SECTION A

NUCLEAR MAGNETIC RESONANCE AND RELAXATION

AN INTRODUCTION
BASIC NMR THEORY

When a nucleus with spin I is placed in a static magnetic field of strength \( H \), the interaction Hamiltonian is given by

\[(A-1.1) \quad \mathcal{H}_Z = -\hat{\mu} \cdot \hat{H}_0 \]

referred to as the Zeeman Hamiltonian. Here, \( \hat{\mu} \) is the magnetic moment operator for the spin \( I \), given by

\[(A-1.2) \quad \hat{\mu} = \gamma \hbar \hat{I} \]

Let the direction of the applied magnetic field \( H \) be chosen as the Z-axis. Then the expression (A-1.1) can be written as

\[(A-1.3) \quad \mathcal{H}_Z = -\gamma \hbar H_0 \hat{I}_Z \]

The Zeeman interaction creates \((2I+1)\) distinct levels of energy with values given by \(-\gamma \hbar H m\), where \( m \) is the magnetic quantum number. The energy difference between any two adjacent levels is given by
At thermal equilibrium, the number of spins occupying different energy levels is given by the Maxwell-Boîtzmann distribution. If $N$ is the total number of spins in the system, then the number of spins present in the energy level denoted by $m$ is

$$N_I = N \exp \left( \frac{-\gamma \hbar H \cdot m_k}{kT} \right)$$

In this expression, $T$ is the lattice temperature and here lattice implies all the translational, rotational and vibrational degrees of freedom of the nuclei. Focusing our attention on a spin 1/2 probe like proton, the spin ensemble is described by two levels of energy and the population in the higher and lower energy states, (which we shall refer to as -1/2 and +1/2 states respectively) are given by $N^0 = N \exp(\gamma \hbar H /2kT)$ and $N^0 = N \exp(-\gamma \hbar H /2kT)$. These expressions show that there is an excess of spins in the lower energy state at any given finite temperature $T$.

When a sinusoidally oscillating magnetic field at the frequency $\omega = \gamma H_o$ is applied in the XY plane, this field couples the two levels and causes transition of spins between these levels. Owing to the excess population of nuclei in the lower energy state, there is a net absorption of energy from such an oscillating field. This happens because of the fact that, the rate at which spins get transferred from +1/2 to -1/2 is greater than the rate at which the spins go from -1/2 to 1/2 state.

In order for the spins to achieve their thermal equilibrium the spin
subsystem will have to interact with all other degrees of freedom (called lattice). If such is not the case, for example, an application of even a weak resonant continuous r.f. perturbation would have led to an eventual equalization of populations (saturation). The interactions among the spins modulated in time due to the motional processes provide the connection between the spin and the lattice degrees of freedom and hence serve as relaxation mechanisms, which try to maintain the equilibrium population difference. Two cases here can be identified. In the first case, which forms the basis of CW-NMR experiments, the amplitude of the applied field is maintained at a sufficiently low value as to avoid saturation of the spin system. Here, the rate at which the energy is absorbed from the applied field is equal to the rate at which this energy is dissipated by the competing relaxation process and the spin system is said to be maintained in a near-equilibrium state. In the second case, which forms the basis for the so-called pulsed-NMR experiments, the amplitude of the applied field is deliberately made large so that within a time interval in which the relaxation effects are negligible, the spin system is disturbed away from equilibrium (saturation being one such state) and the perturbing field is subsequently removed to allow the system to relax back to its thermal equilibrium. This time evolution is monitored to measure the relevant relaxation times.

The molecules (or atoms) in which the nuclei are situated act as carriers of these nuclei and these are subjected to all the translational, rotational and vibrational motions experienced by the carrier molecules (carrier atoms), which are random functions of time. The presence of all other spins causes a local magnetic field at any
given spin, and owing to the above mentioned motional processes this local field fluctuates in time. The component of this fluctuating field perpendicular to the Z-axis can in principle cause transition between the levels and this serves as the path through which spin-lattice relaxation takes place. The inherent dependence of these thermally activated processes on temperature makes the relaxation times too a function of temperature, and measurement of the relaxation times as a function of temperature thus, in principle, provides an opportunity to investigate the dynamic processes present in the system and their relation to other interesting physical phenomena.

As an alternative to the quantum mechanical description of the spin system, a semi-classical description can be given, by which it is more convenient to visualize the evolution of the spins in the presence of the magnetic fields. Let us consider a single spin with a magnetic moment given by \( \mu \) in the presence of an applied magnetic field \( H \). The time rate of change of \( \mu \) is given by

\[
\text{(A-1.6)} \quad \frac{d\mu}{dt} = \mu \times (\gamma H)
\]

Equation (A-1.6) shows that the vector \( \mu \) is moving in a direction perpendicular to the plane containing \( \mu \) and \( H \). This corresponds to the precession of the vector \( \mu \) about the applied field's direction and if \( H \) is constant in time, \( \mu \) subtends a constant angle \( \theta \) about \( H \) and it describes a cone about \( H \), known as Larmor precession. If the applied field is along the \textbf{Z-direction}, the Z-component of the magnetic moment is independent of time but X and Y components are time dependent, from eqn.
This time evolution of \( \mu \) is as seen from the laboratory frame and it will be convenient to transform into a reference frame which rotates with an angular velocity \( \Omega \). It can be shown that the time rate of change of \( \dot{\mu} \) in such a rotating frame can be written as

\[
\frac{\delta \mu}{\delta t} = (1 \times (yH + fi))
\]

Comparing eqns. (A-1.6) and (A-1.7) it is seen that the time evolution of the magnetic moment in the rotating frame is described by an equation similar to that in the lab frame, provided we visualize the net field felt by \( \mu \) to be equal to \((H-n/y)\). If we assume that the field \( H \) is time independent and it is along the Z-axis, denoted by \( H \), we can rewrite (A-1.7) as

\[
\frac{\delta \dot{\mu}}{\delta t} = \mu \times y(H + \Omega/y)
\]

Now, if we choose the frequency of the rotating frame as \( fi = -yH \), then in such a frame the time rate of change of \( \mu \) is zero, and therefore in this frame the magnetic moment is static. The frequency \(-yH\), which we shall denote by \( \omega \), is called the Larmor frequency [Slichter, 1978].

