

A Primer in Nuclear Magnetic Relaxation in Liquids

**By
Nagarajan Murali**

A Primer in Nuclear Magnetic Relaxation is an article based on classic texts in NMR. Contents were developed during a series of lectures given by the author at the National High Magnetic Field Laboratory in early 1996. This article in this present form was edited with the help of Dr. V. V. Krishnan at the Lawrence Livermore National Lab. Section 4 forms a part of a paper submitted recently to JMR. We plan to add examples with simulations soon.

Some of the books used as source of references are:

1. *Principles of Nuclear Magnetism*, A. Abragam, Oxford University Press, 1961.
2. *Principles of Magnetic Resonance*, C.P. Slichter, Springer-Verlag, New York, Heidelberg, Berlin, 1990 (3 edition).
3. *Rotation of Molecules and Nuclear Spin Relaxation*, H. W. Speiss, NMR Basic Principles and Progress (V15), 1978.
4. *High Resolution NMR in Solids (Selective Averaging)*, U. Haeberlen, Advances in Magnetic Resonance (Supplement 1), 1976.

We tried our best to maintain consistency please report any comments to the author at nmurali@magnet.fsu.edu.

A Primer in Nuclear Magnetic Relaxation in Liquids

Nuclear Magnetic Resonance (NMR) spectroscopy has proven to be a valuable technique to understand structure and dynamics of molecular systems. Its ability to yield such information in liquid state is remarkable that its development has been tremendous. The quest for understanding structure and dynamics of ever-larger molecules is pushing the technique to very high fields. Aside from benefits in terms of sensitivity and spectral spread, advantages stemming from relaxation effects at high fields are realized that would aid study of large molecules. It is now predicted that at greater than 1GHz Larmor frequency a 300-kDa protein could yield intelligible spectra and become amenable for study by NMR. Such advantages have been realized by applying relaxation theories, known since the advent of NMR, to systems of such sizes and field strengths.

It is needless to mention that the theory of NMR relaxation in liquids is well established and there exists several classic treatises. It is, however, worthwhile to make a note that while the description of the relaxation theories are no doubt correct their results often focus on a particular situation termed as extreme narrowing limit. It is well known that extreme narrowing limit is valid for small molecules in a very fast motional regime. It is also well known by now that negligible effects in this extreme narrowing limit become discernable in NMR spectrum of macromolecules in slow motion limit. Considering the current trend in NMR applications to larger systems at very high fields, it is thus essential to focus at a general formulation that would cover a wide range of experimental situations. Also, it is worthwhile to point out that there is a wide range of notations used in literature rendering comparison of the same parameter in two different articles often less straightforward.

This article attempts to lay out the well-known relaxation theory from first principles and develop a consistent methodology that can be used for all molecular sizes and motional regimes. This article is intended as a concise source for fresh researchers interested in learning relaxation aspects in NMR. The authors would also like to stress that no originality is claimed in laying out the theory, but care is taken to present a formulation with consistent notation.

The sections are arranged in the following order. In section 1 we derive the Master equation that governs the relaxation in liquids in the density matrix format leading to the famous Redfield relaxation equation. In section 2 the master equation is cast in the operator form. Section 3 describes a general procedure to derive Hamiltonians for various interactions relevant in relaxation theories in liquids. In section 4 we derive correlation (both auto and cross correlation) functions including aspects describing the dynamics in the framework developed by Lipari and Szabo.

Relaxation of the nuclear spins in the solution-state is conveniently described by a semi-classical approach, in which the spins are treated as a quantum mechanical system, while the stochastic interactions of these spins to the lattice as a classical system. It is assumed that the lattice is at thermal equilibrium at all the times and coupled weakly to the spins through time-dependent interactions and hence let the spins to relax back to the required equilibrium Boltzmann distribution. These interactions are assumed to be stochastic (random) in nature and the time dependence is brought upon by the rotational Brownian motion of the molecules in liquid. Further the average over these time-dependent interactions at time lengths longer than the correlation time (time the molecule takes to perform a rotation by one radian) is zero. These sets of rules are rarely violated in the solution NMR spectroscopy and are generally applicable to most bio-molecular NMR experiments performed. Further, these sets of simplified condition draws the necessary framework to extract dynamics information from the various relaxation parameters by using basic equations of quantum mechanics and straightforward analytical methods such as Fourier transform. Bloch first presented a spin relaxation theory in 1946, based on the phenomenological approach in which the behavior of the spin-system is characterized by two rate constants, spin-lattice (T_1) and spin-spin (T_2) relaxation times. In the method proposed by Bloembergen, Purcell and Pound, known as the BPP theory the spin relaxation times are

related to the lattice through molecular motions. Further refinement of the BPP theory finally led to the current general method to describe relaxation of nuclear spins, commonly referred to as Bloch, Wangness and Redfield (BWR) theory.

1. Master Equation for Density Matrix – Redfield Equation

Nuclear spins can be described by a quantum statistical approach in which the ensemble of spins will be considered. Describing the equation of motion by the density matrix will enable to understand the relaxation of the populations but also the various coherences that may be created in any experiment. Writing the fundamental Liouville equation of motion of the density operator σ ,

$$\frac{1}{i} \frac{d\mathbf{s}}{dt} = -[\mathbf{H}_0 + \mathbf{H}_1(t), \mathbf{s}]. \quad [1]$$

In order to remove the time dependence caused by $\mathbf{H}_I(t)$, transforming Eq.[1] to an interaction representation defined by,

$$\mathbf{s}^* = e^{i\mathbf{H}_0 t} \mathbf{s} e^{-i\mathbf{H}_0 t}, \mathbf{H}_1^*(t) = e^{i\mathbf{H}_0 t} \mathbf{H}_1(t) e^{-i\mathbf{H}_0 t}, \quad [2]$$

and rewriting Eq.[1]

$$\frac{1}{i} \frac{d\mathbf{s}^*}{dt} = -[\mathbf{H}_1^*(t), \mathbf{s}^*]. \quad [3]$$

To obtain a solution to Eq.[3], integrate by successive approximation up to second order yields,

$$\mathbf{s}^*(t) = \mathbf{s}^*(0) - i \int_0^t dt' [\mathbf{H}_1^*(t'), \mathbf{s}^*(0)] - \int_0^{t'} dt' \int_0^{t'} dt'' [\mathbf{H}_1^*(t'), [\mathbf{H}_1^*(t''), \mathbf{s}^*(0)]], \quad [4]$$

and then the time derivative is,

$$\frac{d\mathbf{s}^*}{dt} = -i[\mathbf{H}_1^*(t), \mathbf{s}^*(0)] - \int_0^t dt' [\mathbf{H}_1^*(t'), [\mathbf{H}_1^*(t'), \mathbf{s}^*(0)]], \quad [5]$$

and introducing $\mathbf{t} = t - t'$,

$$\frac{d\mathbf{s}^*}{dt} = -i[\mathbf{H}_1^*(t), \mathbf{s}^*(0)] - \int_0^t dt [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t - \mathbf{t}), \mathbf{s}^*(0)]]. \quad [6]$$

Since $\mathbf{H}_1^*(t)$ is a random function of time $\mathbf{s}^*(t)$ is also a random function. Then, an ensemble average of the density matrix is the only relevant only under the important set of assumptions,

(a) $\langle \mathbf{H}_1^*(t) \rangle = 0$ for all matrix elements $\langle \langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{b} \rangle \rangle$. If this is not valid the non-zero part can be added in to a redefined Hamiltonian $\hbar \mathbf{H}_0$.

