CHAPTER I

BASIC THEORY

I.1 INTRODUCTION

It is well known that in solids there is often considerable motion of the whole molecule or of sub-molecular groups about preferred axes. Investigation of internal motions is of immense value in understanding the behaviour of condensed matter. These motions can manifest in different ways. For example, the molecules may move as a whole translating, rotating or reorienting. Also a part or parts of the molecule can sometimes rotate relative to one another, reorient or get exchanged with the surroundings.

NMR is a powerful and sensitive technique for the non-destructive study of matter. In the solid state it offers itself as an excellent probe to study among other things, internal motions and phase transitions. Basic principles of NMR are discussed in detail by Andrew [1], Slichter [2] and Abragam [3]. In this chapter a brief outline of the basic concepts of resonance and relaxation, relevant to the work described in this thesis are presented.
1.2 NUCLEAR MAGNETIC RESONANCE - ELEMENTARY QUANTUM MECHANICAL DESCRIPTION

Many nuclei possess an intrinsic spin angular momentum. If the spin angular momentum of a nucleus is $I\hbar$, the associated magnetic moment $\mu$ is given by

$$\mu = \gamma \hbar I \quad \text{..... I.1}$$

where $\gamma$ is the gyromagnetic ratio of the nucleus.

When such a magnetic dipole is placed in an external magnetic field $H$, the Hamiltonian representing the interaction of $\mu$ with $H$ is given by,

$$\mathcal{H} = -\mu H \quad \text{..... I.2}$$

If $H_0$ is the field along the $z$-axis then

$$\mathcal{H} = -\gamma \hbar H_0 I_z \quad \text{..... I.3}$$

where $I_z$ is the $z$ component of $I$. This interaction results in $(2I+1)$ equally spaced energy levels given by

$$E_m = -\gamma \hbar H_0 m \quad \text{..... I.4}$$
where \( m \) is the magnetic quantum number which can take \((2I+1)\) values given by \( I, I-1, \ldots, -I \).

For the case of \( I = \frac{1}{2} \) (e.g. \(^1\text{H}, ^{19}\text{F} \text{ etc.})\), we have \( m = \pm \frac{1}{2} \) and

\[
E_{-1/2} - E_{1/2} = \Delta E = \gamma \hbar H_0
\]

If a macroscopic sample containing a number of spin \( 1/2 \) nuclei is placed in the magnetic field, the interaction of the nuclei with one another and the other degrees of freedom, brings the spins into thermal equilibrium among themselves and also with the surroundings. Spins exchange energy with the lattice and attain thermal equilibrium with the lattice. The characteristic time constant for this process is called Spin lattice relaxation time \( (T_1) \). Spins exchange energy among themselves and attain a common temperature. The characteristic time required for this process is called spin-spin relaxation time \( (T_2) \). In liquids and gases \( T_1 \approx T_2 \) whereas in solids \( T_1 > T_2 \). The populations \( n_1 \) and \( n_2 \) of the two zeeman levels are governed by the Boltzmann distribution at the temperature of the lattice and the ratio is given by

\[
\frac{n_1}{n_2} = e^{-\Delta E/\kappa T}
\]

To cause transitions between these levels, a radio frequency field \( (\hbar \omega) \) is applied perpendicular to \( H_0 \) such that
\[ \hbar \omega_0 = \Delta E = \gamma \hbar H_0 \]  

The selection rule is \( \Delta m = \pm 1 \) and the transition frequency falls in the region of radio frequency.

**I.3 CLASSICAL DESCRIPTION AND FREE INDUCTION DECAY**

Classically the magnetic resonance phenomenon can be explained in terms of the precessing spins. The pulse methods are first developed by Torrey [4,5] and Hahn [6]. Consider a spin 1/2 system in a magnetic field \( H_0 \) applied along the z direction. Due to the torque (\( \mu \times H_0 \)) exerted by the field, the spins precess around \( H_0 \) with larmor frequency \( \omega_0 = \gamma H_0 \). At equilibrium, the net macroscopic magnetization along the z direction is denoted by \( M_z \). This picture can be simplified by transforming to a rotating coordinate systems \( (x',y',z') \) rotating at the larmor frequency \( \omega_0 = \gamma H_0 \) around \( z' \) axis, which coincides with the z axis of laboratory frame. In this frame of reference the magnetic moment is static and \( H_0 \) vanishes. If a rf field \( H_1 \) is applied along the \( x' \) direction, the effective field in the rotating frame is given by [7].

