CHAPTER 1

INTRODUCTION

Nuclear Magnetic Resonance (NMR) has proved itself to be a powerful, precise and sensitive method for the non-destructive study of matter. In solids, for example, making use of appropriate nuclei, one can probe into a variety of interactions to obtain information regarding the structure, internal motions, phase transitions etc. Basic principles of NMR are discussed in detail, among others, by Andrew\textsuperscript{1}, Slichter\textsuperscript{2} and Abragam\textsuperscript{3}.

As this thesis is concerned with NMR in diamagnetic insulating solids, the theoretical background relevant to the investigations described in the later chapters of this thesis is briefly reviewed in this chapter. An introduction to the basic concepts of resonance and relaxation are given in section 1.1. Section 1.2 describes the nature of the dipolar interaction and its effects on NMR signal shapes. A brief introduction to spin lattice relaxation is given in section 1.3. Spin-rotation interaction in solids is discussed in section 1.4. Modification of the line shape due to tunneling at low temperatures is described in section 1.5.

1.1. RESONANCE AND RELAXATION

Many atomic nuclei which possess an intrinsic non-zero spin angular momentum and also a magnetic moment $\mu = \gamma \hbar \mathbf{l}$ where $\mathbf{l}$ is the spin angular momentum, $\gamma$ is the magnetogyric ratio and $\hbar$ is the Dirac constant. If an assembly of non-interacting nuclear spins are subjected to a magnetic field, the interaction Hamiltonian can be written as

$$\mathcal{H} = -\mu \cdot \mathbf{H} \tag{1.1}$$

If the magnetic field is in the Z-direction i.e., $\mathbf{H} = H_0 \mathbf{k}$

then,

$$\mathcal{H} = -\mu_z k \cdot H_0 k = -\gamma \hbar H_0 I_z \tag{1.2}$$

This interaction results in $(2l + 1)$ energy levels, corresponding to the $(2l + 1)$ eigen values of the operator $I_z$, with energies given by $E = \gamma \hbar H_0 m$ where
\[ m = -I, -I+1, \ldots, +I \]  

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

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

In a macroscopic sample containing such nuclei, the interaction of the spins with one another and with the other degrees of freedom (referred to as the lattice) brings the spin system into thermal equilibrium among themselves and with the surroundings. The populations of the Zeeman levels are then governed by the Boltzmann distribution at the temperature of the lattice, i.e., the lower energy level is more populated than the higher energy level. The application of a radio-frequency (rf) field \( H_1 \cos \omega t \) in a direction perpendicular to \( H_0 \), and with a frequency \( \omega_0 = \gamma H_0 \) causes transitions between adjacent Zeeman levels (selection rule \( \Delta m = \pm 1 \)). The transition probability due to the rf field is proportional to \( 1 < m | m >^4 \). Hence the excess population in the lower level results in a net absorption of rf energy by the spin system with the resonance condition,

\[ \hbar \omega_0 = \hbar \gamma H_0 \]  

\[ \omega_0 = \gamma H_0 \]  

For observing the absorption signal continuously, the strength of the rf field should be small so that the rate at which the spin system absorbs rf energy should be small compared to the rate at which the spin system can exchange its excess energy to the lattice. Otherwise 'saturation' occurs resulting in a fall in the signal intensity. This process by which the spin-system transfers its energy to the lattice is called the spin-lattice relaxation and the time constant governing this process is called the spin-lattice relaxation time \( (T_1) \). \( T_1 \) can also be defined as the time required for the unmagnetized specimen to acquire the total magnetization after the magnetic field is applied. The spin-spin relaxation time \( T_2 \) characterizes the process which destroys any magnetization that may be present in a plane perpendicular to \( H_0 \). This is due to the mutual interaction taking place among the spins themselves and causes the spin system to attain an internal thermal equilibrium (common spin temperature as different from lattice temperature). The spin-spin interactions endow the NMR line with a width, shape and structure.
Considering a spin 1/2 system in the steady state, if \( n_0 \) and \( n \) denote the equilibrium population differences between the two Zeeman levels at time intervals \( t = 0 \) and \( t = t_1 \) respectively, then they are related by the equation

\[
\frac{n_0}{1 + 2WT_1}
\] (1.7)

where \( W \) is the probability of transitions induced by the rf field. The two population differences are equal (i.e., \( n = n_0 \)), when \( 2WT_1 < 1 \). We know that \( W \propto H_1 \), where \( H_1 \) is the amplitude of the rf field. Therefore one has to maintain sufficiently low rf levels to avoid saturation. In practice, for diamagnetic solids, \( T_1 \) can be as small as milliseconds and as large as hours and it is temperature dependent.

