A Primer for Nuclear Magnetic Relaxation in Liquids

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ABSTRACT: This article is a primer that is intended to serve as a concise source of information for researchers interested in learning relaxation aspects in NMR. Explicit expressions have been derived for the equation of motion of nuclear spins in the solution state. General expressions valid for all motional regimes, including anisotropy of spin interactions and molecular motions, are presented. Intricate details that impact the validity of various expressions have been elaborated and efforts have been made to maintain consistent notation. The suitable examples given here should help in the understanding of the concepts developed in the theory. © 2003 Wiley Periodicals, Inc. Concepts Magn Reson Part A 17A: 86–116, 2003

KEY WORDS: NMR; spin relaxation; semiclassical theory; equation of motion; motional limits; rate constants; autocorrelation; cross-correlation

INTRODUCTION

NMR spectroscopy has proved to be a valuable technique to understand the structure and dynamics of molecular systems (*1–15*). Its ability to yield such information in the liquid state is so remarkable that its development has been tremendous (*16*). The quest for understanding the structure and dynamics of large molecules (<100 kDa) is pushing the technique to very high fields (*17–19*). Aside from the benefits in terms of sensitivity and spectral spread, the advantages stemming from relaxation effects at high fields can aid in the study of large molecules. It is predicted that NMR experiments of a 300-kDa protein at very high Larmor frequencies (~1 GHz) would yield intelligible spectra that are suitable for 3-dimensional structure elucidation (*20–24*). Such predications are based on applying relaxation theories, known since the advent of NMR, to systems of such sizes and field strengths. Furthermore, measurements of the anisotropy of spin interactions and motions have been widely used to derive information on structure and dynamics (*13*, *25–29*).

Received 7 August 2002; revised 7 November 2002; accepted 17 November 2002

This article is dedicated to Professor Anil Kumar who is retiring in 2003 from the Indian Institute of Science, Bangalore, India, after an outstanding career in the field of NMR. His research contributions in NMR have helped advance the field significantly. Dr. Kumar is not only a scientist of high caliber but also a fine teacher and a gentleman who always reaches out to his associates and friends in a generous manner. We were quite fortunate to have been associated with him as Ph.D. students and immensely benefited from his thorough knowledge, experience, and guidance.

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Concepts in Magnetic Resonance Part A, Vol. 17A(1) 86–116 (2003)

The theory of relaxation of nuclear spins in liquids is well established and several classic treatises (*1*, *30–34*) and numerous review articles (*7*, *13–15*, *25*, *28*, *35–44*) exist. Most of the descriptions, however, tend to focus on the motional narrowing limit where the rate of rotation due to Brownian motion is much faster than the transition frequency (spectrometer frequency), a situation applicable for the study of small molecules. Present day applications have evolved to include the study of macromolecules, such as proteins, nucleic acids, and their complexes; and it is not always possible to directly use expressions from these works to understand the experimental data. Although it is straightforward to extend the theory to include all motional regimes, presenting such a description from the first principles with a consistent notation is highly desirable and useful.

The purpose of this article is to systematically derive explicit expressions for various relaxation rate constants by following the equation of motion of the nuclear spins in the solution state. General expressions valid for all motional regimes, including internal motions and anisotropic spin interactions, are derived. This article is intended as a concise source of information for researchers interested in learning relaxation aspects in NMR. The formulation of the master equation of motion and the relaxation Hamiltonians closely follow previously published works in classic texts and the general literature, and no originality is claimed. However, in describing the correlation functions we adopted a general framework to include dynamics aspects as laid out by previous researchers. We strived to maintain a consistent notation and elaborate intricate details that impact on the validity of various expressions.

We introduce the general aspects of relaxation in the solution state with master equations in terms of the density matrix and in the operator form. A general method of deriving the various relaxation Hamiltonians responsible for the relaxation mechanisms is described. We derive correlation (both autocorrelation and cross correlation) functions with an emphasis on dynamics information in the framework developed by previous researchers. The application of the theory to realistic problems is discussed.

MASTER EQUATION OF NMR RELAXATION

Relaxation of nuclear spins in the solution state is conveniently described by a semiclassical approach. The static coherent interactions among nuclear spins and with an applied magnetic field are treated in a quantum mechanical framework while a classical approach is used to characterize the stochastic interactions of the nuclear spins with their surroundings, which is called the lattice. The lattice is assumed to have continuous energy levels because of its large number of degrees of freedom, and it possesses a large heat capacity and thus remains in thermal equilibrium at all times. The spins are coupled only weakly to the lattice through time dependent interactions that are random because of the rotational Brownian motion of the molecules. It is assumed that the nature of the randomness is a particular class called the stationary random process, in which the random functions in time are independent of the time origin and depend only on the duration elapsed (also known as the Markovian process). Further, the average over these random, time dependent interactions at time durations longer than the correlation time (the time the molecule takes to perform a rotation by 1 rad) is zero [e.g., see Woessner (*45*)]. These set of rules are rarely violated in solution NMR spectroscopy and provide the necessary framework to extract dynamics information and various relaxation parameters from the evolution of a suitable observable in the form of a NMR spectrum.

In 1946, Bloch (*46*) first presented a spin relaxation theory based on a phenomenological set of equations, known as the Bloch equations, in which the behavior of the spin system is characterized by two rate constants T_1 and T_2, which represent the longitudinal and transverse relaxation times, respectively. In the method proposed by Bloembergen, Purcell, and Pound (*47*), known as BPP theory, the spin relaxation times were derived based on a rigorous treatment of spin–lattice interactions affected by molecular motions. Further refinement of the BPP theory led to the current general method to describe the relaxation of nuclear spins, commonly referred to as the Bloch, Wangness (*48*), and Redfield (*35*, *49*) theory. Several groups have conducted detailed investigations of various aspects of the nuclear spin relaxation (*50–52*), and the articles by Hubbard (*50*, *53*, *54*) are undoubtedly seminal in this area.

Redfield Equation as Master Equation for Density Matrix

A density matrix appropriately describes the quantum and statistical nature of any state of an ensemble of nuclear spins (*55–57*). The equation of motion of the density matrix then yields the time evolution of the populations and the various coherences of the spin system that may be created in an experiment. The fundamental von-Liouville equation of motion of the density matrix σ is

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

where $\mathbf{H}_0$ is the time independent part of the Hamiltonian, which represents the Zeeman interaction of nuclear spins with an applied magnetic field, and it may also contain any static spin–spin interactions; and $\mathbf{H}_1(t)$ is the time dependent Hamiltonian that describes the interaction between nuclear spins and the lattice leading to relaxation. Both $\mathbf{H}_0$ and $\mathbf{H}_1(t)$ are written in Dirac units ($\hbar$), which is Planck's constant (1.0546×10^{-34} J s).

We transform Eq. [1] to an interaction representation defined by

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

in which the evolution or time dependence of the density matrix due to the dominant Zeeman interaction is removed and the slow evolution of the spin system under the relaxation Hamiltonian can be delineated. This rotation is equivalent to a rotating frame transformation of the density matrix to remove the time dependence arising from the radio frequency (RF) field. Substitution of Eq. [2] in Eq. [1] yields an equation of motion in the interaction frame as

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

A general solution to Eq. [3] is given by

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

In general, $\sigma^*(t')$ in the integral on the right-hand side (RHS) is not known and an approximate solution can be obtained by replacing $\sigma^*(t')$ with $\sigma^*(0)$ and integrating by successive approximations up to second order to yield

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

$$-\int_0^t dt'\int_0^{t'} dt''[\mathbf{H}_1^*(t'), [\mathbf{H}_1^*(t''), \sigma^*(0)]] \qquad [5]$$

and then by taking a time derivative, we get an approximate rate equation

$$\frac{d\sigma^*(t)}{dt} = -i[\mathbf{H}_1^*(t), \sigma^*(0)]]$$

$$-\int_0^t dt'[\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t'), \sigma^*(0)]]. \qquad [6]$$

This approach is equivalent to a standard time dependent perturbation approximation carried out up to second order in time (*58*). Because the time dependency is attributable to stationary random processes, we can substitute $\tau = t - t'$. Thus, Eq. [6] is rewritten as

$$\frac{d\sigma^*(t)}{dt} = -i[\mathbf{H}_1^*(t), \sigma^*(0)]$$

$$-\int_0^t d\tau[\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-\tau), \sigma^*(0)]]. \qquad [7]$$

Because $\mathbf{H}_1{}^*(t)$ is a random function of time, $\sigma^*(t)$ also becomes random. Thus, only the evolution of a time averaged density matrix (or equivalently, an ensemble averaged density matrix due to ergodicity) becomes relevant in the description of the state of the spin system under the influence of $\mathbf{H}_1{}^*(t)$. To derive the final equation of motion that describes the nuclear spin relaxation, a few more assumptions need to be taken into account:

1. $\langle \mathbf{H}_1{}^*(t)\rangle = 0$ for all matrix elements $\langle\langle\alpha|\mathbf{H}_1{}^*(t)|\beta\rangle\rangle$. The angle brackets ($\langle\cdot\cdot\cdot\rangle$) represent an average over the ensemble of spins. If this is not valid, the nonzero part can be added in to a redefined static Hamiltonian $\mathbf{H}_0$.
2. Any correlation between $\mathbf{H}_1{}^*(t)$ and $\sigma^*(0)$ is negligible. For $\tau > \tau_c$, where τ_c is the correlation time, the correlation between $\mathbf{H}_1{}^*(t - \tau)$ and $\mathbf{H}_1{}^*(\mathrm{t}\ )$ is negligible, and for $t > \tau$ the correlation between $\mathbf{H}_1{}^*(t)$ and $\sigma^*(0)$ is also negligible. This is a consequence of the stationary random character of the relaxation processes [also known as the first-order Markovian (*59*, *60*) process] in nuclear magnetic relaxation, implying that there is no long time memory of the state of the Hamiltonian.

3. $\sigma^*(0)$ can be replaced by $\sigma^*(t)$ on the RHS of Eq. [7]. The increase is $\{\sigma(t) - \sigma_0\}/\sigma_0 \approx t\langle|\mathbf{H}_1(t)|^2\rangle\tau_c \ll 1$, thus $\sigma^*(0)$ can be replaced by $\sigma^*(t)$.
4. The upper limit of integration in Eq. [7] can be extended to $+\infty$ because for $\tau > \tau_c$ the correlation function decays to zero rapidly.
5. Higher order terms in Eq. [5] can be neglected. Because the ratio of the strengths of terms of order n and $n - 1$ is

$$\left|\frac{A_n}{A_{n-1}}\right| \cong [\langle|\mathbf{H}_1|^2\rangle\tau_c^2]^{1/2} \ll 1$$

for most relaxation mechanisms in NMR, the contributions from higher order terms can be safely ignored. Thus, a limit exists between the time scale of the random motion and the strength of the interaction that is being averaged by the motion for which the relaxation theory is applicable. It also implies that the equation of motion is not valid at time scales of $t \leq \tau_c$.

With all these assumptions, the first term in Eq. [7] goes to zero and the rest is rewritten as

$$\frac{d\langle\sigma^*(t)\rangle}{dt} = -\int_0^\infty d\tau\langle[\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-\tau), \sigma^*(t)]]\rangle. \quad [8]$$

Equation [8] describes the relaxation evolution of the ensemble averaged density matrix. In an alternate approach, Goldman (*44*) derives Eq. [8] without resorting to the method of integration by successive approximation. In his approach the solution given by Eq. [4] is substituted into Eq. [3] and then the same assumptions given here are used to arrive at the final equation that is identical to Eq. [8]. The use of successive approximation (Eq. [5]) to derive Eqs. [7] and [8], however, explicitly takes into account that $\mathbf{H}_1{}^*(t)$ need not commute with each other at different times and that we do not have a priori knowledge of $\sigma^*(t')$ for any t'. We prefer this method of integration by successive approximation because it brings forth rather subtle implications in extending the upper limit of integration to infinity and the size of the correlation time with respect to the strength of the relaxation interactions. The aforementioned assumptions are common in both approaches and they are dictated by the nature of the classical treatment of the random processes.