(b) The correlation between $\mathbf{H}_1^*(t)$ and $\mathbf{s}^*(0)$ can be ignored in taking the ensemble average.

(c) $\mathbf{s}^*(0)$ can be replaced by $\mathbf{s}^*(t)$ on the right hand side of Eq. [6].

(d) The upper limit of integration can be extended to $+\infty$.

(e) The higher order terms can be neglected in Eq. [4].

Then Eq. [6] becomes,

$$\frac{d\mathbf{s}^*}{dt} = -\int_0^{\infty} dt \langle [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-t), \mathbf{s}^*(t)]] \rangle. \quad [7]$$

If we take matrix elements from Eq. [7] in the eigen basis of $\hbar\mathbf{H}_0$ with eigen values $\hbar\mathbf{a}, \hbar\mathbf{b}...$ then,

$$\frac{d\mathbf{s}_{aa'}^*}{dt} = -\int_0^{\infty} dt \langle \mathbf{a} | [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-t), \mathbf{s}^*(t)]] | \mathbf{a}' \rangle. \quad [8]$$

Let us evaluate the right hand side of Eq. [8]

$$\begin{aligned} [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-t), \mathbf{s}^*(t)]] &= \mathbf{H}_1^*(t)\mathbf{H}_1^*(t-t)\mathbf{s}^*(t) \\ &\quad + \mathbf{s}^*(t)\mathbf{H}_1^*(t-t)\mathbf{H}_1^*(t) \\ &\quad - \mathbf{H}_1^*(t-t)\mathbf{s}^*(t)\mathbf{H}_1^*(t) \\ &\quad - \mathbf{H}_1^*(t)\mathbf{s}^*(t)\mathbf{H}_1^*(t-t). \end{aligned} \quad [9]$$

$$\begin{aligned}
\langle \mathbf{a} | [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-t), \mathbf{s}^*(t)]] | \mathbf{a}' \rangle = & \\
& \sum_{\mathbf{b}} \sum_{\mathbf{g}} \langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{g} \rangle \langle \mathbf{g} | \mathbf{H}_1^*(t-t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{a}' \rangle \\
& + \sum_{\mathbf{b}} \sum_{\mathbf{g}} \langle \mathbf{a} | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{H}_1^*(t-t) | \mathbf{g} \rangle \langle \mathbf{g} | \mathbf{H}_1^*(t) | \mathbf{a}' \rangle \\
& - \sum_{\mathbf{b}} \langle \mathbf{a} | \mathbf{H}_1^*(t-t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{H}_1^*(t) | \mathbf{a}' \rangle \\
& - \sum_{\mathbf{b}} \langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{H}_1^*(t-t) | \mathbf{a}' \rangle.
\end{aligned}
\tag{10}$$

$$\begin{aligned}
\langle \mathbf{a} | [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-t), \mathbf{s}^*(t)]] | \mathbf{a}' \rangle = & \\
& \mathbf{d}_{\mathbf{a}'\mathbf{b}} \sum_{\mathbf{b}} \sum_{\mathbf{g}} \langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{g} \rangle \langle \mathbf{g} | \mathbf{H}_1^*(t-t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \\
& + \mathbf{d}_{\mathbf{a}\mathbf{b}} \sum_{\mathbf{b}} \sum_{\mathbf{g}} \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{H}_1^*(t-t) | \mathbf{g} \rangle \langle \mathbf{g} | \mathbf{H}_1^*(t) | \mathbf{a}' \rangle \\
& - \sum_{\mathbf{b}} \langle \mathbf{a} | \mathbf{H}_1^*(t-t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{H}_1^*(t) | \mathbf{a}' \rangle \\
& - \sum_{\mathbf{b}} \langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{s}^*(t) | \mathbf{b} \rangle \langle \mathbf{b} | \mathbf{H}_1^*(t-t) | \mathbf{a}' \rangle.
\end{aligned}$$

[11]

Using the equality,

$$\begin{aligned}
\langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{b} \rangle &= \langle \mathbf{a} | e^{i\mathbf{H}_0 t} | \mathbf{a} \rangle \langle \mathbf{a} | \mathbf{H}_1(t) | \mathbf{b} \rangle \langle \mathbf{b} | e^{-i\mathbf{H}_0 t} | \mathbf{b} \rangle \\
&= \langle \mathbf{a} | \mathbf{H}_1(t) | \mathbf{b} \rangle e^{i(\mathbf{a}-\mathbf{b})t},
\end{aligned}
\tag{12}$$

and defining the correlation function as,

$$G_{\mathbf{a}\mathbf{b}\mathbf{a}'\mathbf{b}'}(t) = \langle \langle \mathbf{a} | \mathbf{H}_1(t) | \mathbf{b} \rangle \langle \mathbf{b}' | \mathbf{H}_1(t+t) | \mathbf{a}' \rangle \rangle
\tag{13}$$

Eq.[33] is rewritten as,

$$\frac{d\mathbf{S}_{aa'}^*}{dt} = \sum_{\mathbf{bb}} \left[\begin{array}{l} -\mathbf{d}_{a'b} \sum_{\mathbf{g}0} \int dt G_{\mathbf{g}\mathbf{g}}(t) e^{-i(\mathbf{g}-\mathbf{b})t} e^{i(\mathbf{a}-\mathbf{b})t} \mathbf{S}_{\mathbf{bb}}^*(t) \\ -\mathbf{d}_{ab} \sum_{\mathbf{g}0} \int dt G_{\mathbf{g}'\mathbf{g}'}(t) e^{-i(\mathbf{g}-\mathbf{b})t} e^{i(\mathbf{b}-\mathbf{a}')t} \mathbf{S}_{\mathbf{bb}}^*(t) \\ + \int_0^{\infty} dt G_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(t) e^{-i(\mathbf{a}-\mathbf{b})t} e^{i(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}')t} \mathbf{S}_{\mathbf{bb}}^*(t) \\ 0 \\ + \int_0^{\infty} dt G_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(t) e^{-i(\mathbf{a}'-\mathbf{b})t} e^{i(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}')t} \mathbf{S}_{\mathbf{bb}}^*(t) \\ 0 \end{array} \right]. \quad [14]$$

The symbol $\langle \rangle$ for the ensemble average has been dropped for convenience

Defining the spectral density functions as,

$$\begin{aligned} j_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(\mathbf{a}'-\mathbf{b}') &= \int_0^{\infty} dt G_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(t) e^{-i(\mathbf{a}'-\mathbf{b}')t} \\ &= \frac{1}{2} \int_{-\infty}^{\infty} dt G_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(t) \cos(\mathbf{a}'-\mathbf{b}')t - i \int_0^{\infty} dt G_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(t) \sin(\mathbf{a}'-\mathbf{b}')t \\ &= \frac{1}{2} J_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(\mathbf{a}'-\mathbf{b}') - i K_{a\mathbf{b}\mathbf{a}'\mathbf{b}'}(\mathbf{a}'-\mathbf{b}'). \end{aligned} \quad [15]$$