### 1.2. DIPOLAR INTERACTION

#### 1.2.1. Dipolar Hamiltonian

The NMR line shape for a system of spin 1/2 nuclei in diamagnetic solids is essentially governed by the nuclear dipole-dipole interactions. This interaction gives rise to a local field \( H_{\text{loc}} \) of the order of one gauss for a typical interspin distance \( r = 2A \) and \( \mu = 10^{-23} \) ergs/gauss for protons.

\[
H_{\text{loc}} = \frac{\mu}{r^3} \sim 1 \text{ Gauss}
\]

The dipolar interaction \( \mathcal{H}_{\text{dp}} \) can be treated as a perturbation on the Zeeman hamiltonian. The total hamiltonian is

\[
\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{\text{dp}}
\] (1.8)

The Zeeman hamiltonian is \( \mathcal{H}_z = \gamma \hbar H_0 \sum \mathbf{l}_z^j \) where the summation runs over all the spins in the solid, with the energy levels given by

\[
E_m^0 = \hbar \omega_0 = -\gamma \hbar H_0 M
\]

where \( M = \sum j m^j \) is an eigen value of \( \mathbf{l}_z = \sum j \mathbf{l}_z^j \)

Therefore \( \omega_0 = \gamma H_0 \)
In general the dipolar Hamiltonian for N spins has the form

$$\chi = \sum_{j<k} d_{jk} = - \frac{\gamma_j \gamma_k}{r_{jk}^3} \left( I_j I_k - 3 \left( I_j \cdot r_{jk} \right) \left( I_k \cdot r_{jk} \right) \right) \left( I_j \times r_{jk} \right) \cdot \left( I_k \times r_{jk} \right)$$

(1.9a)

Considering a pair of spins denoted by $I_j$ and $I_k$, if $\theta$ and $\phi$ are the polar coordinates of the vector $r_{jk}$ describing their relative positions, the Z axis being parallel to the applied field (Fig. 1.1.), $d_{jk}$ can be written as

$$d_{jk} = \frac{\gamma_j \gamma_k}{r_{jk}^3} \left[ I_j I_k - 3 \left( I_j \cdot r_{jk} \right) \left( I_k \cdot r_{jk} \right) \right]$$

$$= \frac{\gamma_j \gamma_k}{r_{jk}^3} \left( I_{jk} \cos \phi + \sin \phi \left( I_{jk} \cdot r_{jk} \right) \right) \left( I_{jk} \cos \phi + \sin \phi \left( I_{jk} \cdot r_{jk} \right) \right)$$

(1.9b)

Where

$$A = I_{jk}^* I_{kj} (1 - 3 \cos^2 \phi)$$

$$B = -(1/4) (1 - 3 \cos^2 \phi) (I_j I_k^* + I_k I_j^*)$$

$$C = -(3/2) \sin \phi \cos \phi e^{-i\phi} (I_j I_k^* + I_k I_j^*)$$

$$D = C^* = -(3/2) \sin \phi \cos \phi e^{i\phi} (I_j I_k^* + I_k I_j^*)$$

$$E = -(3/4) \sin^2 \phi e^{-2i\phi} (I_j I_k^*)$$

$$F = E^* = -(3/4) \sin^2 \phi e^{2i\phi} (I_j I_k^*)$$

(1.9c)

Here $I_j$ and $I_k$ are the ladder operators, $C^*$ and $E^*$ are the Hermitian conjugates of $C$ and $E$ respectively.
Fig. 1.1 Diagram illustrating the free rotation of a pair of identical spins about a common axis.
In perturbation calculation of the nuclear energy levels only the terms A and B of equation (1.9a) which commute with $\hat{H}_z$ will contribute in first order. Therefore only the 'truncated' part of $\hat{H}_{dp}$ is used.

$$\hat{H}_{dp} = \gamma_j \gamma_k \hbar^2 [I_j^z I_k^z - (1/4) (I_j^+ I_k^- + I_j^- I_k^+) (1 - \cos^2 \theta)]$$

The terms C, D, E and F which produce very weak responses at $\omega = 0$ and $\omega = 2\omega_o$ are neglected in the first order. $\hat{H}_{dp}$ gives rise to different local fields $H_{loc}$ at the sites of different spins. This results in a spread of resonance frequency, resulting in the broadening or splitting of the NMR absorption line. Through its dependence on the inter-spin space variables the dipolar broadening is a very useful source of information regarding structure and dynamics in solids.

Pake$^4$ was the first to study the effect of dipolar interaction on NMR signal line shapes for a pair of spins. Later Andrew et al$^5$ studied the problem for three spins (at the vertices of an equilateral triangle) and Gutowsky$^6$, Bersohan and Gutowsky$^7$ andloth et al$^8$ analyzed the problem for a group of four spins arranged in a tetrahedral configuration. It was found that line shape analysis for systems containing groups with more spins was complicated. However it was possible to go beyond a qualitative interpretation by using Van Vleck's method of moments$^9$.