Taking $|\alpha\rangle$, $|\beta\rangle$ as the eigenstates of the unperturbed static Hamiltonian $\mathbf{H}_0$, the eigenvalues α, β, . . . , and rewriting Eq. [8] for the matrix elements, we get

$$\frac{d\langle\sigma^*(t)\rangle_{\alpha\alpha'}}{dt} = -\int_0^\infty d\tau\langle\langle\alpha|[\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-\tau), \sigma^*(t)]]|\alpha'\rangle\rangle. \quad [9]$$

We will first expand the commutator on the RHS,

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

and then take explicit matrix elements by introducing a sum (i.e., Σ) over γ and projection operations such as $\langle\beta|\beta\rangle = 1$, the RHS of Eq. [9] becomes

$$\begin{aligned}\langle\alpha|[\mathbf{H}_1^*(t), [\mathbf{H}_1^*(t-\tau), \sigma^*(t)]]|\alpha'\rangle &= \sum_{\beta\beta'}\sum_{\gamma}\langle\alpha|\mathbf{H}_1^*(t)|\gamma\rangle\\ &\times \langle\gamma|\mathbf{H}_1^*(t-\tau)|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle\langle\beta'|\alpha'\rangle + \sum_{\beta\beta'}\sum_{\gamma}\langle\alpha|\beta\rangle\\ &\times \langle\beta|\sigma^*(t)|\beta'\rangle\langle\beta'|\mathbf{H}_1^*(t-\tau)|\gamma\rangle\langle\gamma|\mathbf{H}_1^*(t)|\alpha'\rangle\\ &- \sum_{\beta\beta'}\langle\alpha|\mathbf{H}_1^*(t-\tau)|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle\langle\beta'|\mathbf{H}_1^*(t)|\alpha'\rangle\\ &- \sum_{\beta\beta'}\langle\alpha|\mathbf{H}_1^*(t)|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle\langle\beta'|\mathbf{H}_1^*(t-\tau)|\alpha'\rangle. \quad [10]\end{aligned}$$

Identifying the transition frequencies using Eq. [2] and using the orthonormal property of the eigenbasis $\langle\beta|\alpha\rangle = \delta_{\alpha\beta}(\delta_{\alpha\beta}$ is the Kronecker δ),

$$\begin{aligned}\langle\alpha|\mathbf{H}_1^*(t)|\beta\rangle &= \langle\alpha|e^{i\mathbf{H}_0t}|\alpha\rangle\langle\alpha|\mathbf{H}_1(t)|\beta\rangle\langle\beta|e^{-i\mathbf{H}_0t}|\beta\rangle\\ &= \langle\alpha|\mathbf{H}_1(t)|\beta\rangle e^{i(\alpha-\beta)t} \quad [11]\end{aligned}$$

and $\langle\alpha|\sigma(t)|\beta\rangle = \sigma_{\alpha\beta}{}^*(t)$, Eq. [10] takes the form

$$\begin{aligned}\langle\alpha|[\mathbf{H}_1^*(t),[\mathbf{H}_1^*(t-\tau),\sigma^*(t)]]|\alpha'\rangle = {} & \sum_{\beta\beta'}\sum_{\gamma}\langle\alpha|\mathbf{H}_1(t)|\gamma\rangle\langle\gamma|\mathbf{H}_1(t-\tau)|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle \\ & \times\langle\beta'|\alpha'\rangle e^{i(\alpha-\gamma)(t-\tau)}e^{i(\gamma-\beta)t} + \sum_{\beta\beta'}\sum_{\gamma}\langle\alpha|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle\langle\beta'|\mathbf{H}_1(t-\tau)|\gamma\rangle \\ & \times\langle\gamma|\mathbf{H}_1(t)|\alpha'\rangle e^{i(\beta'-\gamma)(t-\tau)}e^{i(\gamma-\alpha')t} - \sum_{\beta\beta'}\langle\alpha|\mathbf{H}_1(t-\tau)|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle \\ & \times\langle\beta'|\mathbf{H}_1(t)|\alpha'\rangle e^{i(\alpha-\beta)(t-\tau)}e^{i(\beta'-\alpha')t} - \sum_{\beta\beta'}\langle\alpha|\mathbf{H}_1(t)|\beta\rangle\langle\beta|\sigma^*(t)|\beta'\rangle \\ & \times\langle\beta'|\mathbf{H}_1(t-\tau)|\alpha'\rangle e^{i(\alpha-\beta)(t-\tau)}e^{i(\beta'-\alpha')t}. \qquad [12]\end{aligned}$$

At this stage, it is appropriate to introduce the definition of a time correlation function, an important step that relates the spin relaxation to the molecular motion. If $f_a(t)$ and $f_b(t)$ are random functions of time, any correlation between them is defined as

$$G_{ab}(\tau) = \langle f_a(t)f_b^*(t-\tau)\rangle \qquad [13]$$

where $\langle\cdots\rangle$ represents the time average and $G_{ab}(\tau)$ also obeys the relation $G_{ab}(\tau) = G_{ab}{}^*(\tau) = G_{ab}(-\tau)$. The correlation time τ_c is then defined such that $G_{ab}(\tau)$ is small for $|\tau| \gg \tau_c$. The corresponding spectral density function is given by the Fourier transform of the correlation function as

$$j_{ab}(\omega) = \int_0^\infty G_{ab}(\tau)e^{-i\omega\tau}d\tau. \qquad [14]$$

Using a similar definition for a correlation function for the time dependent relaxation Hamiltonian, $\mathbf{H}_1(t)$, we get

$$G_{\alpha\beta\alpha'\beta'}(\tau) = \langle\langle\alpha|\mathbf{H}_1(t)|\beta\rangle\langle\beta'|\mathbf{H}_1(t+\tau)|\alpha'\rangle\rangle \qquad [15]$$

and substituting Eq. [15] in the master equation (Eq. [9]),

$$\frac{d\sigma^*_{\alpha\alpha'}(t)}{dt} = \frac{1}{2}\sum_{\beta\beta'}$$

$$\times\left[\begin{aligned} & -\delta_{\alpha'\beta'}\sum_{\gamma}\int_0^\infty d\tau G_{\alpha\gamma\beta\alpha}(\tau)e^{-i(\gamma-\alpha)\tau}e^{i(\alpha-\beta)t} \\ & -\delta_{\alpha\beta}\sum_{\gamma}\int_0^\infty d\tau G_{\beta\gamma\alpha'\gamma}(\tau)e^{-i(\gamma-\beta')\tau}e^{+i(\beta'-\alpha')t} \\ & +\int_0^\infty d\tau G_{\alpha\beta\alpha'\beta'}(\tau)e^{-i(\alpha-\beta)\tau}e^{i(\alpha-\beta+\beta'-\alpha')t} \\ & +\int_0^\infty d\tau G_{\alpha\beta\alpha'\beta'}(\tau)e^{-i(\alpha'-\beta')\tau}e^{i(\alpha-\beta+\beta'-\alpha')t}\end{aligned}\right]\sigma^*_{\beta\beta'}(t). \qquad [16]$$

The $\langle\cdots\rangle$ representing the ensemble average has been dropped in Eq. [16] for convenience. Now defining the spectral density functions using Eq. [14], we get

$$j_{\alpha\beta\alpha'\beta'}(\alpha'-\beta') = \int_0^\infty d\tau G_{\alpha\beta\alpha'\beta'}(\tau)e^{-i(\alpha'-\beta')\tau}$$

$$= \frac{1}{2}\int_0^\infty d\tau G_{\alpha\beta\alpha'\beta'}(\tau)\cos(\alpha' - \beta')\tau$$

$$- i\int_0^\infty d\tau G_{\alpha\beta\alpha'\beta'}(\tau)\sin(\alpha' - \beta')\tau$$

$$= \frac{1}{2} J_{\alpha\beta\alpha'\beta'}(\alpha' - \beta') - iK_{\alpha\beta\alpha'\beta'}(\alpha' - \beta'). \qquad [17]$$

In Eq. [17] the real part yields the decay constants and the imaginary part gives rise to a shift known as the *dynamic frequency shift*. The imaginary part, if not too small to neglect, can be included in a redefined unperturbed Hamiltonian $\mathbf{H_0}$, in addition to the term we described in assumption 1. Thus, considering only the real part, Eq. [17] becomes

$$\frac{d\sigma^*_{\alpha\alpha'}(t)}{dt} = \frac{1}{2}\sum_{\beta\beta'}\begin{bmatrix} -\delta_{\alpha'\beta'}\sum_\gamma J_{\gamma\alpha\gamma\beta}(\gamma - \beta)e^{i(\alpha-\beta)t} \\ -\delta_{\alpha\beta}\sum_\gamma J_{\gamma\alpha'\gamma\beta'}(\gamma - \beta')e^{i(\beta'-\alpha')t} \\ +J_{\alpha\beta\alpha'\beta'}(\alpha - \beta)e^{i(\alpha-\beta+\beta'-\alpha')t} \\ +J_{\alpha\beta\alpha'\beta'}(\alpha' - \beta')e^{i(\alpha-\beta+\beta'-\alpha')t} \end{bmatrix}\sigma^*_{\beta\beta'}(t). \qquad [18]$$

Introducing a compact notation, Eq. [18] can be written as

$$\frac{d\sigma^*_{\alpha\alpha'}(t)}{dt} = \sum_{\beta,\beta'} R_{\alpha\alpha'\beta\beta'}e^{i(\alpha-\beta+\beta'-\alpha')t}\sigma^*_{\beta\beta'}(t). \qquad [19]$$

where

$$R_{\alpha\alpha'\beta\beta'} = \frac{1}{2}[J_{\alpha\beta\alpha'\beta'}(\alpha' - \beta') + J_{\alpha\beta\alpha'\beta'}(\alpha - \beta) - \delta_{\alpha'\beta'}\sum_\gamma J_{\gamma\beta\gamma\alpha}(\gamma - \beta) - \delta_{\alpha\beta}\sum_\gamma J_{\gamma\alpha'\gamma\beta'}(\gamma - \beta'). \qquad [20]$$

Equation [19] is known as the Redfield relaxation equation and the rate constants in Eq. [20] are the elements of the Redfield relaxation matrix. Using Eq. [20] in Eq. [19] and replacing $\sigma^*(t)$ by $\sigma^*(t) - \sigma^0$ we get

$$\frac{d\sigma^*_{\alpha\alpha'}(t)}{dt} = \sum_{\beta,\beta'} R_{\alpha\alpha'\beta\beta'}e^{i(\alpha-\beta+\beta'-\alpha')t}(\sigma^*_{\beta\beta'}(t) - \sigma^0_{\beta\beta'}). \qquad [21]$$

For well-resolved spectral lines, terms with $(\alpha - \beta + \beta' - \alpha') \gg 0$ in the RHS rapidly oscillate and their average becomes negligible in comparison with the terms for which $(\alpha - \beta + \beta' - \alpha') = 0$ (known as secular terms). This "secular approximation" [i.e., for terms satisfying the condition $(\alpha - \beta + \beta' - \alpha') = 0$] further simplifies Eq. [21] to

$$\frac{d\sigma^*_{\alpha\alpha'}(t)}{dt} = \sum_{\beta,\beta'}{}' R_{\alpha\alpha'\beta\beta'}(\sigma^*_{\beta\beta'}(t) - \sigma^0_{\beta\beta'}). \qquad [22]$$

The summation $\Sigma'_{\beta\beta'}$ is to states of energies that satisfy the secular condition $(\alpha - \beta + \beta' - \alpha') = 0$. The fact that we replace $\sigma^*(t)$ by $\sigma^*(t) - \sigma(0)$ in Eq. [21] implies that the lattice has a finite heat capacity and is accounted for by this phenomenological approximation. Equation [22] describes the equation of motion for the density matrix elements and a solution of these set of equations will describe the effects of evolution under relaxation. Stringfellow and Farrar (*61*) used a similar approach to formulate a two-spin relaxation problem in the Redfield framework.

Master Equation in Operator Form

In the previous section, the Redfield equation (Eq. [22]) has been derived in the Hilbert space where the basis set is the eigenstates of the unperturbed Hamiltonian of the nuclear spins in an external static magnetic field. For any two weakly coupled spins of $I = 1/2$, the basis set is simply given as $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$, and $|\beta\beta\rangle$. The master equation can also be represented in an operator form, in which the density matrix is represented as an operator given by the sum of products of base nuclear spin angular momentum operators (*62*). Such a description may be more elegant for some applications. Let us take a recourse to Eq. [8]:

$$\frac{d\langle\sigma^*(t)\rangle}{dt} = -\int_0^\infty d\tau\langle[\mathbf{H}^*_\mathbf{1}(t), [\mathbf{H}^*_\mathbf{1}(t - \tau), \sigma^*(t)]]\rangle. \qquad [23]$$

Now we write the relaxation Hamiltonian explicitly as a spin part (A) that is independent of time and a lattice or space part (F) that is dependent on time

$$\mathbf{H_1}(t) = \sum_q (-1)^q F_q(t) A_{-q} \qquad [24]$$

where $F_q(t)$ is the random complex function of time and A_q is non-Hermitian operators acting only on the spin system. However, the Hermiticity of $\mathbf{H_1}(t)$ (i.e., $\mathbf{H_1}^{-1} = \mathbf{H_1}^{*T}$) implies that $F_q(t)$ and A_q also satisfy $F_q^{*}(t) = (-1)^q F_q(t)$ and $A_q^{\dagger} = (-1)^q A_{-q}$. Defining transformations similar to Eq. [2] we get

$$e^{i\mathbf{H_0}t} A_q e^{-i\mathbf{H_0}t} = \sum_p A_{p,q} e^{i\omega_{p,q}t}$$

$$e^{i\mathbf{H_0}t} A_{-q} e^{-i\mathbf{H_0}t} = \sum_p A_{p,-q} e^{i\omega_{p,-q}t}$$

$$\mathbf{H}_1^{*}(t) = e^{i\mathbf{H_0}t}\mathbf{H_1}(t)e^{-i\mathbf{H_0}t} = \sum_{q,p}(-1)^q F_q(t) A_{p,-q} e^{i\omega_{p,-q}t} \qquad [25]$$

and substituting in the master equation (Eq. [23]) and noting that $A_{p,q}$ values are operators only on the spin variables, we get

$$\frac{d\sigma^{*}(t)}{dt} = -\sum_{q,q',p,p'} (-1)^{q+q'} e^{i(\omega_{p,-q}+\omega_{p',-q'})t} \times [A_{p,-q}, [A_{p',-q'}, \sigma^{*}(t)]] \times \int_0^{\infty} \langle F_q(t) F_{q'}^{*}(t-\tau)\rangle e^{-i\omega_{p,-q},\tau} d\tau. \qquad [26]$$