Treating \( \mu \) as the quantum mechanical operator for the magnetic moment, the expectation value of \( \mu \) can be expressed as the sum of the expectation values of the three components, namely,

\[
\langle \hat{\mu} \rangle = \hat{i} \langle \mu_x \rangle + \hat{j} \langle \mu_y \rangle + \hat{k} \langle \mu_z \rangle
\]
It can be shown that the expectation value of this magnetic moment operator $\mu$ obeys a rate equation, similar to (A-1.6), namely,

\begin{equation}
(A-1.10) \quad \frac{d<\mu>/dt}{\gamma H}
\end{equation}

and the $X$ and $Y$ components of the expectation values, $<\mu_x>$ and $<\mu_y>$, are oscillating functions of time with a frequency $\omega = \gamma H$ and $Z$ component of $\mu$, $<\mu_z>$, is independent of time [Slichter, 1978] and these are in accordance with the classical description of the magnetic moment in the presence of the static field $H$.

Let us suppose that an alternating magnetic field $H(t) = iH \cos \omega t$ is applied along the $X$-axis. Such an alternating field can be broken into two circularly rotating components denoted by $H_R$ and $H$. $H_R$ rotates about the $Z$-axis with an angular frequency $\omega$ and $H$ rotates with an angular frequency $-\omega$. When $\omega$ is made close to $\omega$, $H_R$ will rotate in the same sense as the moment $\mu$ and $H$ will rotate in the opposite direction. Thus, we can assume that the effect of $H$ in causing any observable change in the time evolution of $\mu$ is negligible. We shall rewrite $H_R$ by the expression

\begin{equation}
(A-1.11) \quad H_R = H_1 = H_1 (i \cos \omega t + j \sin \omega t)
\end{equation}

In the presence of $H$ and the rotating field $H(t)$, the rate of change of $\mu$ is given by

\begin{equation}
(A-1.12) \quad \frac{d\mu}{dt} = \mu \times \gamma[H_0 + H_1(t)]
\end{equation}
In the rotating frame, in the presence of $H(t)$, the time evolution of $\mu$ can be described by the equation

$$\frac{\delta \mu}{\delta t} = \mu \times \left[ \hat{k}(\omega + \gamma H_0) + i\gamma H_z \right]$$  \hspace{1cm} (A-1.13)$$

It is seen that the time dependence of $H_z$ is removed in this rotating frame, since in the lab frame $H$ also rotates with the same angular frequency $\omega$ as that of the rotating frame. When $\omega = -\gamma H$, which is also called the resonance condition, the $Z$-axis magnetic field in the rotating field becomes zero (A-1.13), and the only non-zero field in this frame is $H$, which is static. Thus, at resonance, in the rotating frame, the magnetic moment $\mu$ precesses about this static field $H$ which is in the XY-plane. The angular frequency of such a precession is given by $\omega = \gamma H$. In a time interval $t$, the spin will precess by an angle $\vartheta = \gamma H \cdot t$. Now, if we choose $t$ in such a way that $\vartheta = \frac{n}{2}$ radians and if $\mu$ was along the $Z$-direction at time $t = 0$, then at $t = t$, the magnetic moment would have been tilted by 90° and it will be in the XY plane. The restricted application of the rotating field $H$ for a short interval of time $t$ is called a pulse and the pulse corresponding to $\vartheta = \frac{n}{2}$ is called the "90 degree pulse" or the "n/2 pulse". Similarly a "n pulse" can be applied such that at the end of $t$ the magnetic moment is along the $-Z$ direction, if it was kept initially along the $+Z$ direction. The magnetic moment after a n/2 pulse precesses about the static field $H$ in the laboratory frame, and if an inductance coil is kept in the XY-plane such a precession causes a time dependent change in the magnetic flux of the coil which induces an e.m.f. and this is the standard method of
detecting NMR signals in pulsed NMR experiments. In the quantum mechanical description the expectation value, in the rotating frame, of the Z-axis magnetic moment $\mu$ can be shown to be [Slichter, 1978]

\[(A-1.14) \quad \langle \mu_z(t) \rangle = \langle \mu_z(0) \rangle \cos \gamma H_1 t \]

where $\langle \mu (0) \rangle$ is the expectation value of the Z-axis magnetic moment time $t = 0$ and we assume here that the magnetic moment is aligned along the Z-axis at time $t = 0$.

The description given so far was confined to an isolated nucleus with a magnetic moment $\mu$. When we have an ensemble of spins we can define a net magnetization $M$ for this ensemble, given for non-interacting spins by

\[(A-1.15) \quad \vec{M} = \sum_i \vec{\mu}_i \]

The azimuthal angle $\phi_i$ of all the individual spins will be randomly distributed and thus the summation of the component of magnetic moments in the XY plane will be zero, and thus the macroscopic magnetization will have only a non-zero component along the Z-axis denoted by $M$, though the individual magnetic moments $\mu_i$ can have non-vanishing components in the XY plane. The assumption of such a random distribution of $\phi_i$ is called the random phase approximation. Thus, in the presence of a static magnetic field $H$ in an ensemble of spins, there will be a net magnetization $\vec{M}$ which is static and lies along the direction of this field.
Bloch's phenomenological equations depict the time evolution of the macroscopic magnetization in the presence of the applied fields and the relaxation processes, and introduces the relaxation times $T_1$ and $T_2$. These equations are given by,

\begin{align}
(A-1.16a) \quad \frac{dM_z}{dt} &= \gamma \left( \hat{M} \times \hat{H} \right)_z - \frac{M_0 - M_z}{T_1} \\
(A-1.16b) \quad \frac{dM_x}{dt} &= \gamma \left( \hat{M} \times \hat{H} \right)_x - \frac{M_x}{T_2} \\
(A-1.16c) \quad \frac{dM_y}{dt} &= \gamma \left( \hat{M} \times \hat{H} \right)_y - \frac{M_y}{T_2}
\end{align}

In the above expressions, $T_1$ is the spin-lattice relaxation time which is the characteristic time associated with the dissipation of excess energy of the spin system to the lattice. After a $\pi/2$ pulse is applied, the magnetization $M$ is tipped onto the XY plane. But, this corresponds to a non-equilibrium condition among the spins, since at equilibrium we expect no net magnetization in XY plane, in the absence of a field component in this plane. Thus, the spin system loses this excess coherence built in the XY plane eventually, and the characteristic time constant associated with the decay of this coherence is the spin-spin relaxation time $T_2$. Now, in order to use these macroscopic relaxation processes to investigate the microscopic dynamics, a suitable theoretical framework is needed providing a connection of $T_1$ and $T_2$ to dynamic variables.

The Bloembergen-Purcell-Pound theory (BPP theory) is one of the
important microscopic theories which provide such a connection and the present investigations are based on it. It may be mentioned in passing that other comprehensive microscopic theories of relaxation are also available in literature, for example, Kubo and Tomita’s linear response theory, Bloch-Wangsness-Redfield theory, and Hebel-Slichter’s theory of nuclear relaxation. In what follows, we shall discuss in detail, the BPP theory and its application to relaxation in solids.