\[ H_{\text{eff}} = H_1 i + (H_0 - \omega/\gamma)k \]  

At resonance, \( H_0 = \omega_0/\gamma \) and the effective field is only \( H_1 \) and is along
the x' axis. As a result in the rotating frame at resonance, the magnetization precesses around \( H_1 \) in the y' z' plane with an angular frequency \( \omega = \gamma H_1 \). If \( H_1 \) is applied for a short duration \( t_p \) then the magnetization would precess through an angle \( \theta \) given by

\[
\theta = \omega t_p = \gamma H_1 t_p
\]

A rf pulse with appropriate width which can tip the magnetization through \( \theta = 90^\circ \), is called a \( \pi/2 \) pulse and a rf pulse which can tip the magnetization by \( 180^\circ \) is called a \( \pi \) pulse. The \( 180^\circ \) pulse inverts the magnetization along the -z direction.

If \( H_1 \) is turned off at the end of a \( \pi/2 \) pulse, the magnetization is tipped from z to y' direction and dephasing of spin vectors occurs due to spin spin interactions and the magnetization in the XY plane decays [Fig. I.1]. This decaying magnetization will be precessing around \( H_0 \) with an angular velocity \( \omega_0 = \gamma H_0 \) and will therefore induce a decaying emf in a coil placed in the transverse plane, which is called the free induction decay (FID). The maximum amplitude of FID is thus proportional to the magnetization in the direction of \( H_0 \) prior to the application of \( \pi/2 \) pulse.

The time constant of decay of FID (transverse magnetization) is the spin-spin relaxation time \( T_2 \). But generally the FID duration is also influenced by field inhomogeneities over the sample volume which cause additional spread in the larmor frequencies and hence faster decay of FID. In such a case the duration of
Fig. I.1. Precession of $\bar{\mu}$ around $\bar{H}_0$ due to torque ($\bar{\mu} \times \bar{H}_0$).

Fig. I.1. Precession of an ensemble of magnetic moments of nuclei ($I=1/2$) generates a net magnetization $M_0$ in equilibrium.
FID is shorter and is denoted by $T_1$ which is less than $T_2$ and in many practical situations the observed FID is a measure of $T_1$ and not $T_2$.

**I.4 SPIN SPIN INTERACTION**

Consider an ensemble of spins embedded in a lattice and placed in an external magnetic field. Each spin produces a small local field of the order of $\mu/r^3$ at another spin where $r$ is the inter nuclear distance. Each spin experiences the resultant of all the local fields due to the neighbouring spins, in addition to the applied magnetic field. The Hamiltonian for a set of interacting spins (dipole-dipole interaction) in a static field $H_0$ is given by

\[
\mathcal{H} = \mathcal{H}_s + \mathcal{H}_d
\]  

where $\mathcal{H}_s$ is the Zeeman Hamiltonian given by

\[
\mathcal{H}_s = -\gamma \hbar H_0 \sum I_z
\]

and $\mathcal{H}_d$ is the perturbing dipolar Hamiltonian given by

\[
\mathcal{H}_d = \sum_{ij} \left[ \frac{\mu_i \mu_j}{r_{ij}^3} - \frac{3 [\mu_i r_{ij}]}{r_{ij}^5} \right]
\]
\[ H_d = \gamma \mu_i \hbar^2 \sum_{i<j} \left[ \frac{I_i I_j}{r_{ij}^3} - \frac{3 [I_i r_{ij}] [I_j r_{ij}]}{r_{ij}^5} \right] \]  

where \( \mu_i \) and \( \mu_j \) are the magnetic moments of the nuclear spins \( i \) and \( j \) respectively and \( r_{ij} \) is the inter nuclear vector. Transforming the above equation using spherical polar coordinates, the dipolar Hamiltonian for identical spins can be written as,

\[ H_d = \gamma^2 \hbar^2 \sum_{i<j} \frac{1}{r_{ij}^3} [A_{ij} + B_{ij} + C_{ij} + D_{ij} + E_{ij} + F_{ij}] \]  

\[ A_{ij} = [1 - 3 \cos^2 \theta_{ij}] I_i \cdot I_j \]  

\[ B_{ij} = -\frac{1}{4} (1 - 3 \cos^2 \theta_{ij}) [(I_i + I_{j-}) + (I_i - I_{j+})] \]  

\[ C_{ij} = -\frac{3}{2} \sin \theta_{ij} \cos \theta_{ij} \exp(-i \phi_{ij}) [I_i I_{j+} + I_{i+} I_j] \]  

\[ D_{ij} = C_{ij}^* \]  

\[ E_{ij} = -\frac{3}{4} \sin^2 \theta_{ij} \exp(-2i \phi_{ij}) I_i I_{j+} \]
\[ F_{ij} = E_{ij} \]  \hspace{1cm} \text{..... I.19}