Introducing the secular approximation (Eqs. [21] and [22]), by setting $\omega_{p',-q'} = -\omega_{p,-q}$ (i.e., $q' = -q$ and $p' = p$), Eq. [26] becomes

$$\frac{d\sigma^{*}(t)}{dt} = -\sum_{q,p} [A_{p,-q}, [A_{p,q}, \sigma^{*}(t)]] \times \int_0^{\infty} \langle F_q(t) F_{-q}^{*}(t-\tau)\rangle e^{-i\omega_{p,q}\tau} d\tau \qquad [27a]$$

and using the property $F_q^{*}(t) = (-1)^q F_q(t)$,

$$\frac{d\sigma^{*}(t)}{dt} = -\sum_{q,p} [A_{p,-q}, [A_{p,-q}^{\dagger}, \sigma^{*}(t)]] \times \int_0^{\infty} \langle F_q(t)(-1)^q F_{-q}(t-\tau)\rangle e^{-i\omega_{pq}\tau} d\tau. \qquad [27b]$$

Using the definition of the correlation function as in Eq. [13] for the time dependent part of F_q and defining

$$g_{qq'}(t) = \langle F_q(t) F_{q'}^{*}(t+\tau)\rangle = \langle F_q(t) F_{q'}^{*}(t-\tau)\rangle = \langle F_q(t)(-1)^q F_{-q}(t-\tau)\rangle \qquad [28]$$

then Eq. [27b] becomes

$$\frac{d\sigma^{*}(t)}{dt} = -\sum_{q,p} [A_{p,-q}, [A_{p,-q}^{\dagger}, \sigma^{*}(t)]] \int_0^{\infty} g_q(\tau) e^{-i\omega_{pq}\tau} d\tau. \qquad [29]$$

The integral in Eq. [29] is the definition of spectral density function (Eq. [14]) and becomes

$$\int_0^{\infty} g_q(\tau) e^{-i\omega_{pq}\tau} d\tau = \frac{1}{2}\int_{-\infty}^{\infty} g_q(\tau)\cos(\omega_{pq}\tau) d\tau - i\int_0^{\infty} g_q(\tau)\sin(\omega_{pq}\tau) d\tau = \frac{1}{2} J_q(\omega_{pq}) - iK_q(\omega_{pq}). \qquad [30]$$

The second term in Eq. [30] gives rise to a dynamic frequency shift and can be treated as stated before (Eq. [17]). Thus, considering only the first term, Eq. [30] becomes

$$\frac{d\sigma^{*}(t)}{dt} = -\frac{1}{2}\sum_{q,p} J_q(\omega_{pq}) [A_{p,-q}, [A_{p,-q}^{\dagger}, \sigma^{*}(t)]]. \qquad [31]$$

Equation [31] is the master equation of the density matrix in the operator form.

Macroscopic Differential Equations

In a NMR experiment the effects of relaxation appear in terms of specific changes in the spectral parameters such as the line position, intensity, and shape. In order to correlate such changes with the associated relaxation processes, we have to cast the equation of motion in observable parameters given by an operator Q and its expectation value q^*

$$q^*(t) = \mathrm{TR}\{\sigma^*(t)Q\} \qquad [32]$$

where TR represents the trace. Multiplying the master equation in operator form (Eq. [31]) on both sides by Q and taking the trace we get

$$\frac{dq^*(t)}{dt} = -\frac{1}{2}\mathrm{TR}\left\{\sum_{q,p} J_q(\omega_{pq})[A_{p,-q}, [A^{\dagger}_{p,-q}, \sigma^*(t)]]Q\right\}. \qquad [33]$$

Using the cyclic property of trace of operators i.e., $\mathrm{Tr}\{[A, [B, C]]D\} = \mathrm{Tr}\{[B, [A, D]]C\}$, Eq. [33] is rearranged to yield

$$\frac{dq^*}{dt} = -\frac{1}{2}\mathrm{TR}\left\{\sum_{q,p} J_q(\omega_{pq})[A^{\dagger}_{p,-q}, [A_{p,-q}, Q]]\sigma^*(t)\right\}. \qquad [34]$$

Defining

$$\widehat{P} = \frac{1}{2}\sum_{q,p} J_q(\omega_{pq})[A^{\dagger}_{p,-q}, [A_{p,-q}, Q]] \qquad [35]$$

and using the definition of the expectation values from Eq. [32], Eq. [34] is written as

$$\frac{dq^*}{dt} = -p^*. \qquad [36]$$

Defining a parameter p_0,

$$p_0 = \frac{1}{2}\mathrm{TR}\left\{\sum_{q,p} J_q(\omega_{pq})[A^{\dagger}_{p,-q}, [A_{p,-q}, Q]]\sigma_0\right\} \qquad [37]$$

corresponding to the equilibrium density operator $\sigma^*(0)$ and $p^* = \mathrm{Tr}\{P\sigma^*(t)\}$ and replacing $\sigma^*(t)$ in Eq. [34] by the deviation $\sigma^*(t) - \sigma^*(0)$, one gets

$$\frac{dq^*}{dt} = -(p^* - p_0) \qquad [38]$$

For example, if the motion of the longitudinal magnetization of a spin I, then $Q = I_z$ and $q^* = \langle Q\rangle = \langle I_z\rangle$. Equation [38] becomes

$$\frac{d\langle I_z\rangle}{dt} = -\{p_z - p_0\}. \qquad [39]$$

Evaluating Eq. [35],

$$\widehat{P} = \frac{1}{2}\sum_{q,p} J_q(\omega_{pq})[A^{\dagger}_{p,-q}, [A_{p,-q}, I_z]] \approx \frac{1}{T_1} \qquad [40]$$

we get

$$\frac{d\langle I_z\rangle}{dt} = -\frac{1}{T_1}\{\langle I_z\rangle - \langle I_0\rangle\}. \qquad [41]$$

The above equation describes the time variation of $\langle I_z\rangle$ by a single exponential as in the case of Bloch equations (*63*). 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 $\langle I_z + S_z\rangle$. With an appropriate choice of Q, it is then possible to characterize the relaxation behavior of any particular operator for a given interaction Hamiltonian.

RELAXATION HAMILTONIANS

Irreducible Tensor Representation

The master equation for the density matrix as given by the Redfield relaxation equation (Eq. [22]) or that given by Eq. [31] can be used to determine rate constants, such as spin–lattice (T_1) or spin–spin (T_2) relaxation times (e.g., see Eq. [41]) and line shape. The exact calculation of such features, however, requires the knowledge of the relaxation Hamiltonian $\mathbf{H_1}$. Thus, this section introduces the relevant Hamiltonians that become time dependent because of molecular motions leading to relaxation. One important feature of these Hamiltonians is that they all can be described uniformly by second rank tensors. In this approach, once these Hamiltonians and their properties are properly formulated, calculation of their contributions to the NMR spectrum can be greatly simplified. A series of articles by Smith et al. (*64–66*) also provides a comprehensive description of the various Hamiltonians.

Let us start with the general definition of the relaxation Hamiltonian (Eq. [24]) in the laboratory frame as

$$\mathbf{H}_1(t) = \sum_q (-1)^q F_q(t) A_{-q} \qquad [42]$$

where $F_q(t)$ is a function describing the time dependence of the space variables alone and the A_{-q} is the spin variable. For NMR, q varies only as ± 2 because of the magnetic dipole nature of the nuclear spin angular moments.

Hamiltonians, when expressed as a tensor of rank *l,* fulfill the unitary transformation defined in terms of its elements T_{lm} (*67*, *68*) as

$$\Im_\Omega T_{lm} \Im_\Omega^{-1} = \sum_{m'=-l}^{l} T_{lm'} \mathbf{D}^{(l)}_{m'm}(\Omega) \qquad [43]$$

where $\Im_\Omega$ is the rotation operator and $\mathbf{D}^{(l)}_{mm'}(\Omega)$ is a component of the Wigner rotation matrix $[\mathbf{D}^{(l)}_{mm'}(\alpha, \beta, \gamma)]$, where α, β, and γ are the Eulerian angles and m takes values between $-l$ and $+l$ (*67*, *68*). Articles by Siminovitch (*69*, *70*) are certainly a good source for other specific examples on the use of Euler rotations. The interaction between any two vectors **V** and **U** in the tensor representation is defined by

$$\begin{aligned} \mathbf{H} \sim \mathbf{V}\Re\mathbf{U} &= \sum_{\alpha,\beta=x,y,z} V_\alpha R_{\alpha\beta} U_\beta \\ &= \sum_{\alpha,\beta=x,y,z} R_{\alpha\beta} T_{\beta\alpha} \qquad [44] \end{aligned}$$

where $\Re$ is a second rank Cartesian tensor. In Eq. [44] the vector components **V** and **U** are expressed as the dyadic $T_{\alpha\beta}$ and are separated from the second rank coupling tensor with the elements $R_{\alpha\beta}$. Equation [44] remains to be expressed in terms of familiar spin operators, such as Cartesian operators. Irreducible tensor representations have been widely used in NMR: Hubbard (*71*) used them to represent correlation functions in his relaxation theory and Stiegel and Spiess (*72*) used them to express the relaxation Hamiltonians. Here we adopt the approach laid out by Stiegel and Spiess.

For a nuclear spin angular moment *I,* the irreducible tensor operator can have nonvanishing matrix elements only for $l \leq 2I$. For example, if $I = 1/2$, then $l \leq 1$. When $I \geq 1$, l can be 2 or more, leading to quadrupole 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 because their coupling to the nuclear magnetic moment, which is a dipole, is ineffective.

For $l = 0$, it is evident from Eq. [43] that the tensor component is a scalar and is rotationally invariant.

For $l = 1$, the irreducible components are

$$\begin{aligned} T_{1\pm1} &= V_{\pm1} = \mp \frac{1}{\sqrt{2}} (V_x \pm iV_y), \\ T_{10} &= V_0 = V_z. \qquad [45] \end{aligned}$$

The linear combination of the Cartesian operators also follows the transformation properties given by Eq. [43]. Higher rank irreducible tensors are then constructed from the irreducible tensor of rank 1 by using the general rule (*67*, *73*),

$$\begin{aligned} T_{l_1} \times T_{l_2} &= \sum_{L=|l_1-l_2|}^{l_1+l_2} T_L, \\ T_{LM} &= \sum_m (l_1 m l_2 M - m | l_1 l_2 L m) T_{l_1} m T_{l_2} M - m \end{aligned} \qquad [46]$$

where the T_{LM} values are the Clebsch–Gordon coefficients (*67*, *68*, *73*). For example, for any two vectors **V** and **U**, the $T_{\beta\alpha}$ are

$$T_{00} = \frac{1}{\sqrt{3}} (V_{+1}U_{-1} + V_{-1}U_{+1} - V_0U_0) \qquad [47a]$$

$$T_{10} = \frac{1}{\sqrt{2}} (V_{+1}U_{-1} - V_{-1}U_{+1}) \qquad [47b]$$

$$T_{1\pm1} = \frac{1}{\sqrt{2}} (\pm V_{\pm1}U_0 \mp V_0U_{\pm1}) \qquad [47c]$$

$$T_{20} = \frac{1}{\sqrt{6}} (V_{+1}U_{-1} + V_{-1}U_{+1} + 2V_0U_0) \qquad [47d]$$

$$T_{2\pm1} = \frac{1}{\sqrt{2}} (V_{\pm1}U_0 + V_0U_{\pm1}) \qquad [47e]$$

$$T_{2\pm2} = (V_{\pm1}U_{\pm1}). \qquad [47f]$$

The expression in Eq. [47a] is different from the scalar product of the two vectors **V** and **U** by a factor of $-1/\sqrt{3}$, and the scalar product is usually given as

$$T_{00} = \mathbf{V} \cdot \mathbf{U} = \sum_{m=-l}^{l} (-1)^m V_{lm} U_{l-m}. \qquad [48]$$

Using Eq. [47d] setting $\mathbf{U} = \mathbf{V} = I$ (e.g., if $I \geq 1$), the expressions for $l = 2$ become

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

$$T^I_{2\pm 1} = \frac{1}{\sqrt{2}}\left[I_0 I_{\pm 1} + I_{\pm 1} I_0\right],$$

$$T^I_{2\pm 2} = I^2_{\pm 2}. \qquad [49]$$

We have thus expressed the two vectors in Eq. [44] in terms of the dyadic $T_{\beta\alpha}$. Using similar sets of rules, the coupling tensor can also be represented by irreducible tensors. The interaction Hamiltonian can be written as a general tensor as

$$\mathbf{H} = T^I_l \times \sum_{l'} T^R_{l'} \qquad [50]$$

with $T^R_{l'}$ as the irreducible tensor that contains all variables other than the spin variables I. Equation [50] is equivalent to Eq. [44]. The rotationally invariant Hamiltonian is obtained only for $\mathbf{H} = T_{00}$, which is valid only when $l' = l$. Thus, forming the scalar product as in Eq. [48],

$$\mathbf{H} \sim T_{00} = \sum_l \sum_{m=-l}^{l} (-1)^m T^I_{lm} T^R_{l-m}. \qquad [51]$$

Equation [51] implies that the rank of the spin tensor and that of the coupling interaction tensor should be identical. In other words, the vector representing a nuclear dipole moment ($l = 1$) can couple only with another vector (e.g., a magnetic field vector).