**Bloembergen-Purcell-Pound theory:**

In the following discussion let us consider only the simple case of spin-1/2 particles unless otherwise specified and take note of the assumptions thereof.

1. The total **Hamiltonian** of the physical system is of the general type

   \[ \hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 \]

   where \( \hat{H}_1 \) is contribution to the total Hamiltonian from the system alone expressed in terms of the spin degrees of freedom, \( \hat{H}_2 \) is the lattice part of the total Hamiltonian, and \( \hat{H}_3 \) expresses the coupling between the spin system and the lattice.

2. The lattice reservoir is assumed to be of infinite thermal capacity because of which even when the spin system exchanges energy with the lattice, the lattice remains at a constant temperature \( T \).

3. In the high-temperature approximation, the energy difference between the spin levels is assumed to be much smaller than \( kT \).
4. In comparison to $H$, $H$ is quite small and a second order
perturbation calculation can be used to calculate the lattice
induced transitions between the different levels of $H$.

5. $H$ is assumed to be a random operator with vanishing ensemble
average and the correlation function $<H(t')H(t'+\tau)>$ is assumed
to be stationary. This function is characterized by a correlation
time $T$.

6. Since a perturbation theory is to be applied, the observation time $t$
has to be much larger than the correlation time $T$ of the lattice
fluctuations.

7. On the time scale of the NMR probe these random processes are
assumed to be Markovian (with no memory effects), leading to time
independent relaxation rates.

Let us consider $N$ spins in a rigid lattice subjected to a strong
Zeeman field $H$ applied in z-direction and an oscillating field $H \cos \omega t$
applied in the xy-plane. The total Hamiltonian of this system can be
written as,

\begin{equation}
H_{\text{tot}} = H_- + \sum_{r,l} n(t) L \cdot SL
\end{equation}

Here $H_{\text{tot}}$ is given by $-M_1 \cos \omega_0 t$. Let us define $\rho$ as the density matrix
over the spin variables for the ensemble of the $N$ spins. Denoting the
spin states by \( \uparrow \rightarrow \) and \( \downarrow \rightarrow \), the probability of occupation of the \( \uparrow \rightarrow \) or \( \downarrow \rightarrow \) energy level is given by \( \sigma \) or \( \sigma \) where,

\[
(A-1.18) \quad \sigma_{i} = \langle \uparrow \sigma \mid \uparrow \rangle = \frac{\exp(-\beta E_{i})}{\sum_{k} \exp(-\beta E_{k})}
\]

where \( \beta = \frac{1}{kT} \) and \( i \) is \( + \) or \( - \). Thus the populations in \( \uparrow \rightarrow \) and \( \downarrow \rightarrow \) levels are given by

\[
(A-1.19) \quad N_{+} = N_{+} \sigma_{+} ; \quad N_{-} = N_{-} \sigma_{-}
\]

The applied r.f. field causes transition between the two energy levels and let \( W_{+} \) and \( W_{-} \) denote the transition probability per unit time induced by the applied field for a transition from \( \uparrow \rightarrow \) to \( \downarrow \rightarrow \) and \( \downarrow \rightarrow \) to \( \uparrow \rightarrow \), respectively. There exists a competing relaxation process mediated by the interaction among the spins which tries to restore the change in the population difference caused by the applied r.f. field, and the transition probability per unit time associated with this process be denoted by \( P_{+} \) and \( P_{-} \). Now the rate of change of population in each level is given by the equations

\[
(A-1.20) \quad \frac{dN_{+}}{dt} = -N_{+} (W_{+} + P_{+}) + N_{-} (W_{-} + P_{-})
\]

\[
(A-1.21) \quad \frac{dN_{-}}{dt} = -N_{-} (W_{-} + P_{-}) + N_{+} (W_{+} + P_{+})
\]

The transition probability per unit time due to the applied field is given by the formula
Equation A-1.25 shows that for a system with a very weak spin lattice coupling, or for a case where $W \gg l/T$, the population difference will eventually go to zero and this condition is the saturation condition. It can also be seen that after the perturbing field is removed the population difference reaches its equilibrium value $n_0$ given by the

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relaxation equation

(A-1.26) \[ n = n_0 [1 - \exp(-t/T)] \]

which also gives the time evolution of the net magnetization \( M \) as it is proportional to the population difference \( n \). Analogous relation can also be derived from the Bloch's equations and the simple picture given so far is able to connect to the macroscopic Bloch's equations.

The spin-lattice relaxation time \( T_1 \), introduced as the inverse of the transition rates induced by the molecular motions, now has to be connected to the microscopic dynamics in the system. We shall do it by considering an explicit form of \( \mathcal{H} \) which will be treated as a perturbation on the Zeeman Hamiltonian \( \mathcal{H} \). In fact, spin-spin relaxation time, \( T_2 \), which we have seen to be the time constant for the magnetization decay in the \( xy \)-plane, is derived naturally to be the inverse of the linewidth of the Zeeman levels, from the above calculation.

Let us consider the dipole-dipole interaction summed over all the spins, given by

\[
\mathcal{H}_{SL} = (1/2) \sum_i \sum_j \gamma_i \gamma_j \hbar^2 \left( \frac{\gamma_j \mathbf{i}_j \cdot \mathbf{i}_i}{r_{ij}^3} - \frac{3 \gamma_j \mathbf{i}_j \cdot \mathbf{r}_{ij}}{r_{ij}^5} \right)
\]

where \( r_{ij} \) is the internuclear vector of any two spins \( i \) and \( j \), and refers to the gyromagnetic ratio of the respective spins. Let
where $V_{ij}$ is given by

\begin{equation}
V_{ij} = \frac{2}{\hbar} r_{ij} (A+B+C+D+E+F)
\end{equation}

and

\begin{align*}
A &= I_{z1} I_{zj} (1 - 3 \cos^2 \theta_{1j}) \\
B &= -1/4 \left[ ((x_1 - i y_1)(x_j + i y_j) + (x_1 + i y_1)(x_j - i y_j)) (1 - 3 \cos^2 \theta_{1j}) \right] \\
C &= -3/2 \left[ ((x_1 - i y_1) I_{zj} + (x_1 + i y_1) I_{z1}) \sin \theta_{1j} \cos \phi_{1j} \exp(-i \phi_{1j}) \exp(i \gamma_H t) \right] \\
D &= -3/2 \left[ ((x_1 - i y_1) I_{zj} + (x_1 + i y_1) I_{z1}) \sin \theta_{1j} \cos \phi_{1j} \exp(i \phi_{1j}) \exp(-i \gamma_H t) \right] \\
E &= -3/4 \left[ (x_1 + i y_1)(x_j + i y_j) \sin^2 \theta_{1j} \exp(-2i \phi_{1j}) \exp(2i \gamma_H t) \right] \\
F &= -3/4 \left[ (x_1 - i y_1)(x_j - i y_j) \sin^2 \theta_{1j} \exp(2i \phi_{1j}) \exp(-2i \gamma_H t) \right]
\end{align*}

