{H}_{LS}$

This represents the coupling between the magnetic moment arising from the spin and orbital motion of the unpaired electrons and can be written as

$$\mathcal{H}_{LS} = \sum_{a,k} a_{j,k} l_j S_k$$  \hspace{1cm} \text{----[1.9]}

If we neglect the electron spin and 'other-orbit' interaction, then the above term can be given in terms of the one-electron spin-orbit coupling constants $\xi_{ii}$.

$$\mathcal{H}_{LS} = \sum_{i} \xi_i l_i S_i$$  \hspace{1cm} \text{----[1.10]}

Within the Russell-Saunders scheme, the interaction reduces to

$$\mathcal{H}_{LS} = \lambda L S$$  \hspace{1cm} \text{----[1.11]}

where $\lambda$ is the spin-orbit coupling constant of the ion and is a function of the effective nuclear charge. For more than half-filled shells, $\lambda$ is negative and for less than half-filled shells, it is positive. In the spin-Hamiltonian formalism, the effect of spin-orbit coupling is assimilated into 'the fictitious' spin concept (vide infra).

Spin-Spin Interaction: $\mathcal{H}_{SS}$

When more than one unpaired electrons are involved in the systems with ground state triplet or higher spin multiplicity, direct dipole-dipole interactions among these spins lead to the splitting of the spin-states via the spin-spin interaction given by

$$\mathcal{H}_{SS} = (g\beta)^2 \sum_{j<k} S_j S_k - 3 \frac{3(r_{jk}S_j)(r_{jk}S_k)}{r_{jk}^3}$$  \hspace{1cm} \text{----[1.12]}

When the external magnetic field is much stronger than the magnitude of spin-spin coupling constant, the above vector dot products can be expanded to give
\[ H_{SS} = (g\beta)^2 (3\cos^2\theta - 1) \frac{S_j S_k}{r_{jk}} \]  

Here \( \theta \) is the angle between the external field and the vector joining \( S_j \) and \( S_k \).

**Hyperfine Interaction:** \( H_{S1} \)

This is a zero-field type interaction connecting the electron magnetic moment and the associated nuclear magnetic moment. This consists of a pure dipole-dipole type interaction described by a tensor due to unpaired p, d, f type spin-densities and an isotropic Fermi contact term for s-type spin-densities. The interaction is written as:

\[ H_{S1} = g\beta g_{\alpha} \beta_n \left[ \sum_{\mu} S_{j\mu} I_{\mu} - \frac{3}{3} \sum_{\mu} \delta(r_{ij}) I_{\mu} S_{j\mu} \right] + \frac{8\pi}{3} \sum_{\mu} \delta(r_{ij}) I_{\mu} \]  

The first term describes an interaction of two point-dipoles and the second containing the Dirac delta function, which when integrated with the wave function vanishes except at \( r_{ij} = 0 \), corresponds to the isotropic interaction. Thus, in the non-relativistic approximation, only s-orbitals can contribute to isotropic coupling to the concerned nuclei.

In a more rigorous treatment, interactions between the orbital magnetic moment and the nuclear spin moment also have to be taken into account. Again, this can be effectively taken into account in the spin Hamiltonian formalism.

**Nuclear Quadrupole Interaction:** \( H_Q \)

This interaction is relevant only to systems having nuclei with spin \( l \geq 1 \) and arises as a result of the interaction of the nuclear electric quadrupole moment with the electric field gradient at the nucleus due to the surrounding electrons. It is expressed as
\[ H_Q = \sum_{n} \left[ e^2 Q / 2 I, (2I, -1)] \left[ r^2 v, I, (I, +1) - 3(r, I, I) \right] r^2 \right. \]  

where \( Q \) is the nuclear electric quadrupole moment.

**Spin Hamiltonian:**

Most EPR data can be described in terms of "Spin-Hamiltonian" involving smaller number of terms by use of an effective fictitious spin without a detailed knowledge of spin-orbit coupling, the magnitude of crystal field splitting, etc.

In Dyad operator notation, the Spin-Hamiltonian can be expressed as

\[ H_S = \beta_e B \cdot g \cdot S + I \cdot A \cdot S + S \cdot D \cdot S + I \cdot Q \cdot I + . \]

where \( g, A, D \) and \( Q \) are second rank tensors, whose principal axes need not coincide. These correspond to the electron g-tensor, hyperfine tensor, zero-field tensor and quadrupole coupling constant tensor respectively.