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

$$\mathfrak{R} = \mathfrak{R}^{(0)} + \mathfrak{R}^{(1)} + \mathfrak{R}^{(2)} \qquad [52]$$

where

$$\mathfrak{R}^{(0)}_{ab} = \frac{1}{3}\mathrm{TR}\mathfrak{R}\delta_{ab} = R\delta_{ab} \qquad [53a]$$

$$\mathfrak{R}^{(1)}_{ab} = \frac{1}{2}(R_{ab} - R_{ba}) \qquad [53b]$$

$$\mathfrak{R}^{(2)}_{ab} = \frac{1}{2}(R_{ab} + R_{ba}) - R\delta_{ab}. \qquad [53c]$$

Equation [53a–c] represents the *isotropic*, *antisymmetric*, and *symmetric* terms, respectively. We can then define a principal axis system (PAS), in which the interaction tensor $\mathfrak{R}^{(0)} + \mathfrak{R}^{(2)}$ is diagonal. The diagonal elements ρ_{XX}, ρ_{YY}, and ρ_{ZZ} are the principal elements, with the convention $|\rho_{ZZ}| \geq |\rho_{XX}| \geq |\rho_{YY}|$ and defining

$$\delta = \rho_{zz}$$

$$\eta = \frac{\rho_{YY} - \rho_{XX}}{\delta} \qquad 0 \leq \eta \leq 1. \qquad [54]$$

Thus, in the PAS, the irreducible tensor components can be represented by 3×3 matrices as follows:

$$\rho^{(0)} = R\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\rho^{(1)} = \begin{pmatrix} 0 & \rho_{XY} & \rho_{XZ} \\ -\rho_{XY} & 0 & \rho_{YZ} \\ -\rho_{XZ} & -\rho_{YZ} & 0 \end{pmatrix}$$

$$\rho^{(2)} = \delta\begin{pmatrix} -\frac{1}{2}(1+\eta) & 0 & 0 \\ 0 & -\frac{1}{2}(1-\eta) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad [55]$$

It should be noted that the antisymmetric part of the tensor cannot be brought into a diagonal form in the PAS. The relation between tensor components in the PAS as Cartesian axes ($\rho^{(l)}_{ab}$) and the corresponding irreducible components (ρ_{lm} or spherical coordinates) can be derived as follows. The interaction Hamiltonian in the PAS as written in Eq. [50] is

$$\mathbf{H} = \mathbf{V}\overset{\rightrightarrows}{\rho}\mathbf{U} \qquad [56]$$

where $\mathbf{V}$ and $\mathbf{U}$ are vector operators and $\overset{\rightrightarrows}{\rho}$ is a second rank coupling tensor given by the sum of the three terms in Eq. [55]. Substituting $\overset{\rightrightarrows}{\rho}$ from Eq. [55] into Eq. [56], then for various values of l,

$$l = 0 : H^{(0)} = R(V_x U_x + V_y U_y + V_z U_z), \qquad [57a]$$

$$\begin{aligned} l = 1 : H^{(1)} &= V_x(\rho_{xy}U_y + \rho_{xz}U_z) + V_y(-\rho_{xy}U_x \\ &\quad + \rho_{yz}U_z) + V_z(-\rho_{xz}U_x - \rho_{yz}U_y) \\ &= (V_xU_y - V_yU_x)\rho_{xy} + (V_xU_z \\ &\quad - V_zU_x)\rho_{xz} + (V_yU_z - V_zU_y)\rho_{yz} \end{aligned} \qquad [57b]$$

$$\begin{aligned} l = 2 : H^{(2)} &= \delta\Big(-V_xU_x \cdot \frac{1}{2}(1+\eta) \\ &\qquad - V_yU_y \cdot \frac{1}{2}(1-\eta) + V_zU_z \Big) \\ &= \frac{1}{2}\delta(-V_xU_x - V_yU_y - V_zU_z + 3V_zU_z) \\ &\quad + \frac{1}{2}\delta\eta(-V_xU_x + V_yU_y). \end{aligned} \qquad [57c]$$

In order to compare these expressions with $\rho_{lm}T_{l-m}$, we first express T_{lm} by Cartesian components. Using the definitions as in Eq. [45] for **V** and **U**,

$$\begin{aligned} V_{\pm 1} &= \mp \frac{1}{\sqrt{2}}(V_x \pm iV_y) \quad V_0 = V_z, \\ U_{\pm 1} &= \mp \frac{1}{\sqrt{2}}(U_x \pm iU_y) \quad U_0 = U_z \end{aligned} \qquad [58]$$

T_{lm} becomes

$$T_{00} = V_xU_x + V_yU_y + V_zU_z \qquad [59a]$$

$$\begin{aligned} T_{10} &= \frac{i}{\sqrt{2}}(V_xU_y - V_yU_x) \\ T_{1\pm 1} &= \frac{1}{2}[-\{(V_x \pm iV_y)U_z + V_z(U_x \pm iU_y)\}]. \end{aligned} \qquad [59b]$$

$$\begin{aligned} T_{20} &= \frac{1}{\sqrt{6}}(V_xU_x - V_yU_y - V_zU_z + 3V_zU_z) \\ T_{2\pm 1} &= \frac{1}{2}[\mp(V_x \pm iV_y)U_z \mp V_z(U_x \pm iU_y)] \\ T_{2\pm 2} &= [V_xU_x - V_yU_y \pm i(V_xU_y + V_yU_x)]. \end{aligned} \qquad [59c]$$

Comparing Eqs. [57] and [59] we get

$$\begin{aligned} &\rho_{00} = R \quad \rho_{20} = \sqrt{\frac{3}{2}}\,\delta, \\ &\rho_{1\pm 1} = (\rho_{xz} + i\rho_{yz}) \quad \rho_{2\pm 1} = 0, \\ &\rho_{10} = -i\sqrt{2}\rho_{xy} \quad \rho_{2\pm 2} = -\frac{1}{2}\delta\eta. \end{aligned} \qquad [60]$$

For nuclear spin relaxation, the rank of the tensor is always 2 ($l = 2$) and hence it is dropped from the notation ($T_{lm} = T_{2m} = T_m$). In Eqs. [43]–[60] the coupling terms have been expressed in terms of irreducible tensor components in the PAS.

Replacing ρ_{lm} by $F_q{}'$ (where the primes denote the PAS frame) and T^{l}_{lm} by A_{-q} the relaxation Hamiltonian $\mathbf{H}_1(t)$ in the PAS frame is given by

$$\mathbf{H}_1^{\mathbf{PAS}}(t) = \sum_q (-1)^q F_q'(t) A_{-q}. \qquad [61]$$

The relaxation Hamiltonian in the laboratory frame is then obtained by transforming Eq. [20], according to the prescription given by Eq. [43], as

$$\mathbf{H}_1(t) = \sum_q \sum_{q'} (-1)^q F_{q'}'(t) D^{(2)}_{q'q}(\Omega) A_{-q} \qquad [62]$$

where $D^{(2)}_{q'q}(\Omega)$ is the Wigner rotation matrix at time t that transforms the PAS to the laboratory frame. However, it is customary to express the Hamiltonian in the laboratory frame in a simple form as

$$\mathbf{H}_1(t) = \sum_q (-1)^q F_q(t) A_{-q} \qquad [63]$$

in which

$$F_q(t) = \sum_{q'} F_{q'}'(t) D^{(2)}_{q'q}(\Omega)$$

implying transformation from the PAS to the laboratory frame (note that in Eq. [63] it is F_q and not F_q').

Expressions for Relaxation Hamiltonians

Once a relaxation mechanism is identified, then the corresponding F_q and A_{-q} can be expressed as second rank irreducible tensors to define the relaxation Hamiltonian. The most common relaxation mechanism for nuclear spins with $I = 1/2$ are due to dipole–dipole (DD) and chemical shift anisotropy (CSA) interactions. Quadrupolar relaxation becomes dominant for spins with higher spin angular momentum, $I > 1/2$. In addition, other less frequently encountered relaxation mechanisms include interactions due to spin–spin coupling (J) and spin rotation (SR). Relaxation Hamiltonians due to CSA, J, and SR mechanisms will have all three (isotropic, antisymmetric, and symmetric) components, but only the isotropic and the traceless symmetric parts are measurable and significant. The antisymmetric part of the 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 relaxation are by nature given by

Table 1 Expressions for Relaxation Mechanisms in Principal Axis System (PAS)

	Relaxation Mechanism		
	Dipole–Dipole	Chemical Shift Anisotropy	Quadrupolar
Vectors	**I** and **S**	**I** and **B**	**S** with itself
Interaction tensor	**D**	σ_I	$\nabla\mathbf{V}$
		PAS Frame	
F'_0	$-\sqrt{\frac{3}{2}}\frac{2\gamma_I\gamma_S\hbar}{r_{IS}^3}$	$\sqrt{\frac{3}{2}}\delta_{zz}$	$\sqrt{\frac{3}{2}}\frac{e^2qQ}{2S(2S-1)}$
$F'_{\pm 1}$	0	0	0
$F'_{\pm 2}$	0	$-\frac{1}{2}\delta_{zz}\eta_{C_I}$	$-\frac{1}{2}\frac{e^2qQ}{2S(2S-1)}\eta_Q$
		Laboratory Frame	
Space part	$F_q^D = -\sqrt{\frac{3}{2}}\frac{2\gamma_I\gamma_S\hbar}{r_{IS}^3} \times D^{(2)}_{0q}(\Omega_D)$	$F_q^{C_I} = \sqrt{\frac{3}{2}}\delta_{zz}\left[D^{(2)}_{0q}(\Omega_{C_I}) - \sqrt{\frac{1}{6}}\eta_{C_I}D^{(2)}_{+2q}(\Omega_{C_I}) - \sqrt{\frac{1}{6}}\eta_{C_I}D^{(2)}_{-2q}(\Omega_{C_I})\right.$	$F_q^Q = \sqrt{\frac{3}{2}}\frac{e^2qQ}{2S(2S-1)\hbar} \times \left[D^{(2)}_{0q}(\Omega_Q) - \sqrt{\frac{1}{6}}\eta_Q D^{(2)}_{+2q}(\Omega_Q) - \sqrt{\frac{1}{6}}\eta_Q D^{(2)}_{-2q}(\Omega_Q)\right]$
		Spin Part	
A_0	$\frac{1}{\sqrt{6}}(3I_zS_z - \mathbf{I}\cdot\mathbf{S})$	$\frac{2}{\sqrt{6}}\omega_I I_z$	$\frac{1}{\sqrt{6}}(3S_z^2 - S(S+1))$
$A_{\pm 1}$	$\mp\frac{1}{2}(I_zS_\pm + I_\pm S_z)$	$\mp\frac{1}{2}\omega_I I_\pm$	$\mp\frac{1}{2}(S_zS_\pm + S_\pm S_z)$
$A_{\pm 2}$	$\frac{1}{2}I_\pm S_\pm$	0	$\frac{1}{2}S_\pm^2$

The dipolar interaction (D) is between spins I and S, the chemical shift anisotropy (C) interaction is between spin I and applied magnetic field **B**, and the quadrupolar (Q) is between spin S and the electric field gradient $\nabla\mathbf{V}$. Transformation from the PAS to the laboratory frame is obtained using Eq. [62] and the values of $D_q^{(2)}(\Omega)$' the Wigner rotation matrix elements, and can be obtained from standard texts (*68*). γ_I and γ_S, the gyromagnetic ratios of spin I and S; $\hbar$, Planck's constant; r_{IS}, internuclear distance between I and S; δ_{zz}, the largest principal value of the chemical shift anisotropy tensor; η, the asymmetric parameters; e^2qQ, the quadrupolar coupling constant (rad/s).

symmetric and traceless tensors. The interaction Hamiltonian for the various relaxation mechanisms can be written in a general form as given in Table 1.

CORRELATION FUNCTIONS

With the knowledge of the relevant relaxation Hamiltonian we can formulate the correlation function given either by Eq. [15] or [28]. Correlation functions can be derived based on specific models that would best describe the molecular motional freedom of a system under study. For example, methyl group rotations in a molecule have been explained in terms of a spherical top motional model along with the overall tumbling of the molecule. In this section we present a general framework for the derivation of the correlation function in which the details of internal motions are included in the framework proposed by Lipari and Szabo (*74*, *75*). In this approach the internal motion is described by an order parameter signifying the restriction for the motion and an effective correlation time indicating the rate of the motion. It is also straightforward to arrive at situations where there are no internal motions by simply setting the order parameter to unity (i.e., completely restricted). Although the connection between the details of the molecular motion and the relaxation data is lost, the simplicity of description and the robustness of fitting the experimental data by this approach are the primary reasons for its choice here. Moreover, any description of dynamics based on a specific model requires additional information on the system that is avoided in the "model free" approach.