1.2.2. The Method of Moments

The method of moments developed by Van Vleck is very useful in that they can be calculated from first principles without having to find the eigen states of the total hamiltonian. For a resonance curve described by a normalized shape function $f(\omega)$ with a maximum at a frequency $\omega_o$, the $n^{th}$ moment with respect to the point $\omega_o$ is defined as

$$M_n = \int (\omega - \omega_o)^n \cdot f(\omega) \cdot d\omega \quad (1.11)$$

If $f(\omega)$ is symmetrical with respect to $\omega_o$ and is an even function, all odd moments vanish. A knowledge of the moments gives information on the shape of the resonance curve and in particular on the rate at which it falls down to zero in the wings, far away from $\omega_o$. In principle the line shape function $f(\omega)$ can be described either by a Gaussian curve (1.12) or Lorentzian (1.13)

$$f(\omega) = \frac{1}{\Lambda \sqrt{2\pi}} \exp \left\{ - (\omega - \omega_o)^2 / 2 \Delta^2 \right\} \quad (1.12)$$
Here $\Delta^2$ is the second moment of the curve about the centre and $\delta$ is the half width at half intensity.

The experimental line shape corresponds very well to the Gaussian shape at low temperatures (rigid lattice case), whereas at high temperatures it would be Lorentzian (the case of rapid motion). In the intermediate temperatures the experimental line shape can be best described by a weighted superimposition of these two line shapes. It should be noted that the total second moment of a line does not change, but only the observed second moment changes. In view of the equation (1.11) the second moment $M_2$ of a NMR line can be written as

$$M_2 = \int \omega^2 f(\omega) \, d\omega \quad ; \quad M_2 = \int h^2 f(h) \, dh$$

(1.14)

$\omega$ is taken as the central frequency.

The second moment of an absorption line is simply the mean square line width. The second moment of an NMR line is completely analogous to the moment of inertia of an object with the same shape of the line. Since moments of a curve are proportional to the derivatives at the origin of its fourier transform,

$$f(\omega) = \Lambda \int_0^\infty G(t) \cdot \cos \omega t \cdot dt$$

(1.15)

where $f(\omega)$ is the normalized shape function, $A$ is the normalization constant and $G(t)$ is an even function defined as

$$G(t) = \frac{2}{\pi A} \int f(\omega) \cos \omega t \, d\omega$$

(1.16)

$$G(t) = \text{Trace} \left( M_x(t), M_x \right)$$

$$G(t) = \text{Trace} \left( e^{i\mathbf{K}t/\hbar} M_x e^{-i\mathbf{K}t/\hbar}, M_x \right), \quad \text{where} \quad M_x = \sum_j m_x j.$$

(1.17)
in which \( M_x = \sum m_{iX} \)

The total hamiltonian is \( \mathcal{H} = \mathcal{H}_0 + \mathcal{H}'_{dp} \)

where \( \mathcal{H}'_{dp} \) represents the truncated part i.e., only A and B terms are taken as they commute with \( \mathcal{H}_0 \).

Hence \( G(t) \) can be rewritten as

\[
G(t) = \text{Tr}\left\{ e^{i\omega I_z t} e^{i\mathcal{H}'_{dp} t} M_x e^{-i\mathcal{H}'_{dp} t} e^{i\omega I_z t} M_x \right\}
\]

(1.18)

Further

\[
e^{-i\omega I_z t} M_x e^{i\omega I_z t} = M_x \cos \omega_0 t + M_y \sin \omega_0 t
\]

\[
G(t) = \cos \omega_0 t \text{Tr} \left\{ e^{i\mathcal{H}'_{dp} t} M_x e^{-i\mathcal{H}'_{dp} t} M_x \right\} + \\
\sin \omega_0 t \text{Tr} \left\{ e^{i\mathcal{H}'_{dp} t} M_x e^{-i\mathcal{H}'_{dp} t} M_y \right\}
\]

(1.19)

The second term vanishes since a rotation of the spins through \( 180^\circ \) around, say, leaves \( \mathcal{H}'_{dp} \) and \( M_x \) unchanged but turns \( M_y \) into \( -M_y \).

Hence \( G(t) \) is replaced by \( G_1(t) \) called the reduced auto- correlation function

\[
G_1(t) = \text{Tr} \left\{ e^{i\mathcal{H}'_{dp} t} M_x e^{-i\mathcal{H}'_{dp} t} M_x \right\}
\]

(1.20)

In turn the various moments of the absorption line can be got from \( G_1(t) \) using the relation,
Here $G_1(t)$ is expanded in powers of $t$, the coefficients of the expansion being traces of operators which are polynomial functions of $g_{ap}$ and $M_x$.

Therefore, we obtain

$$M_2 = \frac{-\text{Tr} \left\{ (X'_{dp}, I_x)^2 \right\}}{\text{Tr} \left( I_x^2 \right)}$$

(1.22)

Using only the truncated part of $X'_{dp}$ (1.10), and evaluation of the traces in the above expression in terms of the coordinates of the nuclei, the expression (1.22) leads to the Van Vleck expression for the second moment for a system of identical spins as

$$M_2 = \frac{3\gamma^4 h^2 I (I+1)}{2N} \sum_{i>k} (1-3\cos^2\theta_{ik})/(r^6_{ik})$$