In a rigid lattice, each spin experiences a static field which is different from the applied field $H$ due to the presence of the neighbouring spins. Since the distribution of spins in the $+1/2$ and $-1/2$ states in the neighbourhood of any given spin varies from site to site, this "local field" also varies from spin to spin. The average of the local field distribution can therefore be expressed as [Bloembergen et al., 1948]
and the mean square deviation in frequency units of the energy level is given by

\[ (A-1.31) \]
\[ <\Delta \omega^2>_{AV} = \gamma^2 <H_{loc}^2>_{AV} \]

Eqn. (A-1.31) gives an expression for the broadening of the resonance line caused by the local field distribution. Term B, which contains the \( I_1 \) and \( I_2 \) operators in pairs, will cause a simultaneous flip of the two spins \( i \) and \( j \) in the opposite directions. This term thus imposes a finite lifetime on a given spin whether it is in the \( |+> \) or \( |-> \) state, and thus this also contributes to the broadening of the energy levels. Now the contribution of this term to the linewidth can be included in the expression for \( <\Delta \omega> \) in the form of a numerical factor and taking this also into account the total broadening caused by term A and term B are given by

\[ (A-1.32) \]
\[ [<\Delta \omega^2>_{AV}]^{1/2} = (1/T_2) = (3/2) \gamma^2 h [I(I+1)/3]^{1/2} \]
\[ \times \left( \sum_{i \neq j} (1-3\cos^2 \theta_{ij})^2 \times r_{ij}^{-6} \right)^{1/2} \]

The spin-spin relaxation time is the shortest in a rigid lattice since the coupling between the spins is strong in the absence of motions and this aids in dissipating the coherence in XY plane more efficiently. It can be shown that lattice motions lead to a time averaging of terms A
and B thereby reducing the linewidth of the resonance line, known as "motional narrowing". In principle, the spin-lattice relaxation process which couples the two levels of energy also contributes to the broadening of the lines [Bloembergen et al., 1948].

**Spin-Lattice relaxation process:**

From eqns. \((A-1.28)\) and \((A-1.29)\), it is seen that terms C and D are capable of coupling the spin levels differing in \(m\) by ±1 and terms E and F couple spin levels differing in their \(m\) by ±2. When motions are present, these terms are modulated in time and they lead to the spin-lattice relaxation. At a finite temperature, motions are present in a system because a finite amount of energy is available to all the lattice degrees of freedom. Normally such thermally activated dynamic processes are random functions of time. These dynamic processes modulate the spatial co-ordinates \((r, \theta, \phi)\) of any given spin randomly in time. Thus, the space part of the terms in the Hamiltonian given in eqn.\((A-1.24)\) are random functions of time. Defining the space dependent terms in the Hamiltonian for some arbitrary test nucleus (i) due to its interactions with a specific j, as

\[
(A-1.33(a)) \quad F_{0j} = (1-3\cos^2\vartheta_{1j})r_{1j}^{-3}
\]

\[
(A-1.33(b)) \quad F_{1j} = \sin\vartheta_{1j}\cos\vartheta_{1j}\exp(i\phi_{1j})r_{1j}^{-3}
\]

\[
(A-1.33(c)) \quad F_{2j} = \sin^2\vartheta_{1j}\exp(2i\phi_{1j})r_{1j}^{-3}
\]
it may be noted that in the presence of isotropic stochastic motions these terms are averaged to zero. The processes are then characterized by the two-time correlation functions. These correlations are quantified by a correlation time $T_c$, which is an average time interval over which the magnitude of the function has not changed appreciably. We can define the autocorrelation function of $F(t)$ as

\begin{equation}
\langle F(t)F^\ast(t+\tau) \rangle_{AV} = K(t, \tau)
\end{equation}

where the average is over the entire ensemble of spins. Assuming that these randomly modulated processes in time are stationary and Markovian the autocorrelation function becomes

\begin{equation}
K(\tau) = \langle F(t)F^\ast(t) \rangle_{AV} \exp(-\tau/\tau_c)
\end{equation}

The spectral density function for $K(\tau)$ is given by

\begin{equation}
J(\nu) = \int K(\tau) \exp(i\omega\tau) d\tau
\end{equation}

and since $K(\tau)$ is real and even, $J(\nu)$ is also real and even. Let us define the spectral density functions $J_0(\nu)$, $J_1(\nu)$ and $J_2(\nu)$ by

\begin{equation}
\langle \Sigma : F_0^2 \rangle_{AV} = \int J_0(\nu) d\nu
\end{equation}

\begin{equation}
\langle \Sigma : F_1^2 \rangle_{AV} = \int J_1(\nu) d\nu
\end{equation}

\begin{equation}
\langle \Sigma : F_2^2 \rangle_{AV} = \int J_2(\nu) d\nu
\end{equation}
The transition probability per unit time caused by these lattice fluctuations, in the case of spin 1/2 particles, can be computed as

\[(A-1.38)\quad P = (9/16)\gamma^4 h^2 [J_1(\nu) + J_2(2\nu)]\]

Though the probability for upward and downward transitions are the same, the overall transition probability for \(\uparrow\rightarrow\downarrow\) transition and \(\downarrow\rightarrow\uparrow\) transition has to be weighted by the respective Boltzmann factors as required by the principle of detailed balance, from which

\[(A-1.39)\quad N_+ P_+ = N_- P_-\]

where

\[(A-1.40)\quad P_{+-} = P \exp(-\gamma\hbar H_0/2kT) ; P_{-+} = P \exp(+\gamma\hbar H_0/2kT)\]

Though this condition is strictly valid only under thermal equilibrium, as long as \(kT >> \gamma\hbar\), this condition can be assumed to be valid even if the spin system is not in thermal equilibrium with the lattice. Therefore, in the high temperature approximation, equation (A-1.40) can be written as

\[(A-1.41)\quad P_{+-} \equiv P [1-(\gamma\hbar H_0/2kT)] ; P_{-+} \equiv P [1+(\gamma\hbar H_0/2kT)]\]