Let us rewrite the time dependent relaxation Hamiltonian as defined in Eq. [63],

$$\mathbf{H}_1(t) = \sum_q (-1)^q F_q(t) A_{-q} \qquad [64]$$

where F_q and A_{-q} are the spin and space parts, respectively. Redefining the correlation function between two functions similar to Eq. [13],

$$g^{AB}_{qq'}(t) = \langle F^{*A}_q(0)\, F^B_{q'}(t)\rangle. \qquad [65]$$

The angle brackets $\langle \cdots \rangle$ represent an ensemble average and the superscripts A and B refer to different relaxation mechanisms. When $A = B$, $g_{qq'}(t)$ is an autocorrelation function; when $A \neq B$, it is a cross-correlation function. Autocorrelation and cross-correlation functions describe correlations of a particular relaxation mechanism with itself and with other mechanisms over time, respectively. The spectral densities are then given by the Fourier transform of the correlation function as (similar to Eq. [14])

$$J^{AB}_{qq'}(\omega) = \int_{-\infty}^{\infty} g^{AB}_{qq'}(t) e^{-i\omega t} dt \qquad [66]$$

In order to evaluate the correlation functions between various relaxation mechanisms it is convenient to first consider the space functions in their respective PASs (signified with a prime) and then transform them into the laboratory frame. In the case of DD relaxation the PAS is defined with its Z axis along the DD vector, and for the other relaxation mechanisms (quadrupolar and CSA) the Z axis is along the symmetry axis of the interaction tensor (or the largest principal value of the tensor). Using the transformation properties of the second rank irreducible tensors and with a sum over q'' for convenience, the space functions of the interaction Hamiltonian are written as

$$F^{\mathrm{Lab}}_q = \sum_{q''=-2}^{2} F'_{q''} D^{(2)}_{q''q}(\Omega) \qquad [67]$$

where Ω is the set of Euler angles defining the orientation of the principal axis frame with respect to the laboratory frame. Substituting Eq. [67] in Eq. [65], the correlation function,

$$g^{AB}_{qq'}(t) = \sum_{q''} \langle (F'_{q''}{}^*)^A D^{(2)*}_{q''q}(\Omega : 0)\, F'_{q''}{}^B D^{(2)}_{q''q'}(\Omega : t)\rangle \qquad [68]$$

where $D^{(2)}_{q''q'}(\Omega{:}t)$ is the rotation matrix at time t. It may be noted that the time dependence is on the Euler angles of transformation. Secular approximation imposes the condition

$$g^{AB}_{qq'}(t) = \delta_{qq'} g^{AB}_q(t) \qquad [69]$$

in Eq. [68].

Autocorrelation Function ($A = B$)

In order to bring out motional details such as internal motion, the autocorrelation 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 autocorrelation function (after substituting the condition given by Eq. [69] into Eq. [68]) is given by

$$g_q(t) = \sum_{q'} \Big\langle \sum_{q''} F'_{q''}{}^* D^{(2)*}_{q''q'}(\Omega' : 0)\, D^{(2)*}_{q'q}(\Omega_M : 0) \times F'_{q''} D^{(2)}_{q''q'}(\Omega' : t)\, D^{(2)*}_{q'q}(\Omega_M : t)\Big\rangle. \qquad [70a]$$

Rearranging the terms in Eq. [70a],

$$g_q(t) = \sum_{q'q''} \langle |F'_{q''}|^2 D^{(2)*}_{q''q'}(\Omega' : 0)\, D^{(2)}_{q'q}(\Omega_M : 0) \times D^{(2)}_{q''q'}(\Omega' : t)\, D^{(2)*}_{q'q}(\Omega_M : t)\rangle. \qquad [70b]$$

In the above equations, $\Omega'{:}t$ describes the orientation of the PAS in the molecular frame at time t and $\Omega_M{:}t$ describes the orientation of the molecular frame with

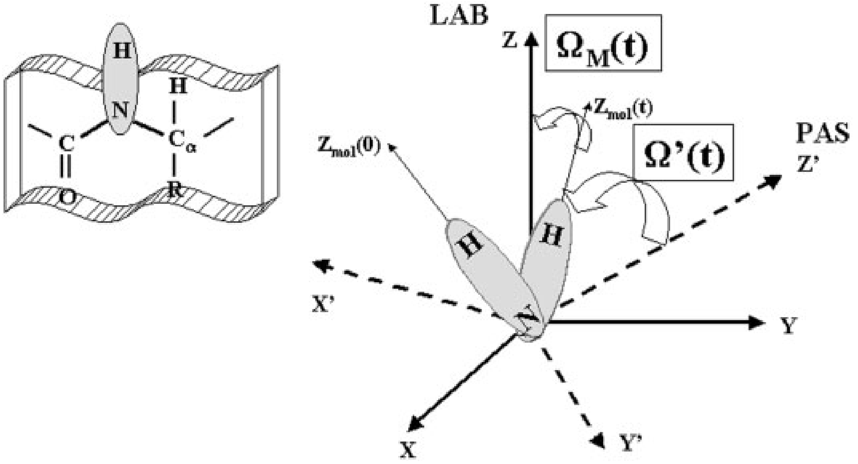

Figure 1 A schematic representation of the coordinate transformation from the principal axis frame (PAS, primed axes) to the laboratory frame (LAB, unprimed axis) of reference in the case of an autocorrelation function. Because of molecular motion, the dipolar vector of a protein backbone (NH) assumes two different orientations at times 0 and t, as represented in their respective molecular frames. [Only the z axes $Z_{\mathrm{mol}}(0)$ and $Z_{\mathrm{mol}}(t)$ are shown.] For example, the first transformation from the PAS to the molecular frame by Euler angles $\Omega'(t)$ is followed by the transformation from the molecular to LAB frame through $\Omega_M(t)$. A similar transformation is performed for the orientation of the vector at time 0 (not shown).

respect to the laboratory frame. Figure 1 schematically represents such transformations for a typical N—H dipolar vector in a protein backbone at time t. If there is no internal motion, then Ω' is independent of time and the correlation function is given in terms of the overall motion that is characterized by the time dependent Ω_M. In the presence of internal motion, it is not straightforward that the internal and overall motion can be separated. However, useful results have been derived when the time scales of internal and overall motions are vastly different (*74*, *75*). In such a situation it is assumed that the total correlation function could be approximated as a product of two correlation functions, one corresponding to the overall motion $C_0(t)$ and the other to the internal motion $C_I(t)$. It has also been shown that such a separation is possible, even for anisotropic overall motion (*76*).

Thus, the autocorrelation function can be written as

$$g_q(t) = C_0(t)C_I(t) \qquad [71]$$

where

$$C_0(t) = \sum_{q'} \langle D^{(2)*}_{q'q}(\Omega_M : 0)\, D^{(2)}_{q'q}(\Omega_M : t)\rangle \qquad [72]$$

and

$$C_I(t) = \sum_{q'q''} |F'_{q''}|^2 \langle D^{(2)*}_{q''q'}(\Omega' : 0)\, D^{(2)}_{q''q'}(\Omega' : t)\rangle. \qquad [73]$$

It is worthwhile to note that Eq. [73] is independent of the variable q. Therefore, it follows that the effect of internal motion appears as a modification of the overall correlation function in a simple way and it is a consequence of the separable form assumed by Eq. [68].

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

$$C_I(t) = |F'_0|^2 \sum_{q'} \langle D^{(2)*}_{0q'}(\Omega' : 0)\, D^{(2)}_{0q'}(\Omega' : t)\rangle. \qquad [74]$$

Following the Lipari and Szabo (*74*, *75*) approach, the correlation function $C_I(t)$ is defined as

$$C_I(t) \approx C_I(\infty) + (C_I(0) - C_I(\infty))e^{-t/\tau_e} \qquad [75]$$

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

$$\frac{1}{8\pi^2}\int_{\Omega} D^{(l)*}_{q_1q_2}(\Omega)\, D^{(l')}_{q_3q_4}(\Omega)\, d\Omega = \frac{1}{2l+1}\,\delta_{ll'}\delta_{q_1q_3}\delta_{q_2q_4}$$

in Eq. [75],

$$C_I(0) = |F'_0|^2 \quad C_I(\infty) = |F'_0|^2 S^2. \qquad [76]$$

Moreover, when the overall motion is isotropic, we may write $C_0(t)$ as

$$C_0(t) = e^{-t/\tau_M}. \qquad [77]$$

Substituting Eqs. [76] and [77] in Eq. [75], the correlation function becomes

$$g(t) = C_I(t) = |F'_0|^2[S^2 e^{-t/\tau_M} + (1 - S^2)e^{-t/\tau}] \qquad [78]$$

where

$$\frac{1}{\tau} = \frac{1}{\tau_M} + \frac{1}{\tau_e}$$

and the subscript q is dropped from $g(t)$ because it is independent of q. For anisotropic overall motion we may again follow the approach of Lipari and Szabo (*74*, *75*) and write $C_0(t)$ as

$$C_0(t) = Ae^{-t/\tau_1} + (1 - A)e^{-t/\tau_2} \qquad [79]$$

where A is an anisotropic factor similar to the order parameter and it is unity when the overall motion is isotropic and can be used instead of Eq. [77] to derive $g(t)$.

Cross-Correlation Function ($A \neq B$)

Let A be the dipolar interaction and B is either the CSA or quadrupolar interaction. It is important that both A and B are represented in the same frame of reference. Hence, for example, A is transformed from its PAS to the molecular reference frame and then finally to the laboratory frame. For mechanism B the sequence of transformations is from its PAS to the dipolar frame (PAS frame of A) to the molecular frame to the laboratory frame. Figure 2 shows a schematic of the transformation for a N—H system in which the nitrogen CSA (interaction B) is transformed from its PAS to that of the dipolar frame (PAS of A) and then to the molecular frame. Mechanism B needs one additional transformation to facilitate the delineation of the time correlation information between the two mechanisms. Thus, for the dipolar relaxation ($A = D$),

$$F_q^D = \sum_{q'q''} F'^{D}_{q''} D^{(2)}_{q''q'}(\Omega'_D)\, D^{(2)}_{q'q}(\Omega_M) \qquad [80]$$

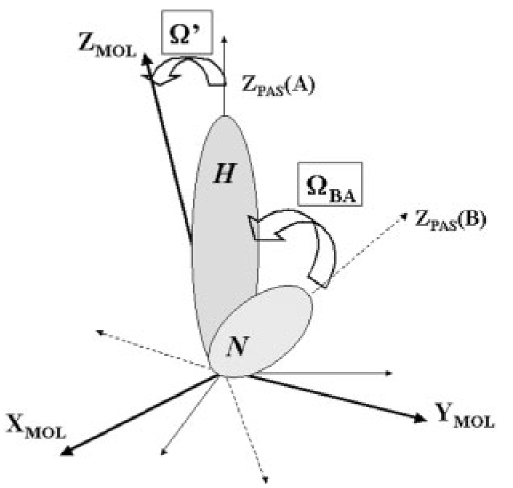

Figure 2 A schematic representation of the coordinate transformation from the principal axis frame (PAS) to the molecular frame (MOL) of reference in the case of a cross-correlation function. The PAS frames of two relaxation mechanisms A (NH-dipolar) and B (N CSA) are arbitrarily assigned. For B, it is necessary to first transform it from its PAS frame [$Z_{\text{PAS}}(B)$) to that of A ($Z_{\text{PAS}}(A)$] and then both A and B are transformed to a common molecular frame. The transformation by Euler angles Ω_M brings the dependence of the molecular geometry (e.g., inter-PAS angles between A and B) into relaxation parameters. The rest of the transformations are similar to those in Fig. 1.

where Ω'_D describes the orientation of the DD vector in the molecular frame. For mechanism B we have

$$F_q^B = \sum_{q'q''q'''} F'^{B}_{q'''} D^{(2)}_{q'''q''}(\Omega_{BD})\, D^{(2)}_{q''q'}(\Omega'_D)\, D^{(2)}_{q'q}(\Omega_M) \qquad [81]$$

where Ω_{BD} describes the orientation of the PAS of interaction B with respect to the dipolar frame. Then the cross-correlation function is

$$g_q^{DB}(t) = \sum_{q'q''q'''} \langle F'^{D*}_{q''} D^{(2)*}_{q''q'}(\Omega'_D : 0)\, D^{(2)*}_{q'q}(\Omega_M : 0)$$
$$\times F'^{B}_{q'''} D^{(2)}_{q'''q''}(\Omega_{BD} : t)\, D^{(2)}_{q''q'}(\Omega'_D : t)\, D^{(2)}_{q'q}(\Omega_M : t)\rangle \qquad [82]$$

For example, the expressions for DD–CSA cross correlations for two-spin and spin calculations are provided in the literature (*13*, *77*) .