\( L_+ \) and \( L_- \) are the ladder operators. The asterisk indicates the Hermitian conjugate. The terms \( A \) and \( B \) (for homonuclear case) are secular and will not cause spin-lattice relaxation. The first term \( A_{ij} \) gives the spread in the larmor frequency and hence the broadening of the resonance lines. The second term \( B_{ij} \) is the spin flip term giving raise to life time broadening. The energy is conserved in this case and hence this term will not give raise to relaxation. Only \( C \) to \( F \) terms will contribute to the spectral density at \( \omega_0 \) (\( \Delta m = \pm 1 \)). The terms \( E \) and \( F \) contribute to spectral density at \( 2\omega_0 \) and causes the simultaneous flipping of two parallel spins \( i \) and \( j \) (\( \Delta m = \pm 2 \)). The result of the dipolar interaction is a spread of resonance frequency resulting in broadening or splitting of the NMR absorption line. The dipolar broadening is a very useful source of information regarding the structure and dynamics in solids.

### I.5 EFFECT OF MOLECULAR MOTIONS AND NUCLEAR SPIN LATTICE RELAXATION

The main interactions which when modulated by internal motions, can produce the required time dependent perturbation to cause spin lattice relaxation in diamagnetic solids are

1. \textbf{Magnetic dipole-dipole interaction}
2. \textbf{Electrical quadrupole interaction}
3. \textbf{Spin - rotation interaction}
(4) Quantum mechanical tunnelling reorientation

The first mechanism is the most important in diamagnetic solids containing symmetric groups of spin 1/2 nuclei and its strength depends on the structure as well as dynamics of the groups. Spin rotation interaction becomes important at higher temperatures while the tunnelling reorientations become important at low temperatures. These mechanisms are briefly described below.

(a) DIPOLE -DIPOLE INTERACTION:

In diamagnetic solids, in the absence of quadrupolar interaction spin lattice relaxation is caused mainly by the modulation of the dipole-dipole interactions by the internal motions. The electronic motions and lattice vibrations are not very effective in causing relaxation through nuclear dipole-dipole interactions as the frequencies at which they occur are very much higher than the larmor frequencies. The effective internal motions which cause spin lattice relaxation are molecular reorientation, torsional oscillation and translational diffusion. As a result of the motion of the molecules, the dipolar field becomes a random function of time since $r$ and $\theta$ fluctuate in time. The Fourier component at $\omega_0$ (resonance frequency) and $2\omega_0$ cause spin lattice relaxation. This is the essence of BPP theory [8]. The Hamiltonian for this time-dependant perturbation can be written as the product of lattice and spin variables [9].
where $F(t)$ is the lattice part which contains information about the molecular motion and $A$ is the spin part. $F(t)$ is a random function of time because of molecular motion and is characterized by an auto correlation function $G(\tau)$.

$$G(\tau) = \sum_i < F_i(t) F_i(t + \tau) > \quad \ldots \quad I.21$$

For a stationary random perturbation

$$G(\tau) = \sum_i < F_i(0) F_i(\tau) > \quad \ldots \quad I.22$$

where the bar denotes the ensemble average. The strength of the Fourier component at $\omega_o$ is indicated by the spectral density $J(\omega)$ which is given by

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(-i\omega \tau) d\tau \quad \ldots \quad I.23$$

The precise form of the spectral density depends on the nature of the molecular motion. An exponential correlation function with a correlation time $\tau_c$ is used to describe the molecular motion. Thus $G(\tau)$ can be expressed as

$$G(\tau) = \frac{1}{|F(0)|^2} \exp \left( \frac{\tau}{\tau_c} \right) \quad \ldots \quad I.24$$
The relaxation rate is proportional to the spectral density at $\omega_0$ i.e.,

$$\frac{1}{T_1} \propto J(\omega_0) = \sum_q \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \right]$$

A plot of $J(\omega)$ versus $\omega$ for three extreme values of $\tau_c$ is shown in Fig(I.2).