(1.23)

and for a system containing unlike spins $S$, the contribution to the second moment of the nuclei of spin $I$, is

$$M_2 = \frac{\gamma_I^2 \gamma_S^2 h^2 S(S+1)}{3N} \sum_{i>k} (1-3\cos^2\theta)/(r^6_{ik})$$

(1.24)

The total second moment of the resonance line of spins $I$ is given by adding the second moment contribution from equations (1.23) and (1.24). For a polycrystalline...
system, the isotropic average of \((1-3\cos^2 \theta)\) yields a factor of \(4/5\). Considering the contributions from identical spins alone, we have

\[
M_{2(\text{powder})} = \frac{3}{10} \frac{I (I+1) \gamma^4 h^2}{\sum_{i>k} \frac{1}{(r_{ik}^G)}}
\]  

However experimentally the second moment \(M_2\) of the absorption lines are obtained by numerical integration of the observed first derivatives using the expression,

\[
M_2 = \frac{1}{3} \frac{\int h^3 f' (h) \, dh}{\int h f' (h) \, dh}
\]  

where \(h = h_0 - H^*\), the deviation from the centre and \(f'(h)\) is the amplitude of the derivative signal at \(h\). The integral is evaluated as a sum over a large number of values for \(h\), obtained by dividing the experimental spectrum into a large number of equally spaced segments. A computer program used for this purpose is given in Appendix A.

1.2.3. Effects of Molecular Motion on the Second Moment.

It is well known that, in many solids where the molecules have symmetric groups like \(\text{NH}_3\), \(\text{CH}_3\), \(\text{NH}_4\), \(\text{N(CH}_3)_4\) etc., there is considerable motion of molecules or submolecular groups about preferred axes. Such a molecular motion can have profound effect on the line shape and the observed second moment. If the spins are in relative motion then the local dipolar field experienced by a nucleus due to its neighbours fluctuates in time and if the molecular motion is faster than the line width of the resonance line, then narrowing of the resonance line occurs. It can also be expressed as

\[
2 \pi \nu_c > \left[ \frac{\Delta H_{\text{loc}} \gamma^2}{2} \right]^{1/2}
\]  

where the bar indicates an average taken over all the spins of the sample and \(\Delta\) is the correlation frequency of the fluctuations in the local field and \((\nu \Delta H)\) is the square
root of the second moment which is a measure of the line broadening. The presence of motion modifies equation (1.18) as

\[ \langle M_2 \rangle = \frac{3 \gamma^4 h^2 I (I+1)}{2N} \sum_{j \neq k} \frac{(1-3\cos^2 \theta_{jk})}{(r_{jk}^\sigma)} \quad (1.28) \]

The calculation of the average quantity on the right hand side of the above equation is in general quite complicated. We consider a simple situation where the two spins \( j \) and \( k \) are rotating about a fixed axis \( ON \) making an angle \( \theta \) with \( Ho \) and an angle \( \gamma_{jk} \) with \( r_{jk} \). \( \theta_{jk} \) is the angle between \( r_{jk} \) and \( Ho \). In such a case \( r_{jk} \) is constant and \( \theta_{jk} \) change with time. Using the addition theorem of spherical harmonics,

\[ \langle (3\cos^2 \theta_{jk} - 1) \rangle = \frac{1}{2} (3\cos^2 \theta - 1) (3\cos^2 \gamma_{jk} - 1) \quad (1.29) \]

\[ M_2 = \frac{3 \gamma^4 h^2 I (I+1)}{8N} (1-3\cos^2 \theta)^2 \sum_{j \neq k} \frac{(1-3\cos^2 \gamma_{jk})^2}{(r_{jk}^\sigma)} \quad (1.30) \]

For a polycrystalline material the above equation may be averaged over \( \theta \) giving a value of 4/5.

\[ M_2 \text{ (powder)} = \frac{3 \gamma^4 h^2 I (I+1)}{40N} \sum_{j \neq k} \frac{(1-3\cos^2 \gamma_{jk})^2}{(r_{jk}^\sigma)} \quad (1.31) \]

A case of special interest is when \( \gamma_{jk} = \pi /2 \) i.e., when the axis of rotation is perpendicular to all the inter nucleus vectors. Then,

\[ M_2 \text{ (powder)} = \frac{3 \gamma^4 h^2 I (I+1) \sum_{j \neq k} 1}{10N} \frac{1}{(r_{jk}^\sigma)} \quad (1.32) \]

Thus under this condition the second moment reduces by a factor of four compared to the rigid lattice case. In the case of isotropic reorientations i.e., when
the axis of rotation is changing rapidly such that all the values of \( \theta_{jk} \) are equally probable.

\[
< (1-3\cos^2\theta^*) > = \int_0^\pi (1-3\cos^2\theta^*) \sin \theta \, d\theta = 0 \quad (1.33)
\]