Recalling equations (A-1.23) through (A-1.25), in the absence of the perturbing r.f. field we can write,
Defining the equilibrium population difference \( n = \frac{N_{2}h\mathcal{H}}{kT} \) under the high temperature approximation and substituting the appropriate expression for \( P_{-} \) and \( P_{-} \) from equation (A-1.41), we can express the rate at which the population difference between the two energy levels changes in time as

\[
\frac{dn}{dt} = 2N_{-}P_{-} - 2N_{+}P_{+}
\]

from which we see that the spin population difference attains its equilibrium value by following a simple exponential law with a characteristic time constant given by

\[
T_{1} = \frac{1}{2P}
\]

Thus the general formula for the spin-lattice relaxation time in the case of spin-1/2 particles can be written as

\[
(1/T_{1}) = \frac{9}{8} \gamma^{2} \hbar^{2} [J_{1}(v) + J_{2}(2v)]
\]

From (A-1.35) the spectral density function can be expressed in a general form as
with \( \omega = 2nv \). Thus, the spin-lattice relaxation time can be expressed in terms of the spectral density functions as

\[
\frac{1}{T_1} = \left( \frac{9}{8} \right) \frac{4\hbar^2}{h} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \right]
\]

Effect of motions on the linewidth:

The equation for the spin-spin relaxation time \( T_2 \) expressed in (A-1.32) is for the rigid lattice and we should reconsider this equation in the presence of the molecular motions. Clearly, the space dependent term in equation (A-1.32) must be replaced by its ensemble average and from the definition of \( J (\nu) \) given in equation (A-1.37a), this ensemble average can be written as

\[
\langle \sum : (1-3\cos^2 \Theta_i(t) \tau_i^3(t) : \rangle_{\text{AV}} = \int J_o(\nu) d\nu
\]

Taking into account the effect of motion, equation (A-1.32) can be modified to express the spin-spin relaxation time as [Bloembergen et al., 1948]
The time modulation of the terms C to F limits the lifetime of the spins in any given energy state and this also contributes to the broadening of the line. In principle, the broadening of the line due to this effect also should be included in determining the overall broadening of the line but in solids where the spin-lattice relaxation time $T_1$ is much larger than the spin-spin relaxation time $T_2$ this effect is negligible. Using equation (A-1.35) we can rewrite equation (A-1.50) as

\begin{equation}
\frac{1}{T_2} = \frac{3}{2} \gamma^2 \hbar \left[ I(I+1) \right]^{1/2} \left[ \int \frac{J_0(n \nu) \, d\nu}{1 + 4 \pi^2 \nu^2 \tau^2_c} \right]^{1/2}
\end{equation}

The limits of the above integral have to be restricted to $(-1/\pi T_1, 1/\pi T_1)$ as terms A and B will represent secular perturbations only when the contribution from $J(\nu)$ is confined to the components which are within the actual width caused by the perturbation. It can be seen that equation (A-1.51) can be recast into

\begin{equation}
\left( \frac{1}{T_2} \right)^2 = C_1 \tan^{-1} \left( \frac{2 \tau_c}{T_2} \right)
\end{equation}

by evaluating the integral within the above said limits. The constant $C_1$ contains the prefactors shown in equation (A-1.51) apart from the value of $|F|$ for the specific case. The general dependence of the spin-spin relaxation time on the correlation time $T$ can be seen from (A-1.52), which shows that for very small $T$, $1/T$ is proportional to $\tau_c$ and with
increasing $T$, $T$ decreases. In fact when $x/T \approx 1$, $T$ reaches its asymptotic value of $T'$ where $T'$ is the spin-spin relaxation time corresponding to the rigid-lattice line width, and $T$ remains at that value with further increase in $x$. Therefore it is seen that the presence of thermally activated motions decreases the linewidth as the line broadening terms get time averaged to a smaller value, and this is referred to as motional narrowing.

Homogeneous and Inhomogeneous broadening:

An important distinction needs to be made in the way the A term and B term contribute to the line broadening. In one case the broadening of the spectral line arises due to the spatial distribution of the spins aligned either parallel or antiparallel to the Zeeman field since this makes the local field felt by any nucleus to be different from site to site and this broadening effect is referred to as inhomogeneous broadening. Term A corresponds to this kind of broadening effect. It is also to be noted that the inherent inhomogeneity present in the Zeeman field also contributes to the inhomogeneous broadening. On the other hand, the finite transition probability provided by the term B for the mutual flipping of a spin pair contributes to the line broadening by making the life time of any given spin pair in their respective energy levels finite. This effect is felt to be the same in intensity on an average by any given spin pair and does not depend on the spatial distribution of any quantity, leading to homogeneous broadening. This difference between term A and B is also brought out by the fact that, even if the spins are not identical, the local field distribution will remain as it was for the
case of identical spins, but term B will not be able to cause the mutual spin-flip between any two non-identical nuclei as this transition does not conserve the total energy of the spin system. Thus its contribution to the broadening by way of limiting the lifetime of the spins in their respective energy states will not be present. An imaginative experiment reported by BPP brings out this difference clearly and this is referred to as the "hole burning" experiment. In recording the absorption spectrum in the frequency domain, the Zeeman field is scanned slowly between two limiting values with a fixed frequency r.f. field and for each quasi-static value of the Zeeman field the absorption is detected as a change in the susceptibility of the sample coil. Instead, if the Zeeman field is fixed at some value within the absorption curve and the r.f. power at a particular frequency within this time is made sufficiently large and after some time if the absorption curve is traced in the regular manner, a "hole" is created in the absorption curve, corresponding to the value of the field value where it was held constant for some time if the line is inhomogeneously broadened. This is because in the case of an inhomogeneously broadened absorption line, only a pocket of spins among all experience a total Zeeman field equal to the value at which the field was locked and only these spins are saturated with prolonged exposure to the r.f. radiation. When the scan of the field is resumed the spin pocket corresponding to this Zeeman field does not have any excess spin in the lower energy state and thus shows zero absorption intensity for this value of H. If the line was homogeneously broadened on the other hand, the increased intensity of r.f. field would have saturated all the spins in the system, as, on an average all the spins in the system experience a Zeeman field of a given value and as consequence

24
one would observe the entire absorption line to saturate. Thus burning a hole in the spectral line is a clear confirmation of the inhomogeneous broadening present in the system.

To summarize, BPP theory provides the necessary expressions for the spin-lattice and spin-spin relaxation time constants expressed in terms of the microscopic variables by treating the dipolar interaction Hamiltonian as a perturbation on the Zeeman Hamiltonian. Part of this Hamiltonian accounts for the broadening of the energy levels and the time dependence of this Hamiltonian brought about by molecular motions leads to spin-lattice relaxation in the system. Since molecular motions are thermally activated, they are stochastic processes in time and they are characterized by a correlation time $T_\tau$, and it is shown that $T$ and $T_\tau$ depend on $T$. The correlation function, being a measure of the randomness of the dynamics concerned, is dependent on temperature and a systematic observation of spin-lattice and spin-spin relaxation times as a function of temperature provides us with the necessary qualitative and quantitative information on all the relevant dynamic processes.