In Eq. [39] the real part yields the decay constants and the imaginary part give rise to a shift and is known as dynamic shift. The imaginary part, if not too small to neglect, can be included in a redefined unperturbed Hamiltonian $\hbar\mathbf{H}_0$. Thus Eq. [38] becomes,

$$\frac{d\mathbf{s}_{aa'}^*}{dt} = \sum_{\mathbf{bb}} \left[\begin{aligned} & \frac{1}{2} [-\mathbf{d}_{a'b} \sum_{\mathbf{g}} J_{\mathbf{g}\mathbf{g}}(\mathbf{g}-\mathbf{b}) e^{i(\mathbf{a}-\mathbf{b})t} \mathbf{s}_{\mathbf{bb}}^*(t) \\ & - \mathbf{d}_{ab} \sum_{\mathbf{g}} J_{\mathbf{g}\mathbf{g}'}(\mathbf{g}-\mathbf{b}') e^{i(\mathbf{b}'-\mathbf{a}')t} \mathbf{s}_{\mathbf{bb}}^*(t) \\ & + J_{\mathbf{aba}'\mathbf{b}}(\mathbf{a}-\mathbf{b}) e^{i(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}')t} \mathbf{s}_{\mathbf{bb}}^*(t) \\ & + J_{\mathbf{aba}'\mathbf{b}}(\mathbf{a}'-\mathbf{b}') e^{i(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}')t} \mathbf{s}_{\mathbf{bb}}^*(t) \end{aligned} \right]. \quad [16]$$

Introducing a compact notation Eq. [16] can be written as,

$$\frac{d\mathbf{s}_{aa'}^*}{dt} = \sum_{\mathbf{b},\mathbf{b}'} R_{aa'\mathbf{bb}'} e^{i(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}')t} \mathbf{s}_{\mathbf{bb}'}^*(t). \quad [17]$$

Where,

$$\begin{aligned} R_{aa'\mathbf{bb}'} = & \frac{1}{2} [J_{\mathbf{aba}'\mathbf{b}}(\mathbf{a}'-\mathbf{b}') + J_{\mathbf{aba}'\mathbf{b}}(\mathbf{a}-\mathbf{b}) \\ & - \mathbf{d}_{a'b} \sum_{\mathbf{g}} J_{\mathbf{g}\mathbf{g}}(\mathbf{g}-\mathbf{b}) \\ & - \mathbf{d}_{ab} \sum_{\mathbf{g}} J_{\mathbf{g}\mathbf{g}'}(\mathbf{g}-\mathbf{b}')]. \end{aligned} \quad [18]$$

Eq. [17] is known as the Redfield relaxation equation and the rate constants in Eq. [18] are the elements of the Redfield relaxation matrix. In Eq. [17] replacing $\mathbf{s}^*(t)$ by $\mathbf{s}^*(t) - \mathbf{s}^0$ we get,

$$\frac{d\mathbf{s}_{aa'}^*}{dt} = \sum_{\mathbf{b},\mathbf{b}'} R_{aa'\mathbf{bb}'} e^{i(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}')t} (\mathbf{s}_{\mathbf{bb}'}^*(t) - \mathbf{s}_{\mathbf{bb}'}^0). \quad [19]$$

The most significant terms valid for well resolved lines, is obtained from Eq [19] by using the secular approximation $(\mathbf{a}-\mathbf{b}+\mathbf{b}'-\mathbf{a}') = 0$,

$$\frac{d\mathbf{s}_{aa'}^*}{dt} = \sum_{\mathbf{b}, \mathbf{b}'} R_{aa'\mathbf{b}\mathbf{b}'} (\mathbf{s}_{\mathbf{b}\mathbf{b}'}^*(t) - \mathbf{s}_{\mathbf{b}\mathbf{b}'}^0). \quad [20]$$

The summation \sum' is to states of energies that satisfy the secular condition.

2. Master Equation in the Operator Form

We start from Eq.[7] again

$$\frac{d\mathbf{s}^*}{dt} = -\int_0^\infty dt \langle [\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-t), \mathbf{s}^*(t)]] \rangle. \quad [21]$$

The random Hamiltonian may be written as,

$$\mathbf{H}_1(t) = \sum_q (-1)^q F_q A_{-q}, \quad [22]$$

so that, $F_q^* = (-1)^q F_{-q}$ and $A_q^\dagger = (-1)^q A_{-q}$. We will explain in the next section the significance of expressing the Hamiltonian in this form. Also introducing the correlation function and the spectral density as,

$$\begin{aligned} g_{qq'}(t) &= \langle F_q(t) F_{q'}^*(t+\mathbf{t}) \rangle = \langle F_q(t) F_{q'}^*(t-\mathbf{t}) \rangle, \\ J_{qq'}(\mathbf{w}) &= \int_{-\infty}^{\infty} g_{qq'}(\mathbf{t}) e^{-i\mathbf{w}\mathbf{t}} d\mathbf{t}, \\ j_{qq'}(\mathbf{w}) &= \int_0^{\infty} g_{qq'}(\mathbf{t}) e^{-i\mathbf{w}\mathbf{t}} d\mathbf{t}. \end{aligned} \quad [23]$$

Using the transformations,

$$\begin{aligned}
e^{i\mathbf{H}_0 t} A_q e^{-i\mathbf{H}_0 t} &= \sum_p A_{p,q} e^{i\mathbf{w}_{p,q} t}, \\
e^{i\mathbf{H}_0 t} A_{-q} e^{-i\mathbf{H}_0 t} &= \sum_p A_{p,-q} e^{i\mathbf{w}_{p,-q} t}, \\
\mathbf{H}_1^*(t) &= e^{i\mathbf{H}_0 t} \mathbf{H}_1(t) e^{-i\mathbf{H}_0 t} = \sum_{q,p} (-1)^q F_q A_{p,-q} e^{i\mathbf{w}_{p,-q} t},
\end{aligned}$$

[24]

and substituting Eq. [24] in Eq. [21],

$$\frac{d\mathbf{s}^*}{dt} = - \sum_{q,q',p,p'} (-1)^{q+q'} e^{i(\mathbf{w}_{p,-q} + \mathbf{w}_{p',-q'})t} [A_{p,-q}, [A_{p',-q'}, \mathbf{s}^*(t)]] \int_0^\infty \langle F_q(t) F_{q'}(t-\mathbf{t}) \rangle e^{-i\mathbf{w}_{p,-q} \mathbf{t}} d\mathbf{t}.$$

[25]

using the secular approximation by setting $\mathbf{w}_{p',-q'} = -\mathbf{w}_{p,-q}$, i.e $q' = -q$, & $p' = p$,

$$\begin{aligned}
\frac{d\mathbf{s}^*}{dt} &= - \sum_{q,p} [A_{p,-q}, [A_{p,q}, \mathbf{s}^*(t)]] \int_0^\infty \langle F_q(t) F_{-q}(t-\mathbf{t}) \rangle e^{-i\mathbf{w}_{p,q} \mathbf{t}} d\mathbf{t}, \\
&= - \sum_{q,p} [A_{p,-q}, [A_{p,-q}^\dagger, \mathbf{s}^*(t)]] \int_0^\infty \langle F_q(t) (-1)^q F_{-q}(t-\mathbf{t}) \rangle e^{-i\mathbf{w}_{p,q} \mathbf{t}} d\mathbf{t} \\
&= - \sum_{q,p} [A_{p,-q}, [A_{p,-q}^\dagger, \mathbf{s}^*(t)]] \int_0^\infty g_q(\mathbf{t}) e^{-i\mathbf{w}_{p,q} \mathbf{t}} d\mathbf{t}
\end{aligned}$$

[26]

$g_q(\mathbf{t})$ is a real and even function of \mathbf{t} , and

$$\begin{aligned}
\int_0^\infty g_q(\mathbf{t}) e^{-i\mathbf{w}_{p,q} \mathbf{t}} d\mathbf{t} &= \frac{1}{2} \int_{-\infty}^\infty g_q(\mathbf{t}) \cos(\mathbf{w}_{p,q} \mathbf{t}) d\mathbf{t} - i \int_0^\infty g_q(\mathbf{t}) \sin(\mathbf{w}_{p,q} \mathbf{t}) d\mathbf{t} \\
&= \frac{1}{2} J_q(\mathbf{w}_{p,q}) - i K_q(\mathbf{w}_{p,q}).
\end{aligned}$$