Axially Symmetric Tensor for Interaction B. The only nonvanishing space functions in the PAS are F'^{D}_0 and F'^{B}_0. Therefore,

$$g_q^{DB}(t) = \sum_{q'q''} \langle F'^{D*}_0 D^{(2)*}_{0q'}(\Omega'_D : 0)\, D^{(2)*}_{q'q}(\Omega_M : 0)\, F'^{B}_0 D^{(2)}_{0q''}$$
$$\times (\Omega_{BD} : t)\, D^{(2)}_{q''q'}(\Omega'_D : t)\, D^{(2)}_{q'q}(\Omega_M : t)\rangle \qquad [83]$$

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

$$C_0(t) = \sum_{q'} \langle D_{q'q}^{(2)*}(\Omega_M : 0)\, D_{q'q}^{(2)}(\Omega_M : t)\rangle \quad [84]$$

and $C_I(t)$ after using the orthogonal property of the Wigner rotation matrix elements is

$$C_I(t) = \sum_{q'} |F_0'^{D*} F_0'^{B}| \langle D_{0q'}^{(2)*}(\Omega_D' : 0)\, D_{q'q'}^{(2)}(\Omega_D' : t) \times D_{00}^{(2)}(\Omega_{BD} : t)\rangle. \quad [85]$$

Again writing $C_I(t) \approx C_I(\infty) + (C_I(0) - C_I(\infty))e^{-t/\tau_e}$ (Eq. [65]), the correlation function becomes

$$\begin{aligned} C_I(0) &= |F_0'^{D*} F_0'^{B}| D_{00}^{(2)}(\Omega_{BD}) \\ &= \frac{1}{2}|F_0'^{D*} F_0'^{B}|(3\cos^2\theta_{BD} - 1) \\ C_I(\infty) &= \frac{1}{2}|F_0'^{D*} F_0'^{B}|(3\cos^2\theta_{BD} - 1)S^2. \end{aligned} \quad [86]$$

Thus, when the overall motion is isotropic, the cross-correlation function is given as

$$g^{DB}(t) = \frac{1}{2}|F_0'^{D*} F_0'^{B}|(3\cos^2\theta_{BD} - 1) \times [S^2 e^{-t/\tau_M} + (1 - S^2)e^{-t/\tau}]. \quad [87]$$

For anisotropic overall motion, we may again use

$$C_0(t) = Ae^{-t/\tau_1} + (1 - A)e^{-t/\tau_2}$$

Thus, a measurement of the cross-correlation spectral density can also yield information on the dynamics of the spin system.

General Tensor for B. For a general tensor and rewriting Eq. [83] we have

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

but for DD relaxation the only nonzero PAS element is $F_0'^{D}$ (see Table 1). Thus,

$$g_q^{DB}(t) = \sum_{q'q''q'''} \langle F_0'^{D*} D_{0q'}^{(2)*}(\Omega_D' : 0)\, D_{q'q}^{(2)*}(\Omega_M : 0) \times F_{q'''}'^{B} D_{q'''q''}^{(2)}(\Omega_{BD} : t)\, D_{q''q'}^{(2)}(\Omega_D' : t)\, D_{q'q}^{(2)}(\Omega_M : t)\rangle. \quad [89]$$

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

$$C_I(t) = \sum_{q'q''q'''} \langle F_0'^{D*} F_{q'''}'^{B} D_{0q'}^{(2)*}(\Omega_D' : 0) \times D_{q''q'}^{(2)}(\Omega_D' : t)\, D_{q'''q''}^{(2)}(\Omega_{BD} : t)\rangle. \quad [90]$$

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

$$C_I(t) = \sum_{q'q'''} \langle F_0'^{D*} F_{q'''}'^{B} D_{0q'}^{(2)*}(\Omega_D' : 0) \times D_{0q'}^{(2)}(\Omega_D' : t)\, D_{q'''0}^{(2)}(\Omega_{BD} : t)\rangle. \quad [91]$$

Thus, when the overall motion is isotropic, the cross-correlation function becomes

$$g^{DB}(t) = \sum_{q'''} F_0'^{D*} F_{q'''}'^{B} D_{q'''0}^{(2)}(\Omega_{BD}) \times [S^2 e^{-t/\tau_M} + (1 - S^2)e^{-t/\tau}]. \quad [92]$$

An extension to the anisotropic overall motion can be formulated as previously.

There is one important implicit assumption in the derivation of the above equations. The relative orientation of the PAS of interaction B and that of the DD vector (or interaction A) is assumed to be constant at all times, even in the presence of internal motion (see Fig. 2). This means that the expressions for cross correlation as given by Eqs. [87] and [92] are valid in situations wherein the same internal motion is affecting the parts of the molecule in which the two interaction tensors represent the relaxation. The situations that one encounters most often, which are ones in which interaction B is due to one of the same spins that participates in the DD interaction, such as a CH vector with CH DD interaction (A) and nitrogen or carbon CSA (B), are adequately described by this method. If the two spins reside in different parts of the same molecule that undergoes different internal motions, then it is not straightforward to formulate the theory. It may be necessary to invoke correlations between the various motions involved and the assumptions on which these expressions are obtained become untenable. Because it is not within the scope of this article, such correlation functions are not considered.

APPLICATION OF THEORY OF SPIN RELAXATION

We have presented a detailed theoretical framework to calculate the effects of various types of relaxation in any given experiment. In this section, we apply the theory to relevant relaxation problems in both the Redfield and operator formulations. A relatively simpler and familiar two-spin relaxation problem is treated first using the operator approach and later a more involved calculation for a slightly more complicated system is presented as an example for the Redfield approach.

Example for Operator Approach

The operator approach is convenient to use in a particular experiment when we know the corresponding observable operator that undergoes relaxation evolution and gives rise to a discernable feature in the NMR spectrum. As an example let us consider two unlike spins denoted by the symbols *I* and *S*. The Zeeman Hamiltonian is given by (*1*)

$$\mathbf{H_0} = \omega_I I_z + \omega_S S_z \qquad [93]$$

In Eq. [93], ω_I and ω_S are the Larmor frequencies of the *I* and *S* spins, respectively. Spins *I* and *S* could either be homonuclear or heteronuclear species. We concentrate on the relaxation of the longitudinal magnetization by the DD relaxation mechanism. We have to solve for the macroscopic observable $\langle I_z \rangle^*$ and $\langle S_z \rangle^*$, where the asterisk denotes interaction representation. The master equation for the macroscopic observable as defined in Eq. [37] is ($q^* = \langle Q \rangle = \mathrm{TR}\{\sigma^*(t)Q\}$),

$$\frac{dq^*}{dt} = -(p^* - p_0) \qquad [94]$$

where

$$p^* = \frac{1}{2}\mathrm{TR}\left\{\sum_{q,p} J_q(\omega_{pq})[A^{\dagger}_{p,-q}, [A_{p,-q}, Q]]\sigma^*\right\},$$

$$p_0 = \frac{1}{2}\mathrm{TR}\left\{\sum_{q,p} J_q(\omega_{pq})[A^{\dagger}_{p,\,-\,q},[A_{p,\,-\,q},Q]]\sigma_0\right\}. \qquad [95]$$

The Hamiltonian for the DD relaxation mechanism in the laboratory frame ([Eq. 64]) is

$$\mathbf{H}_1^D = \sum_q (-1)^q F_q^D A_{-q}^D \qquad [96]$$

where the F_q^D and A_{-q}^D are obtained from Table 1.

$$F_q^D = -\sqrt{\frac{3}{2}}\,\frac{2\gamma_I\gamma_S\hbar}{r_{IS}^3}\,D_{0q}^{(2)}(\Omega_D)$$

$$A_0^D = \frac{1}{\sqrt{6}}(3I_zS_z - \mathbf{I}\cdot\mathbf{S}),$$

$$A_{\pm 1}^D = \mp\frac{1}{2}(I_zS_\pm + I_\pm S_z)$$

$$A_{\pm 2}^D = \frac{1}{2} I_\pm S_\pm. \qquad [97]$$

Using the transformation to interaction representation given by Eq. [2],

$$e^{i\mathbf{H_0}t}A_q e^{-i\mathbf{H_0}t} = \sum_p A_{p,q}e^{i\omega_{p,q}t},$$

$$e^{i\mathbf{H_0}t}A_{-q} e^{-i\mathbf{H_0}t} = \sum_p A_{p,-q}e^{i\omega_{p,-q}t},$$

$$\mathbf{H}_D^*(t) = e^{i\mathbf{H_0}t}\mathbf{H}_D(t)e^{-i\mathbf{H_0}t} = \sum_{q,p}(-1)^q F_q A_{p,-q}e^{i\omega_{p,-q}t} \qquad [98]$$

we get

$$\begin{aligned} e^{i\mathbf{H_0}t}A_0^D e^{-i\mathbf{H_0}t} &= \frac{1}{\sqrt{6}}(3I_zS_z - \mathbf{I}\cdot\mathbf{S}) \\ &= \frac{1}{\sqrt{6}}2I_zS_z - \frac{1}{2}\{e^{i(\omega_I-\omega_S)t}I_+S_- \\ &\quad + e^{-i(\omega_I-\omega_S)t}I_-S_+\} \\ e^{i\mathbf{H_0}t}A_{+1}^D e^{-i\mathbf{H_0}t} &= -\frac{1}{2}(e^{i\omega_I t}I_+S_z + e^{i\omega_S t}I_zS_+), \\ e^{i\mathbf{H_0}t}A_{-1}^D e^{-i\mathbf{H_0}t} &= +\frac{1}{2}(e^{-i\omega_I t}I_-S_z + e^{-i\omega_S t}I_zS_-), \\ e^{i\mathbf{H_0}t}A_{+2}^D e^{-i\mathbf{H_0}t} &= \frac{1}{2}(e^{i(\omega_I+\omega_S)t}I_+S_+ + e^{-i(\omega_I+\omega_S)t}I_-S_-). \end{aligned} \qquad [99]$$

The spectral density $J_q(\omega_{pq})$ is given by (using Eq. [30])

$$
\begin{aligned}
J_q(\omega_{pq}) &= \int_{-\infty}^{\infty} g_q(\tau) e^{-i\omega_{pq}\tau} d\tau \\
&= \delta_{qq'}\delta_{pp'} \int_{-\infty}^{\infty} \langle F_{qp}(t)\, F^{*}_{q'p'}(t-\tau)\rangle e^{-i\omega_{pq}\tau} d\tau \\
&= \langle |F_q^D|^2 \rangle \int_{-\infty}^{\infty} e^{-(|\tau|/\tau_c)} e^{-i\omega_{pq}\tau} d\tau = 2\langle |F_q^D|^2\rangle J(\omega_{pq})
\end{aligned}
\qquad [100]
$$

where

$$
J(\omega_{pq}) = \frac{\tau_c}{1 + \omega_{pq}^2 \tau_c^2} \qquad [101]
$$

which is a Lorentzian spectral density, an outcome of the assumption of an exponential correlation function. The average $\langle |F_q^D|^2 \rangle$ is given as

$$
\begin{aligned}
\langle |F_q^D|^2 \rangle &= 6\, \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \times \left[\frac{1}{8\pi^2} \int_{\Omega_D} D^{(l)*}_{q_1 q_2}(\Omega_D)\, D^{(l')}_{q_3 q_4}(\Omega_D)\, d\Omega_D \right], \\
&= 6\, \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \left[\delta_{ll'} \delta_{q_1 q_3} \delta_{q_2 q_4} \frac{1}{2l+1} \right] \\
&= \frac{6}{5} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6}
\end{aligned}
\qquad [102]
$$

In the above equation $l = 2$. Thus, $J_q(\omega_{pq})$ is given by

$$
J_q(\omega_{pq}) = 2\left(\frac{6}{5} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \right) J(\omega_{pq}) \qquad [103]
$$

Let us evaluate A_z^{I*} given as

$$
\begin{aligned}
A_z^{I*} &= \frac{1}{2} \sum_{q,p} J_q(\omega_{pq}) [A^{\dagger}_{p,-q}, [A_{p,-q}, I_z]] \\
&= \left(\frac{6}{5} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \right) \sum_{q,p} J(\omega_{pq}) [A^{\dagger}_{p,-q}, [A_{p,-q}, I_z]].
\end{aligned}
\qquad [104]
$$

$$
\begin{aligned}
A_z^{I*} = \left(\frac{6\gamma_I^2 \gamma_S^2 \hbar^2}{5\ r_{IS}^6} \right) \Bigg\{ & \frac{4}{6} J(0) [I_z S_z, [I_z S_z, I_z]] \\
& + \frac{1}{24} J(\omega_I - \omega_S) [I_- S_+, [I_+ S_-, I_z]] + HC \\
& + \frac{1}{4} J(\omega_I) [I_- S_z, [I_+ S_z, I_z]] + HC \\
& + \frac{1}{4} J(\omega_I + \omega_S) [I_- S_-, [I_+ S_+, I_z]] + HC \Bigg\}
\end{aligned}
\qquad [105]
$$

where HC stands for Hermitian conjugate. The first and the second term on the RHS of Eq. [105] arise from $q = 0$. The first commutator, however, is zero and the second double commutator can be evaluated (using $[I_+, I_z] = -I_+$ etc.) as

$$
\begin{aligned}
[I_- S_+, [I_+ S_-, I_z]] &= -[I_- S_+, I_+ S_-] \\
&= \{2 I_z S_+ S_- - 2 S_z I_+ I_-\} \\
&= 2 I_z (S_x^2 + S_y^2 - i S_x S_y + i S_y S_x) \\
&\quad - 2 S_z (I_x^2 + I_y^2 - i I_x I_y + i I_y I_x).
\end{aligned}
\qquad [106a]
$$

Using $I_x^2 = I_y^2 = I_z^2 = I(I + 1)/3$, Eq. [106a] reduces to

$$
[I_- S_+, [I_+ S_-, I_z]] = \tfrac{4}{3} S(S + 1) I_z - \tfrac{4}{3} I(I + 1) S_z. \qquad [106b]
$$