The spectral density is large and confined to low frequency for slow motions ($\omega_0 \tau_c >> 1$) whereas for fast motions ($\omega_0 \tau_c << 1$) it is small and flat over a wide frequency range. In both the cases the spectral density is small at the larmor frequency $\omega_0$ and hence $T_1$ is large. But for intermediate values of the correlation time ($\omega_0 \tau_c \approx 1$), $J(\omega)$ at $\omega_0$ is maximum and $T_1$ is minimum. In other words very slow and very fast motions (compared to NMR time scale) are not efficient in causing relaxation. The relaxation rate can be expressed as

$$\frac{1}{T_1} = C \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]$$

where $C = \gamma^4 h^2 / \tau^6$

At higher temperatures ($\omega_0 \tau_c << 1$);

$$\frac{1}{T_1} = 5C \tau_c$$

and $T_1$ is independent of the larmor frequency.

At lower temperatures ($\omega_0 \tau_c >> 1$) we get
Fig.I.2. Spectral density $J(\omega)$ as a function of frequency $\omega$. 
and $T_1$ is proportional to the square of the larmor frequency. When $\omega_0 \tau_c = 0.616$, $T_1$ is minimum and is proportional to $\omega_0$

$$\frac{1}{T_1} = \frac{2C}{\omega_0^2}$$

If a graph of $T_1$ versus temperature is drawn, $T_1$ exhibits a minimum and increases on either side. On the high temperature side of $T_1$ minimum, it is independent of larmor frequency but on the lower temperature side, $T_1$ is dependent on $\omega_0^2$.

For thermally activated motions the correlation time varies exponentially with temperature (Arrhenius law) and can be expressed as [8]

$$\tau_c = \tau_0 \exp \left[ \frac{-E_a}{kT} \right]$$

where $E_a$ is the activation energy and $\tau_0$ is the pre-exponential factor.

If a graph of $\ln \tau_c$ versus $1000/T$ is drawn, the slope of the linear graph gives the activation energy $E_a$. The intercept gives the pre-exponential factor $\tau_0$.

In solids the molecular groups jump discontinuously from one symmetry permitted orientation to another. Each type of reorientation will have a char
istic correlation time. Symmetric rotating groups like $\text{NH}_4$, $\text{N(CH}_3)_4$, $\text{CH}_3$, and $\text{NH}_3$ in solids, can reorient about their three and two-fold symmetry axes ($C_3, C_2$). The motion in which both types of reorientations are equally possible, is called the general reorientation [10-14]. The motional parameters can be studied from the temperature dependence of $T_1$. $C$ can be expressed as

$$C = C_1 \gamma^4 \tau^2$$

where $C_1$ takes different values for different types of reorientations.

For example, for ammonium ion, the values of $C_1$ are given by $\frac{9}{10}, \frac{27}{60}, \frac{9}{10}$ for $C_2, C_3$ and general reorientation [15].

When more than one reorientational motion is present, for eg., $\text{NH}_3$ and $\text{NH}_2$ groups in hydrazinium ion, then the observed spin lattice relaxation time can give different minima at different temperatures corresponding to different group motions.

(b) SPIN-ROTATION INTERACTION :

This interaction has been observed mainly in fluids [16-18]. More recently solids also have been found to exhibit spin rotation interaction [19-26]. This arises due to the interaction between nuclear magnetic moment and the molecular magnetic moment produced because of the rotation of the molecules. The spectral
density available at $\omega_0$ causes the spin lattice relaxation. The interaction Hamiltonian is written as,

$$H_{sr} = -\hbar I C J$$

where $I$ and $J$ are the spin and angular momentum operators and $C$ is the spin rotation interaction tensor. A transient rotation model by Brown et al [17] and Rotation diffusion model by Hubbard [18] were proposed for liquids. In transient rotation model the molecule is assumed to reorient by jumps and the interaction is operative only during the jumps. In rotation diffusion model, the angular momentum of the molecule is assumed to change only during the collision and remains constant in between the collisions.