[27]

The second term in Eq. [27] gives rise to dynamic frequency shift and can be treated as stated before. Then the master equation in the operator form is,

$$\frac{d\mathbf{s}^*}{dt} = -\frac{1}{2} \sum_{q,p} J_q(\mathbf{w}_{pq}) [A_{p,-q}, [A_{p,-q}^\dagger, \mathbf{s}^*(t)]]]. \quad [28]$$

Macroscopic Differential Equations

Let us derive an equation for the expectation value q^* of an observable defined by an operator Q where,

$$q^* = \langle Q \rangle = tr\{\mathbf{s}^*(t)Q\}. \quad [29]$$

Multiplying Eq. [28] on both sides by Q and taking trace,

$$\frac{dq^*}{dt} = -\frac{1}{2} tr\{ \sum_{q,p} J_q(\mathbf{w}_{pq}) [A_{p,-q}, [A_{p,-q}^\dagger, \mathbf{s}^*(t)]Q] \}. \quad [30]$$

Using the cyclic property of trace of an operators i.e., $tr\{[A,[B,C]]D\} = tr\{[B,[A,D]]C\}$,

$$\frac{dq^*}{dt} = -\frac{1}{2} tr\{ \sum_{q,p} J_q(\mathbf{w}_{pq}) [A_{p,-q}^\dagger, [A_{p,-q}, Q]]\mathbf{s}^*(t) \}. \quad [31]$$

Introducing,

$$\hat{A} = \frac{1}{2} \sum_{q,p} J_q(\mathbf{w}_{pq}) [A_{p,-q}^\dagger, [A_{p,-q}, Q]],$$

$$a^* = \langle \hat{A} \rangle^* = tr\{\hat{A}\mathbf{s}^*(t)\},$$

[32]

then Eq. [31] is,

$$\frac{dq^*}{dt} = -a^*. \quad [33]$$

With, $a_0 = \frac{1}{2} \text{tr} \{ \sum_{q,p} J_q(\mathbf{w}_{pq}) [A_{p,-q}^\dagger, [A_{p,-q}, Q]] \mathbf{s}_0 \}$, corresponding to the equilibrium density operator \mathbf{s}_0 , and replacing $\mathbf{s}^*(t)$ by $\mathbf{s}^*(t) - \mathbf{s}_0$, we get,

$$\frac{dq^*}{dt} = -(a^* - a_0). \quad [34]$$

Eq. [34] describes the slow variation q^* due to the coupling of the spins with the lattice.

Suppose if we want to know the motion of the longitudinal magnetization of a spin I, then $Q = I_z$ and $q^* = \langle Q \rangle = \langle I_z \rangle$. Then,

$$\frac{d\langle I_z \rangle}{dt} = -(a_z - a_0). \quad [35]$$

To evaluate the above equation all we have to compute is,

$$\hat{A} = \frac{1}{2} \sum_{q,p} J_q(\mathbf{w}_{pq}) [A_{p,-q}^\dagger, [A_{p,-q}, I_z]] \approx \frac{1}{T_1} I_z, \quad [36]$$

for a given relaxation mechanism. Substituting in Eq. [35],

$$\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1} \{ \langle I_z \rangle - \langle I_0 \rangle \}. \quad [37]$$

The above equation describes the time variation of $\langle I_z \rangle$ by a single exponential. This description is valid even for a system with two "like spins" (each having the same Larmor frequency) where $\langle I_z \rangle$ is replaced by $\langle I_z + S_z \rangle$.

Justifications for the assumptions

Several important assumptions were made in deriving the master equation in terms of the density matrix and in the operator form. These assumptions play the deciding role on the validity of the theory of nuclear spin relaxation and their applicability to specific spin systems of interest. These earlier said assumptions are justified as follows.

(a) $\langle \mathbf{H}_1^*(t) \rangle = 0$ for all matrix elements $\langle \langle \mathbf{a} | \mathbf{H}_1^*(t) | \mathbf{b} \rangle \rangle$. If this is not valid the non-zero part can be added in to a redefined Hamiltonian $\hbar \mathbf{H}_0$. The additional terms, also known as dynamic frequency shift are considered in detail later.

(b) The correlation between $\mathbf{H}_1^*(t)$ and $\mathbf{s}^*(0)$ can be ignored in taking the ensemble average.

For $t > t_c$, where t_c is the correlation time, the correlation between $\mathbf{H}_1^*(t - t)$ and $\mathbf{H}_1^*(t)$ is negligible and for $t > t$ the correlation between $\mathbf{H}_1^*(t)$ and $\mathbf{s}^*(0)$ is again negligible.

(c) $\mathbf{s}^*(0)$ can be replaced by $\mathbf{s}^*(t)$ in the rate Equations. The increase

$\{\mathbf{s}(t) - \mathbf{s}_0\} / \mathbf{s}_0 \approx t \langle |\mathbf{H}_1(t)|^2 \rangle t_c \ll 1$, thus $\mathbf{s}^*(0)$ can be replaced by $\mathbf{s}^*(t)$. The upper limit of integration can be extended to $+\infty$.

(d) The higher order terms can be neglected in Eq. [28]. Since $\left| \frac{A_n}{A_{n-1}} \right| \cong \left[\langle |\mathbf{H}_1|^2 \rangle t_c^2 \right]^{\frac{1}{2}} \ll 1$, for most relaxation mechanisms in NMR, contributions from higher order terms can be safely ignored.

3. Relaxation Hamiltonians

The purpose of this section is to introduce the various forms of interactions for the nuclear spins and their relevant Hamiltonians that become time dependent due to molecular motions leading to relaxation of nuclear spins to their thermal equilibrium state. It is very interesting to note that the most relevant nuclear magnetic interactions causing relaxation can be represented by a second rank tensor and a unified approach can be developed to describe them. Thus, once these Hamiltonians and their properties were properly formulated, calculating their contributions to the NMR spectrum can be greatly simplified.

Our goal, in this section, is to derive Hamiltonian in a general form for any relaxation mechanism as,

$$H(t) = \sum_q (-1)^q F_q(t) A_{-q}, \quad [38]$$

where, $F_q(t)$ is a function describing the time dependence of the space variables alone and A_{-q} 's are spin variables. In NMR the relevant range for q is from -2 to +2. It is particularly convenient to use this form as the transformation properties of Hamiltonians thus expressed will

follow the transformation properties of a second rank tensor under a unitary transformation given by,

$$\mathfrak{S}_\Omega T_{lm} \mathfrak{S}_\Omega^{-1} = \sum_{m'=-l}^l T_{lm'} \mathbf{D}_{m'm}^{(l)}(\Omega). \quad [39]$$

$\mathbf{D}_{mm'}^{(l)}(\Omega)$ is a component of the Wigner rotation matrix ($\mathbf{D}_{mm'}^{(l)}(\mathbf{a}, \mathbf{b}, \mathbf{g})$), where the coordinate of transformation is described by the Eulerian angles.