Consequently, the contribution to \( M_2 \) from interactions within the rotating group vanishes. In the case of rotational motion the centre of rotation of each rotating group, remains constant whereas it varies in the case of translational motion of the spins. In the latter case not only the intramolecular \( M_2 \) but the intermolecular \( M_2 \) also tend to average to zero giving rise to a sharp line as in liquids. Earlier it was mentioned that molecular groups such as \( \text{CH}_3, \text{NH}_3, \text{NH}_4, \text{N(CH}_3)_4 \) exhibit rotation and reorientation. The crystal field provides a potential barrier \( V_o \) hindering such motions. Each group exists in different distinct but energetically equivalent equilibrium positions separated by the barrier height \( V_o \). These rigid rotors move in potential wells consisting of \( N \) equally spaced minima in a \( 360^\circ \) rotation, permitted by the \( N \) fold symmetry axis of the group. (Fig.1.2 shows such a potential barrier). Near the bottom of the well, torsional oscillator states exist. Approaching the top of the barrier, the energy levels begin to resemble those of a 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 the molecular motion. If the energy of the reorienting group is greater than \( V_o \), then relatively free rotation takes place. For energies 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 equivalent well. These reorientational jumps over potential barriers occur due to thermal energy at elevated temperatures. The third possibility is a quantum mechanical tunneling. This becomes important at very low temperatures for symmetric and light (low moment of inertia) molecular groups which are unable to overcome the small potential barrier by a much smaller available thermal energy.

1.2.4. Theoretical Evaluation of the Second Moment

The line shape of an NMR spectrum of a dipolar solid is in general difficult to calculate theoretically, therefore the Van Vleck formula for the second moment is usually used. The direct application of this formula has however, several disadvantages. The tedious calculations must be carried out for each, of the orientation of a single crystal and for a number of evenly distributed orientations sufficiently large to enable an estimate to be made of the average over a powder. Furthermore, it is not clear from the formula how the situation is affected by the
Fig. 1.2 Schematic of the potential barrier for NH$_4^+$ ion in a tetrahedral field. The process ABC corresponds to the classical reorientation and D corresponds to the quantum mechanical tunnelling. $V_0$ is the potential barrier.
symmetry, how many independent parameters one may determine from a set of experimental data, or how averaging over lattice vibrations may be carried out. Evaluation of the second moment will become tedious when the cation $+$ under consideration is executing different types of motions. Gutowsky, et al.\textsuperscript{6} were the first to evaluate $M_2$ theoretically using Van Vleck's second moment formula. They considered NH$_4$ halides in general which have a cubic structure. The X-ray data were used in their calculation and rigid lattice second moment was in good agreement with the experimentally obtained values. They divided the contribution to the second moment into three parts:- (1) Intramolecular (2) Intermolecular and (3) Contribution due to unlike spins. The lattice sum in this case was done by replacing all the H-atoms at the nitrogen site in a CsCl structure. In 1959 McCau and Hamming\textsuperscript{11,12} proposed a method which allowed the separate evaluation of the orientational and structural dependencies of the second moment in rigid solids and found that in general fifteen quantities are sufficient to describe the structural dependence of the second moment. O'reilly and Tsang\textsuperscript{13} published a more comprehensive study of the second moment using the even complex spherical harmonics up to and including fourth order. Making extensive use of group theory, they derived somewhat cumbersome expressions for the symmetry adapted function and tabulated the number of independent structural parameters for the different crystal symmetries. Dereppe\textsuperscript{14} recently extended the procedure to include molecular motion, and also derived a convenient formula for the average over a powder. In 1969, Falaleev et al.\textsuperscript{15,16} introduced a tensor approach which was later supplemented by symmetry considerations. Their method is more convenient than the others referred to but does not include cases involving molecular reorientations. Sjoblom\textsuperscript{17} has discussed a general procedure for the calculation of the theoretical NMR second moment in dipolar solids. He has shown that the second moment of a dipolar solid can be written as a sum of products of real second order spherical harmonic formula. This sum can be contracted to a quadratic form $q s q$ where $q$ depends on the direction of the magnetic field and $s$, the second moment tensor, only on the crystal structure and assumptions made concerning the molecular motions. The effect of symmetry, rigid body reorientations and vibrational motion on $s$ are investigated quantitatively. A formula for the second moment of a powder is also given. This has been applied to oxalic acid dihydrate. A computer program has been written by Sjoblom and Tegenfeldt\textsuperscript{18,19} based on this procedure. This has been successfully applied by them\textsuperscript{20,21} in the case of dimethyl ammonium chloride, trimethyl ammonium chloride and a good agreement between theory and experiment has been found. They have considered three main models in their experiment :- (a) rigid structure, (b) rotation of methyl group around the N-C axis, and (c) reorientation of the methyl groups combined with a reorientation of the whole ion among the possible eight orientations.
Andrew et al\textsuperscript{22} also have done such calculation in mono, di, tri and tetra methyl ammonium chlorides. Their values also agree very well with the experimental results indicating that the model proposed (for such solids) is satisfactory. Tsang and Utton \textsuperscript{23} have done similar calculations in the case of TMACdCl\textsubscript{3}. The effect of lattice vibration on the second moment has been calculated by Polak\textsuperscript{24}. In this case the vibrational frequencies were evaluated from the second moment data and were compared with the IR frequencies.