Both the models proposed for spin-rotation interaction give the same expression for $T_1$.

$$\tau_{sr} \text{ the spin rotation interaction correlation time and } \tau_d \text{ the dipole dipole interaction correlation time are related through the expression [27].}$$

$$\tau_{sr} \cdot \tau_d = \frac{I}{6kT}$$

where $I$ is the moment of inertia of the molecule. If both the interactions are present simultaneously then the composite relaxation rate is given by,
\[
\frac{1}{T_1} = \left[ \frac{1}{T_1} \right]_{d-d} + \left[ \frac{1}{T_1} \right]_{sr} \quad \text{(I.32)}
\]

At lower temperatures the dipolar interaction dominates the relaxation. But as the temperature increases, the efficiency of the dipolar interaction causing relaxation decreases, as the molecular reorientations become faster and \( T_1 \) becomes longer, and spin-rotation interaction may take over. In this temperature region, \( T_1 \) starts decreasing with increase in temperature due to the dominance of spin rotation interaction. At some temperature, \( T_1 \) shows a maximum due to the competition between these opposing interactions,

\[
\left[ \frac{1}{T_1} \right]_{d-d} = 5C_1 \tau_d \quad \text{(I.33)}
\]

where \( C_1 = \frac{9}{20} \frac{\gamma^4 A^2}{\tau^4} \)

\[
\left[ \frac{1}{T_1} \right]_{sr} = \frac{C_2}{C_1} \quad \text{(I.34)}
\]

where \( C_2 = \frac{\rho C^2}{3 \hbar^2} \)

\[
\left[ \frac{1}{T_1} \right]_{sr} = \frac{1}{3} \left[ \frac{\rho C^2}{\hbar^2} \right] \tau_d \quad \text{(I.35)}
\]
Hence $T_1$ due to spin rotation interaction decreases as the temperature increases. The spin rotation interaction is independent of the larmor frequency $\omega_0$. The effective relaxation time due to both the relaxation processes is given by \[ T_1^{-1} = \frac{\tau_d}{C_2 + 5C_1\tau_d^2} \quad \ldots \quad 1.36 \]

(C) QUANTUM MECHANICAL TUNNELLING REORIENTATIONS

In solids containing reorienting molecular groups like CH$_3$, NH$_3$, NH$_4$, N(CH$_3$)$_4$ etc., the intra and intermolecular interactions restrict the mobility of these groups and individual atoms to certain equilibrium orientations. These rigid rotors move in potential wells consisting of $N$ equally spaced minima in 360° rotation permitted by the $N$-fold symmetry of the group. These potential wells are the result of the crystal field caused by the neighbours and the height of the barrier ($v_o$) depends on the structure. Near the bottom of the well, torsional oscillator states exist. Approaching the top of the barrier, the energy levels begin to resemble those of the free rotor and approach them asymptotically at energies well above the height of the barrier. Both the potential barrier and thermal energy determine the nature of molecular motions. If the energy of the reorienting group is greater than $v_o$ then relatively free rotation takes place. If the energy of the reorienting group is less than $v_o$, the group may be excited from one torsional state to another in the same well. Alternatively, a typical reorientational jump occurs when the molecular group is excited from its torsional ground state to a free rotor state, undergoes a classical rotation (as a rigid rotor) and drops into a torsional state in another but equiva-
lent well (Fig.1.3). The third possibility is quantum mechanical tunnelling. This becomes important at very low temperatures for weakly hindered symmetric light molecular groups.

Spin-lattice relaxation studies in a few samples [28-30] have shown additional minima at liquid helium temperatures. The narrow absorption spectra observed at low temperatures (4.2 K) led to the creation of a new model based on the assumption of tunnelling frequency modulations. With this model Allen [31] and Clough [32-35] have explained the additional minima observed at liquid helium temperature. Quantum tunnelling motions become dominant only at sufficiently low temperatures (below 50 K), where effect of thermal reorientations are not encountered [36]. Powels and Gutowsky [37] could successfully explain the line narrowing observed at 4.2 K with the assumption of tunnelling reorientations. The work of Tomita [28] on solid methane and that of Richards and Schafer [29] on ammonium salts provided the early evidence for the observation of tunnelling in solids. The observed effects have been explained by quantum tunnelling theories, developed by Watton et al (with the assumption of spin isomerism) [38], Appayadin and Clough (on the basis of methyl group line shapes) [39], Ikeda and Mcdowell [40], Watton and Petch [41].
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