Thus, the contribution from the $q = 0$ term is

$$
\frac{1}{15} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} 2J(\omega_I - \omega_S) \times \{S(S + 1)\langle I_z \rangle - I(I + 1)\langle S_z \rangle\}. \qquad [107]
$$

Similarly, the contribution from the $q = 1$ term (third term, Eq. [105]) is

$$
\frac{6}{15} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} J(\omega_I) S(S + 1) \langle I_z \rangle \qquad [108]
$$

and the contribution from the $q = 2$ term (fourth term. Eq. [105]) is

$$
\frac{6}{15} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} 2J(\omega_I + \omega_S) \times \{S(S + 1)\langle I_z \rangle + I(I + 1)\langle S_z \rangle\} \qquad [109]
$$

The equation of motion for $\langle I_z\rangle$, after replacing $\langle I_z\rangle$ by $\langle I_z\rangle^* - I_0$ becomes

$$\frac{d}{dt}\langle I_z\rangle = -\frac{1}{T_1^{II}}(\langle I_z\rangle - I_0) - \frac{1}{T_1^{IS}}(\langle S_z\rangle - S_0) \quad [110]$$

where

$$\begin{aligned}\frac{1}{T_1^{II}} &= \frac{1}{15}\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6}S(S+1)\\ &\quad\times[2J(\omega_I-\omega_S)+6J(\omega_I)+12J(\omega_I+\omega_S)],\\ \frac{1}{T_1^{IS}} &= \frac{1}{15}\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6}I(I+1)\\ &\quad\times[-2J(\omega_I-\omega_S)+12J(\omega_I+\omega_S)]. \quad [111]\end{aligned}$$

The equation of motion of $\langle I_z\rangle$ clearly shows its coupling to spin S, and so we need to write a similar equation for S. We can write an equation for $\langle S_z\rangle$ by induction from Eq. [110] as

$$\frac{d}{dt}\langle S_z\rangle = -\frac{1}{T_1^{SS}}(\langle S_z\rangle - S_0) - \frac{1}{T_1^{SI}}(\langle I_z\rangle - I_0) \quad [112]$$

where

$$\begin{aligned}\frac{1}{T_1^{SS}} &= \frac{1}{15}\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6}I(I+1)\\ &\quad\times[2J(\omega_I-\omega_S)+6J(\omega_S)+12J(\omega_I+\omega_S)]\\ \frac{1}{T_1^{SI}} &= \frac{1}{15}\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6}S(S+1)\\ &\quad\times[-2J(\omega_I-\omega_S)+12J(\omega_I+\omega_S)] \quad [113]\end{aligned}$$

For $I = S = 1/2$,

$$\begin{aligned}\frac{1}{T_1^{II}} &= \frac{\gamma_I^2\gamma_S^2\hbar^2}{10r_{IS}^6}[J(\omega_I-\omega_S)+3J(\omega_I)+6J(\omega_I+\omega_S)]\\ \frac{1}{T_1^{SS}} &= \frac{\gamma_I^2\gamma_S^2\hbar^2}{10r_{IS}^6}[J(\omega_I-\omega_S)+3J(\omega_S)+6J(\omega_I+\omega_S)]\\ \frac{1}{T_1^{IS}} &= \frac{1}{T_1^{SI}} = \frac{\gamma_I^2\gamma_S^2\hbar^2}{10r_{IS}^6}[-J(\omega_I-\omega_S)+6J(\omega_I+\omega_S)]\end{aligned}$$

$$[114]$$

For the homonuclear case (i.e., $\omega_I = \omega_S = \omega$)

$$\begin{aligned}\frac{1}{T_1^{II}} &= \frac{1}{T_1^{SS}} = \frac{\gamma^4\hbar^2}{10r_{IS}^6}[J(0)+3J(\omega)+6J(2\omega)]\\ \frac{1}{T_1^{IS}} &= \frac{1}{T_1^{SI}} = \frac{\gamma^4\hbar^2}{10r_{IS}^6}[-J(0)+6J(2\omega)]. \quad [115]\end{aligned}$$

Using Eq. [101], we can write the above equation as

$$\begin{aligned}\frac{1}{T_1^{II}} &= \frac{1}{T_1^{SS}} = \frac{\gamma^4\hbar^2\tau_c}{10r_{IS}^6}\left[1+\frac{3}{1+\omega^2\tau_c^2}+\frac{6}{1+4\omega^2\tau_c^2}\right]\\ \frac{1}{T_1^{IS}} &= \frac{1}{T_1^{SI}} = \frac{\gamma^4\hbar^2\tau_c}{10r_{IS}^6}\left[-1+\frac{6}{1+4\omega^2\tau_c^2}\right]. \quad [116]\end{aligned}$$

We see from Eqs. [110] and [112] taken together that the longitudinal relaxation of the two spins is given by a coupled equation, implying a nonexponential recovery to equilibrium. The term T_1^{IS} (or T_1^{SI}) is known as a cross-relaxation term and leads to the nuclear Overhauser effect (*78*, *79*). We leave it to the readers to evaluate the relaxation rates for the often-used motional limits of $\omega\tau_c \ll 1$ and $\omega\tau_c \gg 1$.

Redfield Approach Example

Let us consider a two-spin system $I = 1/2$, $S = 1$ and we follow the transverse relaxation of the three transitions of spin I (*80*, *81*). We also consider the existence of a scalar coupling between I and S. The Hamiltonian can be written in a doubly rotating frame [given by the operator $R(t) = \exp(i\omega_I I_z t)\exp(i\omega_S S_z t)$] as (similar to Eq. [2])

$$\begin{aligned}\mathbf{H}_0^* &= -(\Delta\omega_I I_z + \Delta\omega_S S_z),\\ \mathbf{H}_J^* &= JI_zS_z \quad [117]\end{aligned}$$

where $\Delta\omega_I I_z$ and $\Delta\omega_S S_z$ are the chemical shifts that appear as offsets from the rotating frame frequencies. In this calculation, the rotating frame and the interaction frame are the same. The six spin-product states $|m_I, m_S\rangle$ of the I–S spin system are

$$|1\rangle = |\tfrac{1}{2}, 1\rangle \quad |2\rangle = |\tfrac{1}{2}, 0\rangle \quad |3\rangle = |\tfrac{1}{2}, -1\rangle$$

$$|4\rangle = |-\tfrac{1}{2}, 1\rangle \quad |5\rangle = |-\tfrac{1}{2}, 0\rangle \quad \text{and} \quad |6\rangle = |-\tfrac{1}{2}, -1\rangle.$$

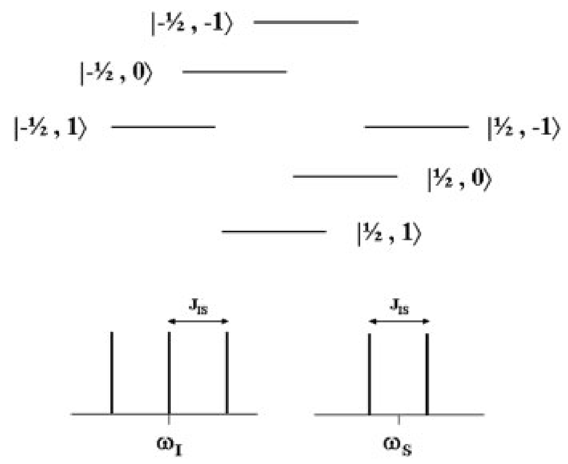

Figure 3 An energy level diagram and the schematic NMR spectrum of a two-spin system, I (spin-1/2) and S (spin 1), with a scalar coupling of J_{IS} between them.

Figure 3 shows the energy level diagram of the spin system and a schematic representation of the NMR spectra of I and S spins. The I-spin spectrum is a triplet with frequencies given by

$$\omega^I_{ab} = \Delta\omega_I + Jm_S \qquad [118]$$

where

$$|a\rangle = |-\tfrac{1}{2}, m_S\rangle \quad \text{and} \quad |b\rangle = |\tfrac{1}{2}, m_S\rangle.$$

The density matrix elements corresponding to the three transitions of I are

$$I_1 = \langle\tfrac{1}{2}, 1|\sigma^*|-\tfrac{1}{2}, 1\rangle = \langle 1|\sigma^*|4\rangle,$$

$$I_2 = \langle\tfrac{1}{2},0|\sigma^*|-\tfrac{1}{2},0\rangle = \langle 2|\sigma^*|5\rangle,$$

$$I_3 = \langle\tfrac{1}{2},-1|\sigma^*|-\tfrac{1}{2},-1\rangle = \langle 3|\sigma^*|6\rangle. \qquad [119]$$

The relevant relaxation mechanisms are the mutual dipolar relaxation between spins I and S, the CSA for spin I, and the quadrupolar relaxation of spin S. Thus, the relaxation Hamiltonian is written as

$$\mathbf{H}_1(t) = \mathbf{H}'^Q(t) + \mathbf{H}'^D(t) + \mathbf{H}'^C(t) \qquad [120]$$

The various relaxation Hamiltonians are given Table 1. The time development of the three elements of the density matrix corresponding to the three I-spin transitions can be described by the following differential equation:

$$\begin{aligned}\frac{d\sigma^*_{\alpha\alpha'}}{dt} &= -i[\mathbf{H}^*_0 + \mathbf{H}^*_\mathbf{J}, \sigma^*]_{\alpha\alpha'} \\ &\quad + \sum_{\beta,\beta'} R_{\alpha\alpha'\beta\beta'} e^{i(\alpha-\beta+\beta'-\alpha')t}(\sigma^*_{\beta\beta'}(t) - \sigma^0_{\beta\beta'}) \\ &\quad - i(L_{\alpha\alpha'\alpha\alpha'}\sigma^*_{\alpha\alpha'})_{\alpha\neq\alpha'} \qquad [121]\end{aligned}$$

The first term on the RHS is the precession arising from the coherent part of the Hamiltonian in the doubly rotating frame, the second term is the relaxation rate constants as described by the Redfield approach (Eq. [19], and the third term is the dynamic shift term (Eq. [17]). We also know from Eq. [20] that

$$\begin{aligned}R_{\alpha\alpha'\beta\beta'} &= \tfrac{1}{2}[J_{\alpha\beta\alpha'\beta'}(\alpha' - \beta') + J_{\alpha\beta\alpha'\beta'}(\alpha - \beta) \\ &\quad - \delta_{\alpha'\beta'}\sum_\gamma J_{\gamma\beta\gamma\alpha}(\gamma - \beta) - \delta_{\alpha\beta}\sum_\gamma J_{\gamma\beta'\gamma\alpha'}(\gamma - \beta') \\ &\qquad [122]\end{aligned}$$

where $J_{\alpha\beta\alpha'\beta'}$ is the Fourier transform of the correlation function (see Eq. [17]),

$$\begin{aligned}G_{\alpha\beta\alpha'\beta'}(\tau) &= \langle\langle\alpha|\mathbf{H}^*_1(t)|\beta\rangle \\ &\quad \times \langle\beta|\mathbf{R}^{-1}(\tau)\mathbf{H}^*_1(t-\tau)\mathbf{R}(\tau)|\alpha'\rangle\rangle. \qquad [123]\end{aligned}$$

For the calculation of $J_{\alpha\beta\alpha'\beta'}$, we express the three relaxation Hamiltonians in terms of their irreducible spherical tensor components as (Table 1)

$$\mathbf{H}_1(t) = \sum_{q=-2}^{2} (-1)^q F_q(t) A_{-q}. \qquad [124]$$

Assuming an isotropic motion described by a correlation time τ_c we get

$$\langle F_q(t)\, F^*_{q'}(t-\tau)\rangle = \delta_{qq'}\langle|F_q|^2\rangle e^{-(|\tau|/\tau_c)} \qquad [125]$$

which is obtained by setting the order parameter $S^2 = 1$ in Eq. [78] (or Eqs. [87] and [92]). Lorentzian spectral densities are obtained through the Fourier transform of the exponential decay term as

$$\frac{1}{2}\int_{-\infty}^{\infty} e^{i\omega_q\tau} e^{(|\tau|/\tau_c)} d\tau = \frac{\tau_c}{1 + \omega^2_q\tau^2_c} = J(\omega_q) \qquad [126]$$

and the spectral densities $J_{\alpha\beta\alpha'\beta'}$ may be expressed as

$$\begin{aligned}\frac{1}{2}J_{\alpha\beta\alpha'\beta'} = {} & \sum_{q=-2}^{2} J(\omega_q^D)\langle|F_q^D|^2\rangle\langle\alpha|A_{-q}^D|\beta\rangle\langle\alpha'|A_{-q}^D|\beta'\rangle^* + \sum_{q=-2}^{2} J(\omega_q^Q)\langle|F_q^Q|^2\rangle\langle\alpha|A_{-q}^Q|\beta\rangle\langle\alpha'|A_{-q}^Q|\beta'\rangle^* \\ & + \sum_{q=-2}^{2} J(\omega_q^{C_I})\langle|F_q^{C_I}|^2\rangle\langle\alpha|A_{-q}^{C_I}|\beta\rangle\langle\alpha'|A_{-q}^{C_I}|\beta'\rangle^* + \sum_{q=-2}^{2} J(\omega_q^Q)\langle|F_q^D F_q^{Q*}|\rangle\langle\alpha|A_{-q}^D|\beta\rangle\langle\alpha'|A_{-q}^Q|\beta'\rangle^* \\ & + \sum_{q=-2}^{2} J(\omega_q^D)\langle|F_q^Q F_q^{D*}|\rangle\langle\alpha|A_{-q}^Q|\beta\rangle\langle\alpha'|A_{-q}^D|\beta'\rangle^* + \sum_{q=-2}^{2} J(\omega_q^{C_I})\langle|F_q^D F_q^{C_I^*}|\rangle\langle\alpha|A_{-q}^D|\beta\rangle\langle\alpha'|A_{-q}^{C_I}|\beta'\rangle^* \\ & + \sum_{q=-2}^{2} J(\omega_q^D)\langle|F_q^{C_I} F_q^{D*}|\rangle\langle\alpha|A_{-q}^{C_I}|\beta'\rangle\langle\alpha'|A_{-q}^D|\beta'\rangle^* \qquad [127]\end{aligned}$$