BPP theory is valid within the purview of the assumptions made in the beginning and its treatment is semiclassical to the extent that the spin part of the dipolar Hamiltonian is treated as quantum mechanical whereas the space part is treated as due to strictly classical random variables. This is enabled by the fact that the dipolar Hamiltonian is expressible as

$$(A-1.53) \quad \mathcal{H}_{SL} = (1/2) \sum_j \sum_k \sum_{q=-2}^2 A_{jk}^{(q)} F_{jk}^{(q)}$$
where $\text{A} - \text{s}$ are the spin functions expressed exclusively in terms of the spin operators, whereas $\text{F} - \text{s}$, the lattice functions, are expressed in terms of the lattice variables $r, \theta$ and $\phi$, which are the ones to pick up the random correlation brought about by the thermal motions. For instance, in Bloch-Wangsness-Redfield theory, this problem is treated differently in that the entire spin system is represented in terms of its density matrix which is subject to both the necessary ensemble and quantum mechanical averaging. But all these microscopic theories address to the general problem of arriving at a rate equation similar to the macroscopic equations of Bloch, from which the respective relaxation rates are naturally derived.

**Method of Moments by Van Vleck:**

In pulsed experiments, we saw that if a perturbing r.f. field whose frequency is equal to $-\gamma H$ is applied suddenly then the magnetization $M$ precesses about this field $H$ and it subtends an angle $90$ with respect to this perturbing field. In contrast, if we apply a very weak, oscillating field with a variable frequency $\omega$ scanned slowly through the spectral region it can be shown that under adiabatic fast passage conditions the magnetization $M$ is always aligned along an effective field $\frac{7}{2} H$ (which is equal to $\frac{1}{2} (\gamma H + [(\omega/\gamma) - H] > 0)$ and this is the basis of the CW experiments [Abragam, 1970; Slichter, 1978]. Here the magnetization induced by the applied field $H$ along X-axis is given by

\[
M_x = H_1 [\chi' (\omega) \cos \omega t + \chi'' (\omega) \sin \omega t ]
\]
where $x'$ and $\chi''$ define the susceptibility of the inductance coil containing the sample. The complex part of the susceptibility $\chi''$ is proportional to the rate of absorption of r.f. energy by the spin system and the real part $\chi'$ gives the dispersion due to the sample, and these are related through Kramers-Kröning equations [Abragam, 1970]. By defining a quantum mechanical operator $M$ corresponding to the X-axis magnetization, a density operator $\rho$ for the ensemble of spins in the sample, and a correlation function $G(t)$, one can derive an expression for the complex part of the susceptibility $\chi''$ as [Abragam, 1970, chap.IV]

\begin{equation}
(A-1.55) \\
\chi''(\omega) = \frac{i \omega V}{kT (2I+1)} \int_0^\infty \cos \omega t' G(t') \, dt'
\end{equation}

Here, $G(t) = \text{trace}(M(t)M^\dagger)$ and $M(t) = e^{iHt}M e^{-iHt}$. $H$ corresponds to the equilibrium Hamiltonian, prior to the application of the perturbing field in the XY plane. Expanding $G(t)$, $\chi''$ can be expressed as

\begin{equation}
(A-1.56) \\
\chi'' = \frac{2\pi \omega V}{(2I+1) 4kT} \sum_{n,n'} |\langle n : M_x^n : n' \rangle|^2
\end{equation}

where the summation is taken only over states which defer in energy $|E_n - E_{n'}| = \hbar \omega$. It is desirable to know $M_x(t)$ so that the complex susceptibility can then be calculated. From the definition of $\chi''(\omega)$, it is clear that the complex susceptibility is proportional to the shape function or absorption curve $f(\omega)$. With the presence of dipolar interaction $M(t)$ obeys the rate equation (Heisenberg picture)

\begin{equation}
(A-1.57) \\
(1/k) \frac{dM_x}{dt} = [H_x + H_1, M_x(t)]
\end{equation}
and in the interaction picture,

\[ \frac{d\hat{M}_x}{dt} = [e^{-i\hat{H}_z t} \hat{H}_1 e^{i\hat{H}_z t}, \hat{M}_x] \]

where \( M \) is given by \( e^{iH_z M e^{iH_z}} \). Choosing a set of basis states of \( h\mathcal{X} \), labelled as \( |E_s\rangle \), where \( s \) is the quantum number to distinguish between the various states of the same energy \( E \), we can write equation (A-1.58) in the matrix form as

\[ (A-1.59) \]

\[ \frac{1}{11} \frac{d}{dt} \langle E'_s | \hat{M}_x | E'_s \rangle = \sum_s \left[ e^{-i(E'_s - E_s) t} \langle E'_s | \hat{H}_1 | E'_s \rangle \langle E'_s | \hat{M}_x | E'_s \rangle \right] 
- \left[ e^{-i(E'_s - E'_s) t} \langle E'_s | \hat{M}_x | E'_s \rangle \langle E'_s | \hat{H}_1 | E'_s \rangle \right] \]

From (A-1.58), we see that in the absence of the perturbation \( \mathcal{H} \), \( \frac{dM}{dt} \) is zero and thus with the inclusion of a small perturbation like \( \mathcal{H} \), the variation of \( M_x \) must be slow, so, it is reasonable to assume that in equation (A-1.59), terms for which \( E' \neq E'' \) or \( E \neq E'' \) contribute a negligible amount to the above summation for small \( \mathcal{H} \). Thus \( (A-1.59) \) can be rewritten as,

\[ (A-1.60) \]

\[ \frac{1}{11} \frac{d}{dt} \langle E'_s | \hat{M}_x | E'_s \rangle = \sum_s \left[ \langle E'_s | \hat{H}_1 | E'_s \rangle \langle E'_s | \hat{M}_x | E'_s \rangle \right] 
- \left[ \langle E'_s | \hat{M}_x | E'_s \rangle \langle E'_s | \hat{H}_1 | E'_s \rangle \right] \]

This is equivalent to considering only those terms in the \( \mathcal{H} \) which are secular with respect to the Zeeman Hamiltonian \( \mathcal{H} \). This implies that
the truncated dipolar Hamiltonian which includes only the terms A and B must be included in the above equation and let this truncated Hamiltonian be denoted by $\mathcal{H}'$. Thus, solving for $M$ and in turn solving for $\chi'$ which is proportional to the shape function translates into finding out all the eigen states for the Hamiltonian,

$$h(\mathcal{H}_Z + \mathcal{H}_1') = \sum_j \mathcal{H}_Z^j + \sum_{j<k} g^2 a_{jk} + B_{jk}$$

(A-1.61)

The problem of finding the shape function leads to finding the complete set of eigen states of the Hamiltonian $\mathcal{H} = \mathcal{H} + \mathcal{H}_1'$, and since $\mathcal{H}'$ does not commute with $\mathcal{H}$ it is not possible to solve this problem exactly. Therefore, only certain statistical properties of the shape function can at best be estimated, involving only traces of relevant operators over these eigen states. In such a case a convenient method to calculate such moments of the distribution function, due to Van Vleck [1948], is very appropriate.