Any coupling between two vectors \mathbf{V} and \mathbf{U} can be described as,

$$\begin{aligned} H \sim \mathbf{V} \mathfrak{R} \mathbf{U} &= \sum_{\mathbf{a}, \mathbf{b}=x,y,z} V_{\mathbf{a}} R_{\mathbf{a}\mathbf{b}} U_{\mathbf{b}} \\ &= \sum_{\mathbf{a}, \mathbf{b}=x,y,z} R_{\mathbf{a}\mathbf{b}} T_{\mathbf{b}\mathbf{a}}. \end{aligned} \quad [40]$$

Where, \mathfrak{R} is a second rank Cartesian tensor. In Eq. [40], we have separated the vector components of \mathbf{V} and \mathbf{U} in terms of the dyadic $T_{\mathbf{b}\mathbf{a}}$ from the second rank coupling tensor with the elements $R_{\mathbf{a}\mathbf{b}}$. Equation [40] is to be expressed in terms of irreducible tensor operators. In order to achieve this goal we need to express the familiar spin operators (Cartesian or raising and lowering operators) and the coupling tensor in terms of components of irreducible tensors. For this, we will follow the approach laid out by Spiess.

Let us first consider the spin part to be expressed by $T_{\mathbf{b}\mathbf{a}}$. For a nuclear spin with spin angular moment I the irreducible tensor operator can have non-vanishing matrix elements only

for $l \leq 2I$. Thus for $I = \frac{1}{2}$, $l \leq 1$ and for $I > 1$ l can be 2 more leading to quadrupole moments and higher order moments. However, it is not necessary to consider any moments greater than 2, as they are of no practical importance in NMR.

For $l=0$, it is evident from Eq.[39] that the tensor component is a scalar and is rotationally invariant.

For $l=1$, the irreducible components for a spin I are,

$$\begin{aligned} T_{1\pm 1} &= V_{\pm 1} = \mp \frac{1}{\sqrt{2}} (I_x \pm iI_y), \\ T_{10} &= V_0 = I_0 = I_z. \end{aligned}$$

[41]

The linear combination of the Cartesian operators follows the transformation properties given by Eq. [39].

Now from irreducible tensor of rank 1, we can construct higher rank irreducible tensors by following the rule,

$$\begin{aligned} T_{l_1} \times T_{l_2} &= \sum_{L=|l_1-l_2|}^{l_1+l_2} T_L, \\ T_{LM} &= \sum_m (l_1 m l_2 M - m | l_1 l_2 L m) T_{l_1 m} T_{l_2 M - m}. \end{aligned}$$

[42]

The coefficients are the Wigner or Clebsch-Gordon coefficients. From the two vectors \mathbf{V} and \mathbf{U} then,

$$T_{00} = \frac{1}{\sqrt{3}} (V_{+1}U_{-1} + V_{-1}U_{+1} - V_0U_0), \quad [43a]$$

$$T_{10} = \frac{1}{\sqrt{2}} (V_{+1}U_{-1} - V_{-1}U_{+1}), \quad [43b]$$

$$T_{1\pm 1} = \frac{1}{\sqrt{2}} (\pm V_{\pm 1} U_0 \mp V_0 U_{\pm 1}), \quad [43c]$$

$$T_{20} = \frac{1}{\sqrt{6}} (V_{+1} U_{-1} + V_{-1} U_{+1} + 2V_0 U_0), \quad [43d]$$

$$T_{2\pm 1} = \frac{1}{\sqrt{2}} (V_{\pm 1} U_0 + V_0 U_{\pm 1}), \quad [43e]$$

$$T_{2\pm 2} = (V_{\pm 1} U_{\pm 1}). \quad [43f]$$

The expression in Eq. [43a] is different from the scalar product of the two vectors \mathbf{V} and \mathbf{U} by a factor $-\frac{1}{\sqrt{3}}$, and the scalar product is usually given as,

$$T_{00} = \mathbf{V} \cdot \mathbf{U} = \sum_{m=-l}^l (-1)^m V_{lm} U_{l-m}. \quad [44]$$

Using Eq. [43d] for \mathbf{V} and setting $\mathbf{U} = \mathbf{V}$ (for example, if $I \geq 1$), we have the expression for $l=2$ as,

$$T_{20}^I = \frac{1}{\sqrt{6}} [3I_0^2 - I(I+1)],$$

$$T_{2\pm 1}^I = \frac{1}{\sqrt{2}} [I_0 I_{\pm 1} + I_{\pm 1} I_0],$$

$$T_{2\pm 2}^I = I_{\pm 2}^2.$$

[45]

We should now express the coupling tensor also in the irreducible tensor representation.

The interaction Hamiltonian can be written as a general tensor coupling as,

$$H = T_l^I \times \sum_{l'} T_{l'}^R, \quad [46]$$

with $T_{l'}^R$ as the irreducible tensor that contain all variables other than the spin variables I . Equation [46] is equivalent to Eq. [40]. The rotationally invariant Hamiltonian is obtained only for $H = T_{00}$, which is valid only when $l'=l$. Thus, forming the scalar product as in Eq. [44],

$$H \sim T_{00} = \sum_l \sum_{m=-l}^l (-1)^m T_{lm}^I T_{l-m}^R. \quad [47]$$

Equation [47] implies the well-known fact that the rank of the spin tensor and that of the coupling interaction tensor should be identical. In other words, the vector nuclear dipole moment ($l=1$) can couple only with another vector (e.g. a magnetic field vector).

The relation between T_{l-m}^R and the elements R_{ab} of the Cartesian coupling tensor can easily be formulated. A general second rank coupling tensor \mathfrak{R} can be expressed in terms of sum of irreducible tensors of rank $l = 0, 1, 2$.

$$\mathfrak{R} = \mathfrak{R}^{(0)} + \mathfrak{R}^{(1)} + \mathfrak{R}^{(2)}. \quad [48]$$

Where,

$$R_{ab}^{(0)} = \frac{1}{3} \text{tr} \mathfrak{R} \mathbf{d}_{ab} = R \mathbf{d}_{ab} \quad [49]$$

$$R_{ab}^{(1)} = \frac{1}{2} (R_{ab} - R_{ba}) \quad [50]$$

$$R_{ab}^{(2)} = \frac{1}{2} (R_{ab} - R_{ba}) \quad [51]$$

Equations [49]-[51] represent the *isotropic*, *anti-symmetric* and *symmetric* terms, respectively. We can define a principal axes system (PAS), fixed in some molecular frame, in which the interaction tensor is diagonal. The diagonal elements, r_{XX} , r_{YY} , r_{ZZ} , are the principal elements. With the convention $|r_{ZZ}| \geq |r_{XX}| \geq |r_{YY}|$, let us define,

$$\begin{aligned} \mathbf{c} &= r_{ZZ}, \\ \mathbf{h} &= \frac{r_{YY} - r_{XX}}{\mathbf{c}}, \quad 0 \leq \mathbf{h} \leq 1. \end{aligned}$$

[52]

Thus in the PAS,

$$\begin{aligned} \mathbf{r}^{(0)} &= R \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \\ \mathbf{r}^{(1)} &= \begin{pmatrix} 0 & r_{XY} & r_{XZ} \\ -r_{XY} & 0 & r_{YZ} \\ -r_{XZ} & -r_{YZ} & 0 \end{pmatrix}; \\ \mathbf{r}^{(2)} &= \mathbf{c} \begin{pmatrix} -\frac{1}{2}(1+\mathbf{h}) & 0 & 0 \\ 0 & -\frac{1}{2}(1-\mathbf{h}) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \end{aligned}$$

[53]