The concept of fictitious spin will be discussed in a more detailed way. It is known that a quantum state described by \( J \) splits it into \((2J+1)\) levels in an external field. Similarly, a system designated with the fictitious spin \( S' \) splits into \((2S'+1)\) levels and transitions are allowed between these according to the selection rules. The only difference between the true spin \( S \) and fictitious spin \( S' \) is that the latter defines the effective spin-angular momentum endowed due to any orbital contribution. In view of the fact that the spin-only g-factor would deviate from the free spin value, due to admixture of higher lying states into the ground state via spin-orbit coupling and hence effectively takes into account of the effect of crystal field terms and spin-orbit term of the generalized Hamiltonian. Since the isotropic g-factor of a free electron is modified
into a tensor when orbital momentum is not completely quenched in the principal axis system of the g-tensor, the Hamiltonian is written as

$$\mathcal{H} = \beta (B_\alpha g_{\alpha\alpha} S_x + B_{\gamma\gamma} g_{\gamma\gamma} S_y + B_{\alpha\alpha} g_{\beta\beta} S_z)$$  \[1.17\]

If the tensor is spherically symmetric, $g_{\alpha\alpha} = g_{\gamma\gamma} = g_{\beta\beta} = g$ and $B_\alpha = B_\gamma = B_\beta = B$, then

$$\mathcal{H} = \beta [B g S]$$  \[1.18\]

And if the tensor is axially symmetric,

$$\mathcal{H} = \beta [B_\alpha g_{\alpha\alpha} S_z + g_{\beta\beta} (B_\beta S_x + B_\gamma S_y)]$$  \[1.19\]

Likewise, the hyperfine terms, which consist of a dipolar part and isotropic part, are generally written as:

$$\mathcal{H} = A_{\alpha\alpha} I_x S_x + A_{\gamma\gamma} I_y S_y + A_{\beta\beta} I_z S_z$$  \[1.20\]

If the unpaired electron is purely s-type, then

$$\mathcal{H} = a I_z S_z$$ and $a = (8\pi/3) g \beta g_0 \beta_n |\psi(0)|^2$  \[1.21\]

where $|\psi(0)|^2$ is the squared amplitude of the unpaired s-electron density at the nucleus. Isotropic hyperfine interaction arises due to (a) direct unpaired spin-density in an s-orbital or in a molecular orbital (MO) with s-orbital contribution, (b) spin-polarization, due to isotropic hyperfine coupling in an isolated paramagnetic atom or ion, where the electron is in a p or d orbital arises via polarization of core-s-electrons, (c) also configuration interaction between a ground state MO orbital with no s-orbital contribution and states with finite s-orbital contribution.

Dipolar coupling arises out of point dipole interaction between p or d orbital with the nucleus and follows a $(3 \cos^2 \theta - 1)$ variation given by
\[ \mathcal{H}_d = g \beta g_u (3 \cos^2 \theta - 1) \left(1/r^3\right) \]  

In \( p^3 \) or \( d^3 \) high spin configuration, due to spherical charge distribution, dipolar-coupling vanishes. Also in paramagnetic systems in solutions, where the molecule tumbles rapidly, it averages to zero, being represented by a traceless tensor.

The signs of the experimental principal values of the hyperfine tensor cannot be inferred from EPR spectra. However, a sensible choice (often made easier, if the isotropic coupling can be independently determined) can always be made with the ratio of unpaired \( p \) and \( s \) densities in simple free–radicals depends on the hybridization and hence leads to an estimation of bond angles [6]. Often hyperfine coupling to ligand-magnetic nuclei in transition metal complexes, when the unpaired electron ‘formally’ occupies a metal nd orbital can lead to an estimate of the covalence of the metal ligand bonds.

In systems with more than one unpaired electron, the spin-degeneracy is removed even in the absence of external magnetic field by a second spin-orbital coupling known as the zero-field interaction. This is also a dipolar type interaction and is expressed in the spin Hamiltonian as

\[ \mathcal{H}_{ss} = D[S_z^2 - 1/3 S(S+1)] + E(S_x^2 - S_y^2) \]

\[ = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2 \]  