Definition:

For an absorption curve which is represented by a normalized symmetric function $f(\omega)$ with a maximum at $\omega = \omega_0$, the $n$ moment is defined by

$$M_n = \int (\omega - \omega_0)^n f(\omega) \, d\omega$$

(A-1.62)

If $f(\omega)$ is symmetric about $\omega$ all odd moments vanish. The shape function $f(\omega)$ is related to the correlation function $G(t)$ by
(A-1.63) \[ f(\omega) = \mathcal{A} \int_0^\infty G(t) \cos \omega t \, dt \]

and conversely,

(A-1.64) \[ G(t) = \frac{2}{\pi \mathcal{A}} \int_0^\infty f(\omega) \cos \omega t \, d\omega \]

Here \( A \) is given by the normalization of the function \( f(\omega) \). \( M(t) \) is given by \( M(t) = e^{-\mathcal{K}t} \) where, \( \mathcal{K} \) is given by

(A-1.65) \[ \mathcal{K}(t) = \mathcal{K}_Z + \mathcal{K}_1' \]

Substitution of this definition leads to

(A-1.66) \[ G_1(t) \cos \omega_0 t = \frac{2}{\pi \mathcal{A}} \int_{-\omega_0}^{\omega_0} f(\omega_0 + u) \cos(\omega_0 + u)t \, du, \]

where \( G(t) \) is called the reduced correlation function, given by

(A-1.67) \[ G_1(t) = \text{tr} \{ e^{i\mathcal{K}_1't} M e^{-i\mathcal{K}_1't} \} \]

Let us also define \( h(u) = f(\omega + u) \) and utilizing the fact that the shape function is a sharp enough line, one can show that

(A-1.68) \[ G_1(t) = \frac{2}{\pi \mathcal{A}} \int_{-\infty}^{\infty} h(u) \cos ut \, du \]

and the various even moments of the absorption curve are defined by
Expanding $G(t)$,

\begin{equation}
G_1(t) = \frac{2}{\pi A} \int_{-\infty}^{\infty} h(u) \left[ 1 + \frac{u^2 t^2}{2!} \right] \, du
\end{equation}

\begin{equation}
= \frac{2}{\pi A} \left[ \int h(u) \, du + \frac{t^2}{2!} \int u^2 h(u) \, du + \ldots \right]
\end{equation}

\begin{equation}
= \frac{2}{\pi A} \left[ 1 + \frac{t^2}{2!} M_2 + \frac{t^4}{4!} M_4 + \ldots \right]
\end{equation}

Thus the function $G(t)$ can be derived to different \textit{approximations} by including more terms. From the definition of $G(t)$, the moments can also expressed as,

\begin{equation}
M_{2n} = (-1)^n \frac{(1/2)^n}{n!} \pi A \frac{d^{2n} G_1(t)}{dt^{2n}} \bigg|_{t=0}
\end{equation}

It can be shown that at $t = 0$

\begin{equation}
\frac{d^p G_1(t)}{dt^p} = (i)^p \text{tr} \left[ \left[ [H_1', [H_1', [\ldots, [H_1', M_x] \ldots]] M_x \right] \right]
\end{equation}

The advantage of the method of moments is the fact that the trace in the above given formula is independent of the specific basis set within the
vector space in which one evaluates them. Thus one can evaluate the
moments in a representation where the values of \( m_j = \frac{J_j}{Z} \) of the individual
spins are good quantum numbers, thus circumventing the insoluble problem
of finding all the eigen states \( |n> \) of the total Hamiltonian.

From the above the second and fourth moments can be expressed for
instance as

\[
M_2 = - \frac{\text{tr} \{ [H', I_x]^2 \}}{\text{tr} \{ I_x^2 \}}
\]

and

\[
M_4 = \frac{\text{tr} \{ [H', [H', I_x]]^2 \}}{\text{tr} \{ I_x^2 \}}
\]

From (A-1.75) and (A-1.76) it can be deduced that any interaction which
commutes with \( I_x \) does not contribute to the second or the fourth moment
and in fact such a term in the Hamiltonian will not contribute to the
higher order moments as well.

Expression for \( M \):

Substituting the appropriate expression for the truncated
Hamiltonian given by (A-1.65) in terms of \( A \) and \( B \), the second moment of
the absorption curve for a crystalline lattice is derived to be
For a polycrystalline compound which has a uniform angular distribution of crystallites in space, \( M_2 \) is given by

\[
M_2 = \frac{(3/4) \gamma^4 h^2 I(I+1) \sum_k (1-3\cos^2 \theta_{jk})}{r^6_{jk}}
\]

These are the well known Van Vleck's formulae for the second moment. From (A-1.75) and (A-1.76) it can be deduced that any interaction which commutes with \( I_x \) does not contribute to the moments. Since \( M_2 \) varies as \( 1/r \), it is sufficient to consider the nearest neighbours in evaluating the lattice sum, and one can calculate \( M_2 \) knowing the specific information on a given crystal structure. For instance, in the case of a simple cubic lattice and a polycrystalline compound, \( M \) is given by

\[
M_2 = \frac{(3/5) \gamma^4 h^2 I(I+1) \sum_k 1}{r^6_{jk}}
\]

where \( d \) is the lattice constant.

Since the moments are derived from the absorption curve, they should essentially reflect the dependence of the lineshape on temperature or changes in dynamic environment. The moments for any given system can be experimentally obtained by recording the absorption spectrum in the frequency domain and numerically calculating the moments adapting the
definition given in (A-1.62). Calculation of second moment as a function of temperature is a popular scheme to observe the effects of motions in solids, and $M$ values reflect the onset of different dynamic processes, both qualitatively and quantitatively, as a function of temperature. Starting from a sufficiently high temperature where the motions are very rapid, progressive cooling of the sample may lead to freezing of different motions in a specific sequence, and $M_\omega$ measured as a function of temperature develops a step like structure for every motion which undergoes a linewidth transition given by the condition $\omega T = 1$ where $\omega$ is the dipolar linewidth of the absorption curve. Another advantage of measuring $M$ to observe the dynamical changes is the fact that $M_\omega$ is a very sensitive function of the shape function values which are far away from the central frequency of the absorption curve, and small changes in the lineshape which may not reflect to a great extent in the linewidth will also affect $M_\omega$ considerably. In some favourable cases, knowledge of $M_\omega$ provides with the information about the inter-nuclear distances also, and in fact by measuring $M$ in a single crystal, Van Vleck formula can be conveniently used to estimate the inter nuclear distances.