Relation between $\mathbf{r}_{ab}^{(l)}$ (tensor components in the PAS) and $\mathbf{r}_{lm} = T_{l-m}^R$ (components of irreducible tensor for coupling) can be derived as follows. The interaction Hamiltonian written as in Eq.[40] is,

$$H = \mathbf{V} \bar{\mathbf{r}} \mathbf{U}. \quad [54]$$

Where, \mathbf{V} and \mathbf{U} are vector operators and $\bar{\mathbf{r}}$ is a second rank coupling tensor given by the sum of the three terms in Eq. [53]. Substituting $\bar{\mathbf{r}}$ from Eq.[543] into Eq.[54] we can write for,

$$l = 0 : H^{(0)} = R(V_x U_x + V_y U_y + V_z U_z), \quad [55a]$$

$$\begin{aligned} l = 1 : H^{(1)} &= V_x (\mathbf{r}_{xy} U_y + \mathbf{r}_{xz} U_z) \\ &+ V_y (-\mathbf{r}_{xy} U_x + \mathbf{r}_{yz} U_z) \\ &+ V_z (-\mathbf{r}_{xz} U_x - \mathbf{r}_{yz} U_y) \\ &= (V_x U_y - V_y U_x) \mathbf{r}_{xy} \\ &+ (V_x U_z - V_z U_x) \mathbf{r}_{xz} \\ &+ (V_y U_z - V_z U_y) \mathbf{r}_{yz}, \end{aligned} \quad [55b]$$

and

$$\begin{aligned} l = 2 : H^{(2)} &= \mathbf{d} (-V_x U_x \cdot \frac{1}{2} (1 + \mathbf{h}) - V_y U_y \cdot \frac{1}{2} (1 - \mathbf{h}) + V_z U_z) \\ &= \frac{1}{2} \mathbf{d} (-V_x U_x - V_y U_y - V_z U_z + 3V_z U_z) \\ &+ \frac{1}{2} \mathbf{d} (-V_x U_x + V_y U_y). \end{aligned} \quad [55c]$$

In order to compare these expressions with $\mathbf{r}_{lm}T_{l-m}$, let us express T_{lm} by Cartesian components. Using definitions as in Eq. [41] for \mathbf{V} and \mathbf{U} ,

$$\begin{aligned} V_{\pm 1} &= \mp \frac{1}{\sqrt{2}}(V_x \pm iV_y), V_0 = V_z, \\ U_{\pm 1} &= \mp \frac{1}{\sqrt{2}}(U_x \pm iU_y), U_0 = U_z, \end{aligned} \tag{56}$$

we get,

$$T_{00} = V_x U_x + V_y U_y + V_z U_z \tag{57}$$

$$\begin{aligned} T_{10} &= \frac{i}{\sqrt{2}}(V_x U_y - V_y U_x), \\ T_{1\pm 1} &= \frac{1}{2}[-\{(V_x \pm iV_y)U_z + V_z(U_x \pm iU_y)\}] \end{aligned} \tag{58}$$

$$\begin{aligned} T_{20} &= \frac{1}{\sqrt{6}}(V_x U_x - V_y U_y - V_z U_z + 3V_z U_z), \\ T_{2\pm 1} &= \frac{1}{2}[\mp(V_x \pm iV_y)U_z \mp V_z(U_x \pm iU_y)], \\ T_{2\pm 2} &= [V_x U_x - V_y U_y \pm i(V_x U_y + V_y U_x)]. \end{aligned} \tag{59}$$

Comparing Eqs. [55a], [55b] and [55c] with Eqs. [57]-[59],

$$\begin{aligned} r_{00} &= R, & r_{20} &= \sqrt{\frac{3}{2}}\mathbf{d} \\ r_{1\pm 1} &= (\mathbf{r}_{xz} + i\mathbf{r}_{yz}), & r_{2\pm 1} &= 0, \\ r_{10} &= -i\sqrt{2}\mathbf{r}_{xy}, & r_{2\pm 2} &= -\frac{1}{2}\mathbf{ch}. \end{aligned} \tag{60}$$

For relaxation in NMR l is invariably 2 (we shall see this shortly) and can be dropped from the notation and replacing $r_{lm} = T_{l-m}^R$ by F_q (including various constants) and T_{lm}^I by A_{-q} , we have

$$H(t) = \sum_q (-1)^q F_q(t) A_{-q}, \quad [61]$$

As the molecule tumbles the space variable F_q becomes dependent and gives rise to relaxation.

It remains to evaluate F_q (and A_{-q}) for various relaxation mechanism also

We have, thus, represented the interaction Hamiltonian in terms of irreducible tensor operators.

Chemical shift anisotropy (CSA), spin-spin coupling (J), and spin rotation interaction (SR), can have all three components described above. Only the isotropic and the traceless symmetric parts are measurable and important. The anti-symmetric tensor of rank 2 has been shown to yield a second order shift in line position and will be dropped from further discussion. Dipolar and quadrupolar relaxations are by nature given by symmetric and traceless tensors.

Expressing the space function in the principal axis by a superscript prime, Eq. [48] can be written as,

$$H = \sum_q \sum_{q'} (-1)^q F_{q'} D_{q'q}^{(2)}(\Omega) A_{-q}. \quad [62]$$

Where, $D_{q'q}^{(2)}(\Omega)$ Wigner rotation matrix that transforms the PAS to the laboratory frame. The interaction in the various relaxation mechanisms can be written as follows,

| | | | |
|----------------------|----------------|--------------------|----------------|
| Relaxation Mechanism | \mathbf{V} | \mathfrak{R} | \mathbf{U} |
| Dipole-Dipole | \mathbf{I}_i | \mathbf{D} | \mathbf{I}_j |
| CSA | \mathbf{I}_i | \mathbf{S}_i | \mathbf{B} |
| Quadrupolar | \mathbf{I}_i | $\nabla\mathbf{V}$ | \mathbf{I}_i |

For dipole - dipole relaxation between I and S:

$$F_0' = -\sqrt{\frac{3}{2}} \frac{2\mathbf{g}_I\mathbf{g}_S\hbar}{r_{IS}^3}; F_{\pm 1}' = 0; F_{\pm 2}' = 0. \quad [63]$$

For chemical shift anisotropy of spin I:

$$F_0' = \sqrt{\frac{3}{2}} \mathbf{d}_{zz}'; F_{\pm 1}' = 0; F_{\pm 2}' = -\frac{1}{2} \mathbf{d}_{zz}' C_I. \quad [64]$$

For the case of quadrupolar relaxation of spin with spin angular momentum S:

$$F_0' = \sqrt{\frac{3}{2}} \frac{e^2qQ}{2S(2S-1)}; F_{\pm 1}' = 0; F_{\pm 2}' = -\frac{1}{2} \frac{e^2qQ}{2S(2S-1)} \mathbf{h}_Q. \quad [65]$$

Thus the relaxation Hamiltonians in the laboratory frame is summarized as follows:

| <u>Quadrupolar relaxation</u> | <u>Dipolar relaxation</u> | <u>CSA relaxation</u> |
|--|--|--|
| $F_q^Q = \sqrt{\frac{3}{2}} \frac{e^2 q Q}{2S(2S-1)\hbar}$ $- \sqrt{\frac{1}{6}} \mathbf{h}_Q D_{+2q}^{(2)}(\Omega_Q)$ $- \sqrt{\frac{1}{6}} \mathbf{h}_Q D_{-2q}^{(2)}(\Omega_Q)].$ $A_0^Q = \frac{1}{\sqrt{6}} (3S_z^2 - S(S+1))$ $A_{\pm 1}^Q = \mp \frac{1}{2} (S_z S_{\pm} + S_{\pm} S_z)$ $A_{\pm 2}^Q = \frac{1}{2} S_{\pm}^2.$ | $F_q^D = -\sqrt{\frac{3}{2}} \frac{2\mathbf{g}_I \mathbf{g}_S \hbar}{r_{IS}^3}$ $D_{0q}^{(2)}(\Omega_D).$ $A_0^D = \frac{1}{\sqrt{6}} (3I_z S_z - \mathbf{I} \cdot \mathbf{S})$ $A_{\pm 1}^D = \mp \frac{1}{2} (I_z S_{\pm} + I_{\pm} S_z)$ $A_{\pm 2}^D = \frac{1}{2} I_{\pm} S_{\pm}.$ | $F_q^{C_I} = \sqrt{\frac{3}{2}} \mathbf{d}_{zz}$ $[D_{0q}^{(2)}(\Omega_{C_I})$ $- \sqrt{\frac{1}{6}} \mathbf{h}_{C_I} D_{+2q}^{(2)}(\Omega_{C_I})$ $- \sqrt{\frac{1}{6}} \mathbf{h}_{C_I} D_{-2q}^{(2)}(\Omega_{C_I})].$ $A_0^{C_I} = \frac{2}{\sqrt{6}} \mathbf{w}_I I_z$ $A_{\pm 1}^{C_I} = \mp \frac{1}{2} \mathbf{w}_I I_{\pm}$ $A_{\pm 2}^{C_I} = 0.$ |