The \( D \)'s are the principal values of the \( D \)-tensor and \( E \) is an asymmetry parameter, depending on the deviation of the \( D \)-tensor from axial symmetry. The relative magnitudes of \( D \) and \( g \beta B \) are to be noted in any perturbation treatment of the spin-Hamiltonian.
The quadrupolar term in the spin-Hamiltonian is quite analogous to the zero-field term and is given by

$$\mathcal{H}_Q = Q_{xx}I_x^2 + Q_{yy}I_y^2 + Q_{zz}I_z^2$$

$$= Q'[I_x^2 - 1/3 I(I+1)] + Q''[I_x^2 - I_y^2]$$

where $Q_n$'s are the principal values of the quadrupole coupling constant tensor. Here, $Q'$ is similar to $D$ and $Q''$ to $E$. The effect of quadrupolar interaction in EPR is twofold. Firstly, since there will be a competition between the electric field gradient at the nucleus and the hyperfine field to quantize the nuclear spin-angular momentum about their respective axes, the $|m_I>$'s are no longer good quantum numbers: hence the selection rule $\Delta M_S = \pm 1, \Delta m_I = 0$, breaks down and 'forbidden' transitions with $\Delta m_I = \pm 1, \pm 2$ become allowed. Secondly, quadrupolar effects cause the intensities of normal transitions and hyperfine spacing to become unequal, the latter showing progressive increase or decrease from the ends towards the center. In single crystals, especially when the external field is perpendicular to the symmetry axis, the analysis becomes difficult due to the presence, sometimes, of intense forbidden transitions [23].

An appropriate choice of the spin Hamiltonian based on the symmetry of the paramagnetic species often leads to a correct solution of the spin Hamiltonian parameters such as $g$, $A$, $D$, $Q$ etc. The parameters are also derived theoretically from the knowledge of the ground state molecular orbital and optical spectroscopic data with the use of perturbation theory. The methodology of obtaining M.O. coefficients from the observed magnetic resonance parameters has been described in detail in the literature [24, 25]. It is possible, in favorable cases, therefore to obtain bonding parameters for transition metal complexes from EPR data.
The fundamental theorem of Jahn-Teller [26] may be stated as, if a molecule or crystalline defect has orbital electronic degeneracy when nuclei are in a symmetric configuration, then the molecule or the defect is unstable with respect to at least one asymmetric displacement of the nuclei which lifts the degeneracy. The only exception to the rule is the linear molecule. The theorem has been illustrated in Figure 1.2. Let $E_o$ denote the energy of the doubly degenerate electronic state in a symmetric configuration. Then according to the theorem, there is some distortion $Q$ that splits the electronic degeneracy and cause the lower split-off state to have an energy $E_-$ such that $(E_o - E_-)$ increases linearly with $Q$ for small $Q$ (except for the linear molecule, there is always at least one $Q$ that produces such a linear splitting, unless of course the coupling coefficient for this mode of distortion happens accidentally to be exactly zero), the two split electronic states are the two eigen-states that become degenerate at $Q = 0$, and their energies $E_+(Q)$ and $E_-(Q)$ are associated eigen-values. Since the elastic energy associated with the distortion is proportional to $Q^2$ (the symmetric configuration denoted by $Q = 0$ is assumed to be a configuration of stable equilibrium apart from the coupling to degenerated electronic state), the system can lower its energy by distorting to a definite $Q$. The symmetric configuration is therefore unstable with respect to this distortion.

It is now necessary to mention about the Kramers theorem [27]. This deals with the restrictions to the amount of degeneracy, which can be removed by the purely electrostatic field. If the system contains an odd number of electrons, such an electronic field can not reduce the degeneracy of any level below two. Each pair is
Figure 1.2  Energy splitting of a doubly degenerate electronic state under a distortion that lifts the degeneracy in first order, showing the Jahn-Teller instability of the symmetric configuration. Here, $E_0$ is energy of doubly degenerate state, $E_+$ and $E_-$ are the energies of the electronic states and $Q$ is distortion.
known as Kramer's doublet, which can be only separated by an external magnetic field. Thus it is always possible in principle to observe electron spin resonance in such systems, though not necessarily in practice. On the other hand, in a system with even number of electrons, the degeneracy of lower orbital triplet or quintet may be completely removed by the crystal field and the levels so separated that transitions between states differing in $M_z$ by one unit need more energy than can be supplied by the microwave field.