Relaxation in Solids:

Here we shall attempt to provide a general scheme to adapt the results of BPP theory to the case of solids. The expression for the spin-lattice relaxation rate ($\text{spin-1/2 particles}$) is given by
Normally, the dynamics in the solids are thermally activated and these Arrhenius processes have temperature dependent $T$ given by

\[
\text{(A-1.80)} \quad \frac{1}{T_1} = \left(\frac{9}{8}\right) \gamma^4 R^2 \left( \frac{\langle |F_1|^2 \rangle_{\text{AV}}}{1 + \omega^2 \tau_c^2} \right) + \left( \frac{\langle |F_2|^2 \rangle_{\text{AV}}}{1 + 4\omega^2 \tau_c^2} \right)
\]

where $E$ is the activation energy associated with this process. A random fluctuation, especially in a solid, can be thought of as a jump process where a given molecular group jumps from one equivalent orientation to another. In a solid all the atoms are subjected to the electrostatic potentials created by the presence of the next of the atoms, and a given orientation in which a molecule exists is its "equilibrium" configuration. But, conducive to the overall structure of the solid, a molecule may have more than one such "equilibrium" orientation but it costs energy for the molecule to change itself from one such orientation to the other as it has to cross a hindering potential barrier. The size of the potential barrier the molecular group may have to overcome depends on the surrounding molecular groups at a given site. Depending on the availability of kinetic energy to the rotational, vibrational and translational degrees of freedom, the molecule may reorient from one equilibrium position to another frequently or rarely, and the correlation
time in this context can be thought of as the average dwell time in a given equilibrium orientation. Considering all such processes being inherently stochastic, the probability of occupancy quantified by such 'dwell' times can be expressed by eqn. (A-1.81). In this context, $E$ is the hindering potential a given group has to overcome and $\tau$ is a prefactor formally corresponding to the correlation time at infinite temperature ($T$ indicates the extent to which the molecular group couples with the available thermal energy spectrum or phonons).

Often, the problem of arriving at an expression for the spin-lattice relaxation rate is reduced to finding out the ensemble average of the lattice functions $F_i$. In view of the present investigations on the reorientational dynamics of groups like $(\text{CH}_3)_3\text{N}^+$, $(\text{CH}_3)_3\text{NH}^+$, $(\text{CH}_3)_2\text{NH}_2^+$, $(\text{CH})\text{NH}$, $\text{NH}$ and $\text{CH}$, one focuses on molecular dynamics of symmetric groups in solids.

Such random motions in molecular solids with symmetric groups often involve discrete rotational motion about different symmetric axes, and so the problem of performing such ensemble averages corresponds in solids to building suitable stochastic models taking care of these motions over the intermolecular potential barriers. All these molecular groups have one or more axes of symmetry about which "reorientation" or a "rotational jump" can take place between a few well defined positions. For instance, in the case of $\text{CH}_n$ groups, there is one 3-fold axis of symmetry and the $\text{CH}_3$ group has three well defined positions at which the potential felt by the molecule is minimum. The hindering potential that the molecule has to overcome to jump from one position to the other is then given by the
activation energy $E$ (Eqn. A-1.81).

Depending on the complexity of a given molecular group we can have reorientation of the group as a whole as well as internal reorientations within the molecule of smaller constituent groups. A typical example is that of the trimethylammonium cation where reorientation of the entire cation takes place about the triad axis passing through the N-H bond, and methyl group reorientations about their 3-fold axes about the bond connecting the C and N atoms can also take place. For this kind of groups, where the number of orientations are limited, we can assign an occupational probability $p$ for a given pair of positions "$ij$" and our intention is to consider a given pair of nuclei at a time. We also note that it is the modulation of the dipolar interaction among each individual pairs of spins that is responsible for the relaxation.

We can write a rate equation for the probability of each possible pair of sites and it can be shown that this rate consists of an inward flux into the given site $ij$ which is proportional to the occupational probabilities of the other pairs, and has an outward flux which is proportional to the occupational probability of pair $ij$ itself. An illustrative form of such an equation can be given as

\[
\frac{dp_{ij}}{dt} = -R^{ij} p_{ij} + \sum_{l \neq ij} R^{lm} p_{lm}
\]

(A-1.82)

Here, $R$ refers to the rate of reorientation of given rotational jump...
process and in principle R can contain the sum of reorientational rates corresponding to some internal motions mentioned above. By symmetry considerations the number of these equations can be restricted and by a proper recombination of variables, these coupled equations can be separated and solved. Even without getting into the finer details, the functional form of these equations suggest that the probabilities are going to be exponentially decaying functions of time with the preexponential factors given by the combination of the relevant reorientation rates.

Once we are equipped with the solution to these rate equations, it is in principle simple to connect these probabilities to the relaxation rates. From BPP theory, it is established that the relaxation rate is given by

\[ 1/T_1 = (9/8) \gamma^4 h^2 [J_1(\omega) + J_2(2\omega)] \]  

(A-1.83)

\[ j^\mu(\omega) = \int_{-\infty}^{\infty} G^\mu(t) e^{i\omega t} \, dt \]  

(A-1.84)

where \( G(t) \) is the correlation function of the relevant lattice function \( F \) given by \( \langle F_{ij}(0) F_{ij}(\tau) \rangle \). In the present case this average corresponds to the averaging of the function \( F \) over all the possible equivalent sites \( ij \). It can be stated as

\[ G^\mu(\tau) = \sum_{ij} \langle F_{ij}^\mu F_{ij}(\tau) \rangle_{AV} \]  

(A-1.85)

Now for each \( ij \), we can show that
and thus we can substitute the expressions for \( p_i \)'s we have obtained into the above equation.

With the relevant crystal structure data on a given molecular group, we can actually evaluate terms like \( |F_{ij}|^2 \) or \( F_{ij}^* F_{lm} \), in equation (A-1.86) to get the necessary relaxation constants. What we have outlined here is a brief summary of a general procedure for the computation of the relaxation rate in the case of symmetric molecular group reorientations applicable to the type of solids we have investigated. In latter sections, relevant dynamic models are discussed in order to obtain formulae for spin lattice relaxation rates appropriate for the particular type of molecular groups studied thereof.
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