4. Auto and Cross Correlations in Relaxation

Expressions for various relaxation parameters, such as spin-lattice and spin-spin relaxation times (T_1 and T_2) can be easily derived from the description of the set of expressions derived so far. These will be clear when the specific expressions are given in the following section. In this sub-section, expressions for correlation functions are presented. A general framework including internal motions following the approach laid out by Lipari and Szabo is used. The internal motion is described in terms of an order parameter signifying the restriction for the motion and a effective correlation time indicating the rate of the motion. It is then straightforward to arrive at situations where there are no internal motions by simply setting the order parameter to unity.

The time dependent relaxation Hamiltonian (Eq.[61]) is given as,

$$H(t) = \sum_q (-1)^q F_q(t) A_{-q}, \quad [66]$$

where F_q 's are the space functions and A_{-q} 's represent spin operators as defined earlier with the following properties,

$$F_q^* = (-1)^q F_{-q}; A_q^\dagger = (-1)^q A_{-q}; \quad [67]$$

and transformation properties of an irreducible tensor of rank 2,

$$F_q = \sum_{q'=-2}^2 F_{q'} D_{q'q}^{(2)}(\Omega), \quad [68]$$

where $D_{q'q}^{(2)}(\Omega)$ is the Wigner rotation matrix that transforms the space functions from primed coordinate system to the un-primed coordinate system and Ω is the set of Euler angles corresponding to the particular transformation.

The correlation function is given as,

$$g_{qq'}^{AB}(t) = \langle F_q^*(0) F_{q'}^B(t) \rangle, \quad [69]$$

$\langle \rangle$ represents ensemble average and the superscripts A and B refer to different relaxation mechanisms. If A=B one gets auto correlation function and when A \neq B one gets cross correlation function. The spectral densities are then given by,

$$J_{qq'}^{AB}(\omega) = \int_{-\infty}^{\infty} g_{qq'}^{AB}(t) e^{-i\omega t} dt. \quad [70]$$

In order to evaluate the correlation functions for various relaxation mechanisms and their cross-correlations, it is convenient to first consider the space functions for the various relaxation mechanisms in their respective principal axis system (PAS) with a prime and then transform them into the laboratory frame. In the case of dipole-dipole relaxation the PAS is defined with its Z-axis along the dipole-dipole vector, and for the other relaxation mechanisms (quadrupolar and CSA) the Z-axis is along the symmetry axis of the interaction tensor.

$$F_q^{Lab} = \sum_{q''=-2}^2 F_{q''} D_{q''q}^{(2)}(\Omega), \quad [71]$$

where Ω is the set of Euler angles defining the orientation of the principal axis frame with respect to the laboratory frame. Substituting Eq.[71] in Eq.[69] we get,

$$g_{qq'}^{AB}(t) = \sum_{q''} \left\langle \left(F_{q''}^* \right)^A D_{q''q}^{(2)*}(\Omega:0) F_{q''}^B D_{q''q}^{(2)}(\Omega:t) \right\rangle, \quad [72]$$

where $D_{q''q}^{(2)}(\Omega:t)$ is the rotation matrix at time t. Secular approximation imposes a condition,

$$g_{qq'}^{AB}(t) = \mathbf{d}_{qq'} g_q^{AB}(t). \quad [73]$$

Auto Correlation (A=B):

Let us first consider the auto correlation function by setting A=B in Eq. [73]. In order to bring out motional details such as internal motion, the auto correlation function is computed first by transforming the space functions from the PAS to a molecular fixed frame and then transforming it to the laboratory frame. In the molecular frame if internal motions are present they can be identified uniquely facilitating their quantification. Thus, the auto correlation function is given by,

$$g_q(t) = \sum_{q'} \left\langle \sum_{q''} F_{q''}^* D_{q''q'}^{(2)*}(\Omega':0) D_{q'q}^{(2)*}(\Omega_M:0) F_{q''} D_{q''q'}^{(2)}(\Omega':t) D_{q'q}^{(2)*}(\Omega_M:t) \right\rangle, \quad [74a]$$

$$g_q(t) = \sum_{q'q''} \left\langle \left| F_{q''}^* \right|^2 D_{q''q'}^{(2)*}(\Omega':0) D_{q'q}^{(2)*}(\Omega_M:0) D_{q''q'}^{(2)}(\Omega':t) D_{q'q}^{(2)*}(\Omega_M:t) \right\rangle. \quad [74b]$$

In the above equations, $\Omega':t$ describes orientation of the PAS in the molecular frame at time t and $\Omega_M:t$ describes the orientation of the molecular frame with respect to the laboratory frame. If there is no internal motion, then Ω' is time independent and the correlation function is governed only by the overall motion characterized by the time dependent Ω_M . In the presence of internal motion, it is not straightforward (from the above equations) that the internal and overall motion could be separated. The sum over q' present both in internal and overall motion show mutual influence on each other. However, useful results have been derived when the time scales of internal and the overall motions are different (internal motion in the extreme narrowing limit). In such a situation it is assumed that the total correlation function could be approximated as a product of two correlation functions corresponding to one the overall motion and the other to the internal motion. It has also been shown that such a separation is possible even for anisotropic overall motion.

Thus the auto correlation function can be written as,

$$g_q(t) = C_0(t)C_I(t), \quad [75]$$

where,

$$C_0(t) = \sum_{q'} \left\langle D_{q'q}^{(2)*}(\Omega_M:0) D_{q'q}^{(2)}(\Omega_M:t) \right\rangle, \quad [76]$$

and

$$C_I(t) = \sum_{q'q''} \left| F_{q''} \right|^2 \left\langle D_{q''q'}^{(2)*}(\Omega':0) D_{q''q'}^{(2)}(\Omega':t) \right\rangle. \quad [77]$$

In the case of axially symmetric second rank tensor (e.g. dipole-dipole interaction and interactions such as CSA or quadrupolar with asymmetry parameter set to 0) the only relevant non vanishing space function in the PAS is when $q''=0$. Then, the internal motion is given as,

$$C_I(t) = \left| F_0 \right|^2 \sum_{q'} \left\langle D_{0q'}^{(2)*}(\Omega':0) D_{0q'}^{(2)}(\Omega':t) \right\rangle. \quad [78]$$

Following Lipari and Szabo approach,

$$C_I(t) \approx C_I(\infty) + (C_I(0) - C_I(\infty)) e^{-t/\tau_e}, \quad [79]$$

where the expression is exact only at times zero and t , and τ_e is an effective correlation time describing the internal motion.