**Crystal field parameters for d electrons:**

Both $d^1$ and $d^9$ systems have a single unpaired electron in the outermost $d$-orbital and hence, give rise to $^2D$ in the free ion state. The energy level splitting for $d^1$ and $d^9$ systems is the same but the ordering of the energy levels is inverted for both ions in any symmetry like octahedral, tetrahedral, square planar etc. In octahedral symmetry, six ligands are arranged octahedrally around the central d-metal ion and it is clear that the repulsive forces exerted by the ligands would be strongest along the direction of the X, Y and Z- axes, because in $O_h$ field all ligands are aligned along X, Y and Z- axes. We know that $d_{x^2}$ and $d_{z^2}$ orbitals (known as $e_g$ set) of the d-metal ion are aligned along the X, Y and Z- axes respectively and the remaining $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals (known as $t_{2g}$ set) are directed between the X, Y and Z- axes. In other words, in $O_h$ field, the repulsion effects on orbital $e_g$ will be more than on the $t_{2g}$ set. As a result, the $^2D$ term splits into $e_g$ and $t_{2g}$ levels in $O_h$ field. Figures 1 3 and 1 4 show the splitting of $d$-orbitals under various symmetry environments of the metal ion. In the
Figure 13  Representation of the splitting of d-orbitals under various crystal field symmetries.
Figure 14  Crystal field splitting of the d-orbitals in (a) octahedral (b) octahedral with tetragonal distortion (c) square planar and (d) distorted square planar symmetries.
case of $d^9$ electronic configuration with $O_h$ field, the $t_{2g}$ level is lower and the two
levels have the energies

$$< t_{2g} | V_{oct} | t_{2g} > = -4Dq$$

$$< e_g | V_{oct} | e_g > = 6Dq$$

The energy difference between these two levels is $10Dq$, where $Dq$ is a measure of the
interaction of the ion with the crystal field and is usually treated as a semi-empirical
parameter, which can be obtained from the experimental results. The $Dq$ value in a
complex depends on the geometrical shape, the nature of the central metal ion and the
nature of the ligands. The $Dq$ value for an octahedral complex is greater than that of a
tetrahedral complex within the same ligands, which are at the same distance from the
central ion. This is because of the geometrical shape and also the number of ligands
present in the complex [28]. $Dq$ also depends on the effective charge ($Z_{eff}$) and the
valency of the central metal ion. This effect is probably due to the fact that the central
metal ions with higher charge will polarize the ligands more effectively. The ligand
field effects contribute more to the variation in $Dq$ value for a given central ion and a
given geometry. A ligand exerting a strong field will give a low $Dq$ value.

However, many complexes seem to possess symmetry lower than octahedral.
Deviations from octahedral symmetry are usually treated as perturbations on the high
symmetry and would cause splitting in the degenerate levels as shown in Figure 1.3. In
the present investigation, the symmetry of the metal ions in all the lattices is lower than
octahedral. In such a situation, the ground state is not purely due to a single d-orbital,
because, the orbital contribution to the spin Hamiltonian is due to the mixing of the
excited state wave function with the ground state through spin-orbit coupling.
Therefore, in the most general situation, the ground state is the linear combination of all five orbitals. Without resorting to any symmetry considerations, the coefficients of the d-orbitals and hence the ground state can be calculated using the procedure developed by Swalen et al. [29]. They used the experimentally observed g-values to determine the five coefficients of the Kramers' doublet. There are only three g-values and a normalization condition to determine five coefficients. The fifth equation is obtained by assuming the coefficients of the $d_{xz}$ and $d_{yz}$ orbitals to be equal.

Magnitude of the crystal field:

The magnitude of the crystal field is also of great importance since it governs the extent of the orbital levels. In order to incorporate the effect of the crystal field into the general spin Hamiltonian for the ion, three levels of interactions are to be recognized. They are

a) Smaller effect: The rare earth ions have unpaired 4f electrons, partially shielded by the electrons of outer orbitals. So the electrostatic forces at central metal ion, already rather weak, are further attenuated. In these ions, L and S remain coupled and precess about resultant J, which in turn precesses about the electric field. Thus $M_J$ is a good quantum number. In calculating the energy values, one must first consider the spin-orbit coupling term ($\mathcal{H}_{LS}$) and then, the crystal field ($\mathcal{H}_V$) as a perturbation. The g approximates to free ion value in many cases.

b) Moderate effect: In the iron group transition metal elements, the unpaired electrons are less well shielded. In such cases, the crystal field is strong enough to decouple L and S, which then precess independently (so $M_L$ and $M_S$ are proper
quantum numbers). The splitting between levels with different $M_L$ is of the order of $10^3 \text{ cm}^{-1}$ so that only the lowest level is occupied at normal temperature, and the orbital angular momentum is largely quenched. Spin-orbit coupling then mixes in contributions from higher orbital to counteract the quenching to a greater or lesser extent, g would deviate from the value 2.00.