Reynhardt et al\textsuperscript{25} have theoretically evaluated the M\textsubscript{2} values for both proton and fluorine in NH\textsubscript{4}HF\textsubscript{2} with all possible types of motions and their effect on second moment. Their model was able to explain the M\textsubscript{2} transitions for both \textsuperscript{1}H and \textsuperscript{19}F absorptions. Jagannathan et al\textsuperscript{26} have evaluated M\textsubscript{2} values for \textsuperscript{1}H in ammonium acetate. They have used the same method as that of Sjoblom et al\textsuperscript{18,19} and found a good agreement between theory and experiment.

1.3. SPIN LATTICE RELAXATION

1.3.1. Introduction to Pulsed NMR

NMR in solids by using pulsed methods was introduced by Torrey\textsuperscript{27} and Hahn\textsuperscript{28}. The important difference between the pulsed and CW techniques is that in the latter, the signal is observed in the presence of the rf field whereas, in the former the observation is done in the absence of the rf field which has a perturbing influence on the spins. The spin system is subjected to a powerful rf pulse, then it is turned off and the response of the spin system induces an emf in the receiver coil by the freely precessing resonant spins known as the free induction decay (FID). Thus pulsed NMR is observed in the time domain in contrast to CW NMR which is observed in the frequency domain. The relaxation times of the spins can be determined from the response of the spin system to a chosen sequence of rf pulses. A brief discussion regarding the origin of the FID and its relation to relaxation times is given below.

Let us consider a spin 1/2 system in a static magnetic field (H\textsubscript{0}) applied along the Z-direction. Due to the torque (mxH\textsubscript{0}) exerted by the field, the spins precess around H\textsubscript{0} with the Larmour frequency $\omega_0 = \gamma H_0$ (Fig.1.3.). At equilibrium, $M_z$ the net macroscopic magnetization along the Z-direction is denoted by $M_0$. This picture can be simplified by transforming into a rotating coordinate system $(X', Y', Z')$ rotating with a frequency $\omega_0 = \gamma H_0$ around $Z'$axis which coincide with the Z axis of the laboratory frame. In this frame of reference, the magnetic moment vector looks static (Fig. 1.4.) 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
Fig. 1.3a Precession of $\tilde{\mu}$ around $\tilde{H}_o$ due to torque ($\tilde{\mu} \times \tilde{H}_o$).

Fig. 1.3b Precession of an ensemble of magnetic moments of nuclei ($J = 1/2$) generates a net magnetization $M_o$ in equilibrium.
Fig. 1.4 Diagram of behaviour of spin vectors under the action of a $\pi/2$ pulse.
(a) Equilibrium magnetization ($M_0$); (b-c) Effect of $\pi/2$ pulse on $M_0$,
(d-e) Spin-Spin relaxation in progress; (f) Free induction decay signal.
At resonance, $\omega / \gamma$ nullifies the effect of $H_o$ and the effective field is $H_1$ only. As a result, in the rotating frame at resonance, the magnetization precesses around $H_1$, in the Y'Z' plane, with an angular velocity $\omega = \gamma H_1$. If $H_1$ is applied for a short duration, $t_p$, then the magnetization would precess through an angle $\theta$ given by

$$\theta = \omega t_p = \gamma H_1 t_p.$$ 

An rf pulse whose duration is such that the magnetization tips through an angle of $90^\circ$ is called a $\pi / 2$ pulse. After the application of such a pulse, the magnetization is turned through $90^\circ$ and is along the Y-direction. The pulse for which the magnetization is turned away from the Z direction through $180^\circ$ and aligned along the -Z direction is called a $\pi$ pulse. This would invert the magnetization.

If $H_1$ is turned off at the end of a $\pi / 2$ pulse, the magnetization which is initially tipped from Z to Y' direction by this pulse begins to precess around $H_o$. Due to spin-spin interactions, dephasing of spin vectors occurs and the magnetization in the XY'-plane decays. This decaying magnetization will be precessing around $H_o$ (Fig.1.5.) with an angular velocity $\omega_o = \gamma H_o$ and will induce an emf in a coil placed in the transverse plane (the XY plane) and is called the free induction decay (FID). The maximum amplitude of the FID is thus proportional to the magnetization in the direction of $H_o$, prior to the application of the $\pi / 2$ pulse.

The time constant of decay of the FID (transverse magnetization) is the spin-spin relaxation time ($T_2$). But generally the FID duration is also influenced by (static) magnetic field inhomogeneities over the sample volume which provides additional spread in the larmour frequencies and cause faster decay of the FID. In such a case the duration of the FID is shorter and is characterized by $T_2^*$. Normally $T_2^*$ is less than $T_2$ and in many practical situations the observed FID indicates $T_2^*$ and not $T_2$.

The classical picture of precessing magnetization gives useful insight into the spin-lattice relaxation processes also. At the end of a $\pi / 2$ pulse, there is no net magnetization along the Z'-axis. The spin system exchanges energy with the lattice and starts relaxing towards the equilibrium state, during which process $M_Z$ component develops continuously till it attains the thermal equilibrium value $M_Z = M_0$ (Fig. 1.5.). This growth of $M_Z$ along the $H_o$ direction, in general is exponential with a characteristic time $T_1$, the spin lattice relaxation time.