$$\text{Using the property } \frac{1}{8\pi^2} \int_{\Omega} D_{q_1q_2}^{(l)*}(\Omega) D_{q_3q_4}^{(l)}(\Omega) d\Omega = \frac{1}{2l+1} \mathbf{d}_{l'q_1q_3} \mathbf{d}_{lq_2q_4}, \text{ we have}$$

therefore ,

$$C_I(0) = \left| F_0 \right|^2; C_I(\infty) = \left| F_0 \right|^2 S^2, \quad [80]$$

when the overall motion is isotropic

$$C_0(t) = e^{-t/\tau_M}, \quad [81]$$

and

$$g(t) = \left| F_0 \right|^2 \left[S^2 e^{-t/\tau_M} + (1 - S^2) e^{-t/\tau} \right], \quad [82]$$

where $\frac{1}{t} = \frac{1}{t_M} + \frac{1}{t_e}$ and the subscript q is dropped from g(t) as it is independent of q. For anisotropic overall motion we may write following again Lipari and Szabo approach,

$$C_0(t) = Ae^{-t/t_1} + (1-A)e^{-t/t_2} \quad [83]$$

where A is an anisotropic factor similar to the order parameter and is unity when the overall motion is isotropic and can be used to get g(t).

Cross Correlation (A ≠ B)

Let us say A is dipolar interaction and B is either CSA or quadrupolar interaction. For the interaction A the transformations will be: PAS to molecular frame to laboratory frame. For interaction B the sequence of transformations will be PAS to dipolar frame to molecular frame to Laboratory frame.

$$F_q^D = \sum_{q'q''} F_{q''}^D D_{q''q'}^{(2)}(\Omega_D') D_{q'q}^{(2)}(\Omega_M), \quad [84]$$

where Ω_D' describes the orientation of the dipole-dipole vector in the molecular frame.

$$F_q^B = \sum_{q'q''q'''} F_{q'''}^B D_{q'''}^{(2)}(\Omega_{BD}) D_{q''q'}^{(2)}(\Omega_D') D_{q'q}^{(2)}(\Omega_M), \quad [85]$$

where Ω_{BD} describes the orientation of PAS with respect to dipolar frame.

$$g_q^{DB}(t) = \sum_{q'q''q'''} \left\langle F_{q''}^D D_{q''q'}^{(2)*}(\Omega_D':0) D_{q'q}^{(2)*}(\Omega_M:0) F_{q'''}^B D_{q'''}^{(2)}(\Omega_{BD}:t) D_{q''q'}^{(2)}(\Omega_D':t) D_{q'q}^{(2)}(\Omega_M:t) \right\rangle$$

[86]

Case:1 Axially symmetric tensor for interaction B:

The only non-vanishing space functions in the PAS are $F_0'^D$ and $F_0'^B$. Therefore,

$$g_q^{DB}(t) = \sum_{q'q''} \left\langle F_0'^{D*} D_{0q'}^{(2)*}(\Omega_D' : 0) D_{q'q}^{(2)*}(\Omega_M : 0) F_0'^B D_{0q''}^{(2)}(\Omega_{BD} : t) D_{q''q'}^{(2)}(\Omega_D' : t) D_{q'q}^{(2)}(\Omega_M : t) \right\rangle. \quad [87]$$

Writing $g_q^{DB}(t) = C_0(t)C_I(t)$, we have for

$$g_q^{DB}(t) = \sum_{q'q''} F_0'^{D*} D_{0q'}^{(2)*}(\Omega_D' : 0) D_{q'q}^{(2)*}(\Omega_M : 0) F_0'^B D_{0q''}^{(2)}(\Omega_{BD} : t) D_{q''q'}^{(2)}(\Omega_D' : t) D_{q'q}^{(2)}(\Omega_M : t). \quad [88]$$

From the orthogonal property of the Wigner rotation matrix elements,

$$C_I(t) = \sum_{q'} \left| F_0'^{D*} F_0'^B \right| \left\langle D_{0q'}^{(2)*}(\Omega_D' : 0) D_{q''q'}^{(2)}(\Omega_D' : t) D_{00}^{(2)}(\Omega_{BD} : t) \right\rangle. \quad [89]$$

Again writing $C_I(t) \approx C_I(\infty) + (C_I(0) - C_I(\infty))e^{-t/t_e}$, we have

$$\begin{aligned} C_I(0) &= \left| F_0'^{D*} F_0'^B \right| D_{00}^{(2)}(\Omega_{BD}) = \frac{1}{2} \left| F_0'^{D*} F_0'^B \right| \left(3 \cos^2 \mathbf{q}_{BD} - 1 \right), \\ C_I(\infty) &= \frac{1}{2} \left| F_0'^{D*} F_0'^B \right| \left(3 \cos^2 \mathbf{q}_{BD} - 1 \right) S^2 \end{aligned} \quad [90a,b]$$

Thus when the overall motion is isotropic,

$$g^{DB}(t) = \frac{1}{2} \left| F_0'^{D*} F_0'^B \right| \left[\left(3 \cos^2 \mathbf{q}_{BD} - 1 \right) S^2 e^{-t/t_M} + (1 - S^2) e^{-t/t} \right]. \quad [91]$$

For anisotropic overall motion we again use $C_0(t) = Ae^{-t/\tau_1} + (1-A)e^{-t/\tau_2}$. Thus a measurement of cross correlation spectral density can also yield information on the dynamics of the spin system.

Case 2: General tensor for B:

Now let us not make the assumption that the interaction tensor for B is axially symmetric.

We have,

$$g_q^{DB}(t) = \sum_{q'q''q'''} \left\langle F_{q''}^{D*} D_{q''q'}^{(2)*}(\Omega_D' : 0) D_{q'q}^{(2)*}(\Omega_M : 0) F_{q'''}^B D_{q''q'''}^{(2)}(\Omega_{BD} : t) D_{q''q'}^{(2)}(\Omega_D' : t) D_{q'q}^{(2)}(\Omega_M : t) \right\rangle$$

[92]

But for dipole-dipole relaxation the only non-zero PAS element is $F_0^{D'}$, thus

$$g_q^{DB}(t) = \sum_{q'q''q'''} \left\langle F_0^{D*} D_{0q'}^{(2)*}(\Omega_D' : 0) D_{q'q}^{(2)*}(\Omega_M : 0) F_{q'''}^B D_{q''q'''}^{(2)}(\Omega_{BD} : t) D_{q''q'}^{(2)}(\Omega_D' : t) D_{q'q}^{(2)}(\Omega_M : t) \right\rangle$$

[93]

Again, as before, separating the overall and internal motion, we have for internal motion

$$C_I(t) = \sum_{q'q''q'''} \left\langle F_0^{D*} F_{q'''}^B D_{0q'}^{(2)*}(\Omega_D' : 0) D_{q''q'}^{(2)*}(\Omega_D' : t) D_{q''q'''}^{(2)}(\Omega_{BD} : t) \right\rangle.$$

[94]

But orthogonality requires $q''=0$, so

$$C_I(t) = \sum_{q'q'''} \left\langle F_0^{D*} F_{q'''}^B D_{0q'}^{(2)*}(\Omega_D' : 0) D_{0q'}^{(2)*}(\Omega_D' : t) D_{q'''}^{(2)}(\Omega_{BD} : t) \right\rangle.$$

[95]

Thus when the overall motion is isotropic we can write,

$$g^{DB}(t) = \sum_{q'''} F_0^{D*} F_{q'''}^{B} D_{q'''}^{(2)}(\Omega_{BD}) \left[S^2 e^{-t/t_M} + (1 - S^2) e^{-t/t} \right]. \quad [96]$$

Extension to anisotropic overall motion can be formulated as before.