c) Stronger effect: In the case of copper complexes such as copper chelates, iron group cyanides, etc., not only the coupling between the L and S broke down, but often between l and s for individual electrons. These then tend to pair off as far as possible leaving a single unpaired electron if the total number is odd. This behaves much like the unpaired electron in a free radical, and g-factor is close to the free spin value of 2.00

Relaxation [30]

The excess of population in the ground state ($M_s = -1/2$) over that in the upper state ($M_s = +1/2$), for a single spin system, is extremely small. At a temperature of 300 K, for a species with $g = 2$, the population ratio is 0.9986 with a magnetic field of 300 mT. Thus the excess population in the ground state is only about 0.07%, yet the whole phenomenon of EPR absorption depends on this difference. The probability of transitions upwards equals that for transitions downwards, therefore if the unpaired spins are isolated from their surroundings, the two levels would be rapidly become equally populated and absorption cease. There must therefore be other mechanisms by which energy absorbed and stored in the upper state can be dissipated in such a manner
as to permit return to the ground state. Such mechanisms are called relaxation processes.

In the spin Hamiltonian formalism outlined above, the paramagnetic entities are treated as in isolation. Such an ideal system of ‘non-interacting’ spins is hardly ever attainable in practice. The interactions among neighboring spins spoil the coherent precession of the net magnetization vector about B, leading to time-independent transitions. Also the systems of spins are energetically coupled to the ‘lattice’ via spin-lattice interaction, which affects the life-time of the excited state by transferring the energy to lattice via radiationless processes. In an exact solution of the dynamics of the energy transfer between the microwave field and the magnetic dipoles, these two processes have to be taken into account (Bloch Equations [31]).

The spin-lattice relaxation, or the longitudinal relaxation ($T_1$), measures the efficiency with which the spins can transfer their energy to the surrounding medium. The energy of the magnetic dipoles is not conserved in this process and leads to the establishment of spin populations governed by Boltzmann distribution.

The spin-spin relaxation or transverse relaxation time ($T_2$) is a measure of the rate at which the assembly of spins comes to internal equilibrium at a given temperature, and bears no immediate relationship to the lattice temperature. The energy of the system is conserved in this process. The spin-spin relaxation controls the natural width of resonance when complication from ‘saturation’ does not occur.

In ‘neat’ paramagnetic systems, the $T_2$ process leads to very broad resonance and often these may be even beyond detection. Usually, paramagnetic compounds are doped into isomorphous diamagnetic host-lattices to reduce the dipolar broadening.
The spin-lattice relaxation is more of a property of the individual system and can be altered only by temperature variation. Due to the presence of local fluctuating magnetic dipoles, not all the spins in an ensemble have the same Larmor frequency. In other words, even if phase coherence of all spins is achieved by some external perturbation, very soon this coherence will decay (i.e., the phases of the spin become randomized) with characteristic first order kinetics. This process, which is responsible for natural line width or resonance absorption, is known as the spin—spin or transverse relaxation time, $T_2$. Now, we will discuss linewidth of resonance

Line widths [3]:

The spectral lines can be classified into two kinds as homogeneously broadened and inhomogeneously broadened. Homogeneous broadening will occur for a set of spins when all these see the same net magnetic field and have the same spin Hamiltonian parameters (the local field need not be identical at any one instant, but the need only give the same time-averaged field over sufficiently short intervals.) This means that the line shape (i.e., the transition probability as the function of magnetic field) is the same for each dipole. The resulting line usually has Lorentzian shape. Figure 1.5 This is in accord with the predicted Bloch absorption line shape,

$$P_a = \frac{\pi}{\mu_0} \left[ B_1^2/(1+\gamma^2 B_1^2 T_1 T_2) \right] \omega B \chi^2$$

$P_a$ is the power absorbed by the magnetic systems from the linearly polarized excitation field. This is Lorentzian with a linewidth (half - width at half-height) in frequency units of $T_2^{-1}$ under non saturating conditions. In general, one often can define an
Figure 15: Lorentzian line shapes: (a) absorption spectrum, (b) first derivative spectrum and (c) second derivative spectrum
effective $T_2$ by equating it to $|\kappa \gamma_e \Gamma|^{-1}$, where $\Gamma$ (mT) now is half the line width at half-height in the absence of microwave power saturation and $\kappa$ is relative permeability

$$\Gamma = \left[ \frac{1}{|\gamma_e| T_2} \right] \left( 1 + \gamma_e^2 B_1^2 T_1 T_2 \right)^{1/2}$$