The phenomenological equations governing the growth of magnetization including the effects of relaxation have been postulated by Bloch$^{29}$ and are given below.
Fig. 1.5. Spin-lattice relaxation in progress.

(a) Dephasing of spin vectors
(b-c) Growth of $M_z$
(d) Thermal equilibrium ($M_z = M_0$)
Here $M_x$, $M_y$ and $M_z$ represent the instantaneous magnetization along the X, Y and Z directions respectively, and other symbols have their usual significance.

1.3.2. Effect of Molecular Motion on Spin Lattice Relaxation.

Spin-lattice relaxation arises because each spin experiences a fluctuating field at its site because of the random nature of the internal motions. The first successful relaxation theory was proposed by Bloembergen, Pound and Purcell (BPP)\textsuperscript{30} for liquids and can be applied for solids also. If the fourier spectrum of this fluctuating field contains a frequency component at $\omega$, the transitions are induced between the spins and the lattice. The interactions among the spins are weak compared to Zeeman interaction, and hence can be taken as a perturbation to the Zeeman interaction. The hamiltonian for this time-dependent perturbation can be written as a product of lattice and spin variables\textsuperscript{10}.

$$\mathcal{H}(t) = \sum (-1)^q F^q(t) A^q \quad (1.36)$$

where $F^q(t)$ is the lattice part which contains information about the molecular motion and $A^q$ is the spin part. The lattice variables $F^q(t)$ is a random function of time because of molecular motions and is characterized by an auto correlation function

$$G(\tau) = \sum \langle F^q(t) F^q(t+\tau) \rangle \quad (1.37)$$

For a stationary random perturbation,
\[ G(\tau) = \sum_q < F^q(0) F^q(\tau) > \]  

(1.38)

where the bar denotes the ensemble average. The strength of the Fourier component in the fluctuation, at \( \omega_0 \) is indicated by the spectral density \( J(\omega) \) which is given by

\[ J(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{-i\omega \tau} d\tau \]  

(1.39)

The relaxation rate is proportional to the spectral density at \( \omega_0 \), i.e.,

\[ \frac{1}{T_1} = J(\omega_0) \]  

(1.40)

The precise form of the spectral density depends upon the nature of the molecular motion. Usually an exponential correlation function with a characteristic correlation time is used to describe these thermally activated molecular motions. Thus,

\[ G(\tau) = \sum_q < F^q(0) >^2 \exp\left(-\frac{\tau_0}{\tau_c}\right) \]

\[ \frac{1}{T_1} = J(\omega) = \sum_q < F^q(0) >^2 \frac{\tau_c}{\tau_c} \]  

(1.41)

Fig. 1.6. shows the plot of \( J(\omega) \) vs \( \omega \). If \( \tau_c \) is long, the motions are slow and the spectral density is large at low frequencies. If \( \tau_c \) is short the molecular motions are fast and the spectral density is constant over a wide spectrum of frequencies. The \( T1 \) not only depends on the spectral density at \( \omega_0 \) but also depends on the strength of the perturbing interaction. Out of several possible interactions which can couple spins to the lattice the important one is the magnetic dipole-dipole interaction.

The dipolar interaction hamiltonian discussed in section (1.2.1.) shows that A and B (for homo nuclear case) are secular and will not cause spin lattice relaxation. The first term A gives the spread in the larmour frequency and hence the broadening of the resonance lines. The second term B is the spin-flip term giving rise to life-time broadening. The energy is conserved in this case and this term will not give rise to relaxation. Only C to F terms will contribute to relaxation of spins. The terms C and D contribute to the spectral density at \( \omega_0 \) (\( \Delta m = \pm 1 \)), the terms E and F contribute
Fig. 1.6 Spectral density $J(\omega)$ as a function of frequency $\omega$. 
to spectral density at $2\omega_0$ and cause the simultaneous flipping of two parallel spins $i$ and $j$ ($\Delta m = \pm 2$).

The final expression for $T_1$ can be written as

$$\frac{1}{T_1} = \frac{3}{2} \gamma^2 h^2 I (I+1) \left\{ J_1(\omega_0) + J_2(2\omega_0) \right\}$$  \hspace{1cm} (1.42)

The spectral densities at $\omega_0$ and $2\omega_0$ are calculated from $C$ and $D$ and $E$ and $F$ terms respectively and the expression for $T_1$ becomes

$$\frac{1}{T_1} = C \left\{ \frac{\tau_c}{1 + \omega^2 \tau_c} 2^+ \frac{\tau_c}{1 + 4 \omega^2 \tau_c} 2^- \right\}$$  \hspace{1cm} (1.43)

where $\tau_c$ is the correlation time for the molecular motion under consideration, $\omega$ is the Larmor frequency and $C$ indicates the strength of the relaxation interaction.

The above equation can be discussed under three cases.

**Case I:** $\omega \tau_c << 1$

This region is called the white spectral region. As the temperature is increased, $\tau_c$ will decrease and hence $T_1$ will increase. $T_1$ is independent of the operating frequency in this region.

$$\frac{1}{T_1} = 5C \tau_c$$  \hspace{1cm} (1.44)

**Case II:** $\omega \tau_c >> 1$

In this region $T_1$ is proportional to the square of the operating frequency. When the temperature is decreased, $\tau_c$ will increase hence $T_1$ will increase.

$$\frac{1}{T_1} = \frac{2C}{\omega^2 \tau_c}$$  \hspace{1cm} (1.45)

**Case III:** $\omega \tau_c \approx 1$

This is in between the cases I and II. It shows a minimum in $T_1$ and the value of $T_1$ depends on the operating frequency. From the above discussion it is seen that $T_1$ vs temperature shows a minimum in $T_1$ at $\omega \tau_c = 0.62$. 

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The correlation times vary with temperature according to Arrhenius law, since these motions are thermally activated

$$\tau_c = \tau_c^0 \exp \left( \frac{E_a}{RT} \right)$$

(1.47)

where $E_a$ is the activation energy required to overcome the potential barrier and is equal to the energy separation of the lowest ground state and the free rotor state. $\tau_c^0$, the pre exponential factor is largely determined by the life time of the free rotor states.

The correlation times are determined from experimental values of $T_1$ using BPP equation (1.43). From the Arrhenius law (1.47) the plot of $\ln \tau_c$ vs $1000/T$ is obtained which is linear. The slope of the straight line gives the magnitude of $E_a$. Thus the temperature dependence of $T_1$ gives quantitative information about rates of motion over a wide range of frequencies ($10^6 - 10^{13}$ Hz).

When more than one rotational mechanism is present then the correlation times will be different for different motions which have a pronounced effects on the observed relaxation.

1.4. SPIN ROTATION INTERACTION

This interaction has been found to be one of the dominant relaxation mechanisms in gases and liquids for a long time. More recently, it is found to be present in many solids also. This arises due to the interaction between the nuclear magnetic moment and the molecular magnetic moment produced by the electronic charge distribution in the molecule. This interaction when modulated by internal motions can cause relaxation. The hamiltonian for spin-rotation interaction can be described as,

$$\mathcal{H}_{sr} = -\hbar I C J$$

(1.48)

where $I$ and $J$ are the nuclear spin and angular momentum operator and $C$ is the spin-rotation tensor. The molecular motion changes the value of angular momentum and modulates the field at the nuclear site in a given molecule. This interaction was first observed in liquids. Brown et al. have advanced a 'transient rotation model' in which the molecule jumps from one orientation to another at random and this interaction operates only during the short jump time. Hubbard has proposed an alternate mechanism based on 'rotational diffusion model' which assumes that only during collision with other molecules angular momentum changes and remains constant in between collisions. The above two models apply for fluids. Till now no
A comparison of dipole-dipole and spin-rotation interaction reveals some interesting features. For the spin-rotation interaction, it is the fluctuation in the angular velocity which is important in contrast to the dipole-dipole interaction where the fluctuations in co-ordinates are instrumental in causing relaxation. Both these processes have got opposite temperature effects. At low temperatures, the relaxation is dominated by the dipolar interaction. With increase in temperature, the efficiency of relaxation due to dipolar interaction goes down and \( T_1 \) becomes longer, whereas at high temperatures spin-rotation interaction becomes a dominant relaxation mechanism. Thus \( T_1 \) shows a maximum due to these competing mechanisms.

1.5. TUNNELING EFFECTS AT LOW TEMPERATURES.

The semiclassical theory predicts that at sufficiently low temperatures, the motion of the molecular groups will be frozen with respect to the NMR time scale and hence NMR lines should broaden. But there are many experimental observations where lines remain narrow even down to liquid helium temperatures instead of attaining the rigid lattice value\(^{44,45}\). Also spin- lattice relaxation time shows multiple minima in this temperature range which could not be accounted for by the classical theory\(^{46,47}\). According to semiclassical theory of relaxation (BPP theory) the changes in \( T_1 \) and line width are determined by variations in the rate of random thermal reorientations. As a consequence, there should be an agreement between the various nuclear resonance observations with regard to their predicted random molecular jump rates, which indeed is so in the intermediate and high temperature regions but not in the very low temperature regions. To explain this, quantum mechanical tunneling, has been invoked.

When the activation energy is sufficiently small (weakly hindered solids) the wave functions of the spins in the different potential wells overlap appreciably. This causes the tunneling splitting of the torsional oscillator ground states. Then the tunneling of the protons from one well to another becomes possible and this leads to narrowing of the resonance lines. The additional minima in \( T_1 \), occur when the tunnel splitting are equal to integral multiples of Zeeman splittings\(^{48,49}\). There are excellent reviews\(^{50-53}\) which discuss in detail the effects of tunneling on line shapes and relaxation.
REFERENCES