---[1.26]

the factor that depends on the line shape. For Lorentzian lines $\kappa = 1$, whereas for the Gaussian lines $\kappa = (\pi \ln 2)^{1/2}$

To visualize the possible contribution to $T_2$, the individual spins have to be considered. It has been established that $T_2$ often is the measure of the interaction between spins. In this case, if $T_2 = \infty$, the spins are completely isolated from each other, whereas $T_2 = 0$ implies very strong coupling, such that there is no local variation in the spin temperature. The mutual spin flips of paired spins cause no change in the energy of the spins state but do affect the lifetime ($T_1$) of the each spin ($M$). The propagation of magnetization through the lattice via such flips, called spin diffusion, causes equilibration to the same spin temperature throughout the system of equivalent spin, $T_2$ is the measure of this rate.

Another model invoking random sudden fast events consider collisions (eg., in gas-phase radicals) that re-orient the spin magnetic moments. This leads to Bloch type equations where now $T_1 = T_2$ is the mean time period between collision [32].

The actual linewidth is determined by $(2T_1)^{-1} (1 + \gamma_e^2 B_1^2 T_1 T_2)^{1/2} T_2^{-1}$ rather than by the second term alone (Eq 1.26). The lifetime broadening produced by the first term is missing in the Bloch formulation (which predicts a Dirac $\delta$-function absorption in the limit $T_2 \rightarrow \infty$). The factor 2 in the first term arises since the transition probability $\approx 2T_1$.
In inhomogeneous case, the line broadening mechanism distributes the resonance frequencies over an unresolved band, without broadening the line arising from individual equivalent spins. Generally, the unpaired electrons in a sample are not all subjected to exactly the same B values. Thus, at any time, only the small fraction of spins is in resonance as the external magnetic field is swept through the "line". The observed line is then a superposition of a large number of individual components (referred to as "spin packets"), each slightly shifted from the other. The resultant envelop often has approximately a Gaussian shape (Figure 16). It thus is possible to choose $B_1$ so as to power saturate some selected portion of the EPR line, decreasing the intensity there (this is known as "hole burning"). The following are some causes of inhomogeneous broadening for a given spin (chemical) species:

a) An inhomogeneous external magnetic field

b) Unresolved hyperfine structure (e.g., for F centers in KCl), occurring the number of hyperfine components from nearby nuclei is so great that no structure is observed. Hence one deduces the envelop of a multitude of lines.

c) Anisotropic interaction in randomly oriented systems in the solid state. Here the distribution of local magnetic fields resulting from the anisotropic g and hyperfine interactions give rise to the inhomogeneity. In this case, the line shape is highly unsymmetrical.

d) Dipolar interaction with other fixed paramagnetic centers. These may impose the random local field at a given unpaired electron, arising from dipolar fields from other electron spins.
Figure 16: Gaussian line shapes (a) absorption spectrum, (b) first-derivative spectrum and (c) second-derivative spectrum
The values of $T_1$ and $T_2$ may be the same for all packets, or they may differ. Experimental techniques (e.g., double field modulation) exist to detect homogeneous spin-packet lines within an inhomogeneously broadened EPR line [33]. In some of the above cases, the local magnetic field gives rise to inhomogeneous broadening.

**Magnetically and chemically inequivalent sites:**

A paramagnetic system with anisotropic $g$ and $A$ tensors will give rise to EPR resonances depending on the orientation of the magnetic field $B$ with respect to the tensor axes. In single crystals, depending on the space group and the number of molecules per unit cell ($Z$), there will be several different spatial orientations of the paramagnetic sites. Species that are chemically identical (i.e., they are described by identical spin Hamiltonian parameters) but are spatially oriented differently are referred to as magnetically distinct sites. It is also possible that due to charge compensation process [34, 35] in the lattice, depending upon different relative configurations of the 'radical vacancy' directions, there exist many different sets of spin Hamiltonian parameters (although these may differ only slightly). The species themselves would be expected to be identical when the charge-compensating vacancies are not taken into account. Such sites are referred to as chemically distinct sites. These chemically distinct sites are necessarily magnetically distinct, whereas the converse need not necessarily hold.

In the present thesis, we could identify two magnetically inequivalent sites in Cu(II) incorporated hexaimidazole cobalt dichloride tetrahydrate (HCDT) and hexaimidazole Nickel dichloride tetrahydrate (HNDT) and are discussed in Chapter 3.
Chemically and magnetically different sites have been identified in the case of VO(II) doped in zinc sodium phosphate hexahydrate (ZSPH), as discussed in detail in Chapter 6.
References:


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