In Eq. [127] the first three terms are the autocorrelation relaxation rates, the fourth and fifth terms are the cross correlations between dipole and quadrupole relaxation mechanisms, and the last two terms are the cross correlations between the dipole and CSA relaxation mechanisms. It is important to note that there is no cross-correlation term between the quadrupole and CSA relaxation in the above equation. The spin part of the quadrupole (spin S) and CSA (spin I) contain only single spin operators of spins S and I, respectively. So the quadrupole–CSA cross-correlation term does not survive the double commutators either with the I or S spin single quantum coherences. However, it will make a contribution to multiple quantum coherences. Using the orthogonality of the Wigner rotation matrices and the various averages in Eq. [102],

$$\langle|F_q^D|^2\rangle = \frac{6}{5}\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6},$$

$$\langle|F_q^Q|^2\rangle = \frac{3}{40}\frac{(e^2qQ)^2}{[S(2S-1)]^2}\left(1+\frac{\eta_Q^2}{3}\right),$$

$$\langle|F_q^{C_I}|^2\rangle = \frac{3}{10}\delta_{zz}^2\left(1+\frac{\eta_{C_I}^2}{3}\right),$$

$$\begin{aligned}\langle|F_q^D F_q^{Q*}|\rangle &= \langle|F_q^Q F_q^{D*}|\rangle \\ &= -\frac{3}{10}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\frac{(e^2qQ)}{2S(2S-1)}[(3\cos^2\theta_{Q-D}-1) \\ &\quad - \eta_Q\sin^2\theta_{Q-D}\cos2\phi_{Q-D}],\end{aligned}$$

$$\begin{aligned}\langle|F_q^D F_q^{C_I^*}|\rangle &= \langle|F_q^{C_I} F_q^{D*}|\rangle \\ &= -\frac{3}{10}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\delta_{zz}[(3\cos^2\theta_{C_I-D}-1) \\ &\quad - \eta_{C_I}\sin^2\theta_{C_I-D}\cos2\phi_{C_I-D}] \qquad [128]\end{aligned}$$

In calculating the last two averages, first the quadrupole and CSA tensors are transformed to the dipolar frame and the angles ($\theta_{Q-D}/\theta_{CI-D}$) and ($\phi_{Q-D}/\phi_{CI-D}$) are the polar and azimuthal angles, respectively, of the dipolar vector in the PAS of the quadrupolar–CSA tensor (Fig. 2). The dynamic shifts represented by $L_{\alpha\alpha'\alpha'\alpha} = \delta_{\alpha\alpha'}$ are given by

$$L_{\alpha\alpha'\alpha'\alpha} = K_{\alpha\alpha\alpha'\alpha'} + K_{\alpha'\alpha'\alpha\alpha} - \sum_{\gamma} K_{\alpha\gamma\alpha\gamma} - \sum_{\gamma} K_{\gamma\alpha'\gamma\alpha'}$$

$$K_{\alpha\beta\alpha'\beta'} = \mathrm{Im}\left(\int_0^\infty \langle\langle\alpha|\mathbf{H}_1(t)|\beta\rangle \times \langle\alpha'|\mathbf{R}^{-1}(\tau)\mathbf{H}_1(t-\tau)\mathbf{R}(\tau)|\beta'\rangle^*\rangle d\tau\right) \qquad [129]$$

where Im stands for the imaginary part.

In order to calculate the various spectral density functions we need to know the matrices corresponding to all the A_q values for the various relaxation mechanisms (*81*). The explicit expressions for the spin part of the quadruploar, dipolar and CSA relax-

Table 2 Components of Quadrupolar and Dipolar Relaxation Elements

Tensor	Cartesian Operator	Matrix
	Quadrupolar Relaxation Elements	
A^Q_0	$\frac{1}{\sqrt{6}}\{3S_z^2 - S(S+1)\}$	$\frac{1}{\sqrt{6}}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$
A^Q_{+1}	$-\frac{1}{2}(S_zS_+ + S_+S_z)$	$\frac{1}{2}\begin{pmatrix} 0 & -\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
A^Q_{-1}	$\frac{1}{2}(S_zS_- + S_-S_z)$	$\frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{2} & 0 \end{pmatrix}$
A^Q_{+2}	$\frac{1}{2}S_+^2$	$\begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
A^Q_{-2}	$\frac{1}{2}S_-^2$	$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$

ation mechanisms are listed in Tables 2, 3, and 4, respectively. The Redfield element corresponding to the transition I_1 given by the density matrix element

$$\sigma^*_{14} = \langle \tfrac{1}{2}, 1|\sigma^*| -\tfrac{1}{2}, 1\rangle$$

is

$$\begin{aligned} R_{1414} = \tfrac{1}{2}\{&2J_{1144}(0) - J_{1111}(0) - J_{4444}(0) - J_{2121}(\omega_S) \\ &- J_{5454}(\omega_S) - J_{3131}(2\omega_S) - J_{6464}(2\omega_S) \\ &- J_{4141}(\omega_I) - J_{1414}(\omega_I) - J_{2424}(\omega_I - \omega_S) \\ &- J_{3434}(\omega_I - 2\omega_S) - J_{5151}(\omega_I + \omega_S) \\ &- J_{6161}(\omega_I + 2\omega_S)\} \end{aligned} \qquad [130]$$

Using Eq. [127] and the various matrices given in Tables 2–4, we can evaluate all the relevant Redfield elements. Thus, the matrix equation for the evolution of the three I-spin transitions is

Table 3 Components of the Dipolar Relaxation Elements

Tensor	Cartesian Operator	Matrix
A_0^D	$(1/\sqrt{6})(3I_zS_z - \mathbf{I}\cdot\mathbf{S})$ $= (1/\sqrt{6})\left\{2I_zS_z - \frac{1}{2}(I_+S_- + I_-S_+)\right\}$	$(1/\sqrt{6})2I_zS_z = \frac{1}{\sqrt{6}}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$
		$(1/\sqrt{6})\left\{-\frac{1}{2}(I_+S_- + I_-S_+)\right\} = -\frac{1}{\sqrt{12}}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
A_{+1}^D	$-\frac{1}{2}(I_zS_+ + I_+S_z)$	$\frac{1}{2}\begin{pmatrix} 0 & -1/2\sqrt{2} & 0 & -1/2 & 0 & 0 \\ 0 & 0 & -1/2\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2 \\ 0 & 0 & 0 & 0 & 1/2\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2\sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
A_{-1}^D	$\frac{1}{2}(I_zS_- + I_-S_z)$	$\frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 1/2\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2\sqrt{2} & 0 & 0 & 0 & 0 \\ 1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2\sqrt{2} & 0 & 0 \\ 0 & 0 & -1/2 & 0 & -1/2\sqrt{2} & 0 \end{pmatrix}$
A_{+2}^D	$\frac{1}{2}I_+S_+$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
A_{-2}^D	$\frac{1}{2}I_-S_-$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}$

$$\frac{d}{dt}\begin{pmatrix} \sigma_{14}^* \\ \sigma_{25}^* \\ \sigma_{36}^* \end{pmatrix} = \begin{pmatrix} -i(\Delta\omega_I + J + \delta\omega_{+1}) + R_{1414} & R_{1425} & R_{1436} \\ R_{2514} & -i(\Delta\omega_I + \delta\omega_0) + R_{2525} & R_{2536} \\ R_{3614} & R_{3625} & -i(\Delta\omega_I - J + \delta\omega_{-1}) + R_{3636} \end{pmatrix}\begin{pmatrix} \sigma_{14}^* \\ \sigma_{25}^* \\ \sigma_{36}^* \end{pmatrix} \tag{131}$$

Table 4 Components of CSA Relaxation Elements

Tensor	Cartesian Operator	Matrix
$A_0^{C_I}$	$\frac{2\omega_I}{\sqrt{6}} I$	$\frac{\omega_I}{\sqrt{6}} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}$
$A_{+1}^{C_I}$	$-\frac{\omega_I}{2} I_+$	$\frac{\omega_I}{2} \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
$A_{-1}^{C_I}$	$\frac{\omega_I}{2} I_-$	$\frac{\omega_I}{2} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$
$A_{-1}^{C_I}$	0	0

where the dynamic shifts $\delta\omega$ in the above matrix are given as

$$\begin{aligned} \delta\omega_{\pm 1} &= -4L^{Q-D}(\omega_S) \pm L^{C_I-D}(\omega_I) \\ \delta\omega_0 &= 8L^{Q-D}(\omega_S) \end{aligned} \qquad [132]$$

The Redfield relaxation elements appearing in the matrix are given in Table 5.

Equation [121] can be written as

$$\frac{d\sigma^*}{dt} = \mathbf{A}\sigma^* \qquad [133]$$

where A is a 3×3 matrix equal to the sum of the coherent and relaxation part of the Hamiltonian. A formal solution of Eq. [131] may be written as (*81*)

$$\sigma^*(t) = e^{\mathbf{A}t}\sigma^*(0) \qquad [134]$$

where $\sigma^*(0)$ is the density matrix immediately following a $\pi/2$ pulse on the I spin and is given by a unit column vector. The time-domain signal arising from the free induction decay of the three I-spin transitions (I_1, I_2, and I_3) can be represented as (*30*)

$$G(t) = \mathbf{X}\sigma^*(t) = \mathbf{X}e^{\mathbf{A}t}\sigma^*(0) \qquad [135]$$

Table 5 Redfield Matrix Elements for *I* = 1/2 and *S* = 1

$R_{1414/3636} = -\Big[4J^Q(\omega_S) + 8J^Q(2\omega_S) + \frac{8}{3}J^D(0) + \frac{1}{3}J^D(\omega_I - \omega_S)$ $+ 2J^D(\omega_I) + J^D(\omega_S) + 2J^D(\omega_I + \omega_S) + \frac{2}{3}J^{C_I}(0) + \frac{1}{2}J^{C_I}(\omega_I)\Big]$ $\pm \Big[\frac{4}{3}J^{C_I-D}(0) + J^{C_I-D}(\omega_I)\Big]$	$R_{2525} = -\Big[8J^Q(\omega_S) + \frac{2}{3}J^D(\omega_I - \omega_S)$ $+ 2J^D(\omega_S) + 4J^D(\omega_I + \omega_S)$ $+ \frac{2}{3}J^{C_I}(0) + \frac{1}{2}J^{C_I}(\omega_I)\Big]$
$R_{1425} = R_{2514} = 4J^Q(\omega_S) - J^D(\omega_S)$	$R_{1436} = R_{3614} = 8J^Q(2\omega_S)$

The autocorrelation spectral density functions are the following:

$$\begin{aligned} J^Q(\omega) &= \frac{3}{160}(e^2qQ)^2\left(1 + \frac{\eta_Q^2}{3}\right)\frac{\tau_c}{1 + \omega^2\tau_c^2}, \\ J^D(\omega) &= \frac{3}{10}\left(\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6}\right)\frac{\tau_c}{1 + \omega^2\tau_c^2}, \\ J^{C_I}(\omega) &= \frac{3}{10}\omega_I^2\delta_{zz}^2\left(1 + \frac{\eta_{C_I}^2}{3}\right)\frac{\tau_c}{1 + \omega^2\tau_c^2}. \end{aligned}$$

The cross-correlation spectral density functions are

$$\begin{aligned} J^{Q-D}(\omega) &= \frac{3}{80}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}(e^2qQ)[(3\cos^2\theta_{Q-D} - 1) - \eta_Q\sin^2\theta_{Q-D}\cos 2\phi_{Q-D}]\frac{\tau_c}{1 + \omega^2\tau_c^2}, \\ J^{C_I-D}(\omega) &= \frac{3}{10}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\omega_I\delta_{zz}[(3\cos^2\theta_{C_I-D} - 1) - \eta_{C_I}\sin^2\theta_{C_I-D}\cos 2\phi_{C_I-D}]\frac{\tau_c}{1 + \omega^2\tau_c^2}. \end{aligned}$$

The dynamic frequency shifts are

$$\begin{aligned} L^{Q-D}(\omega) &= \omega\tau_c J^{Q-D}(\omega), \\ L^{C_I-D}(\omega) &= \omega\tau_c J^{C_I-D}(\omega). \end{aligned}$$

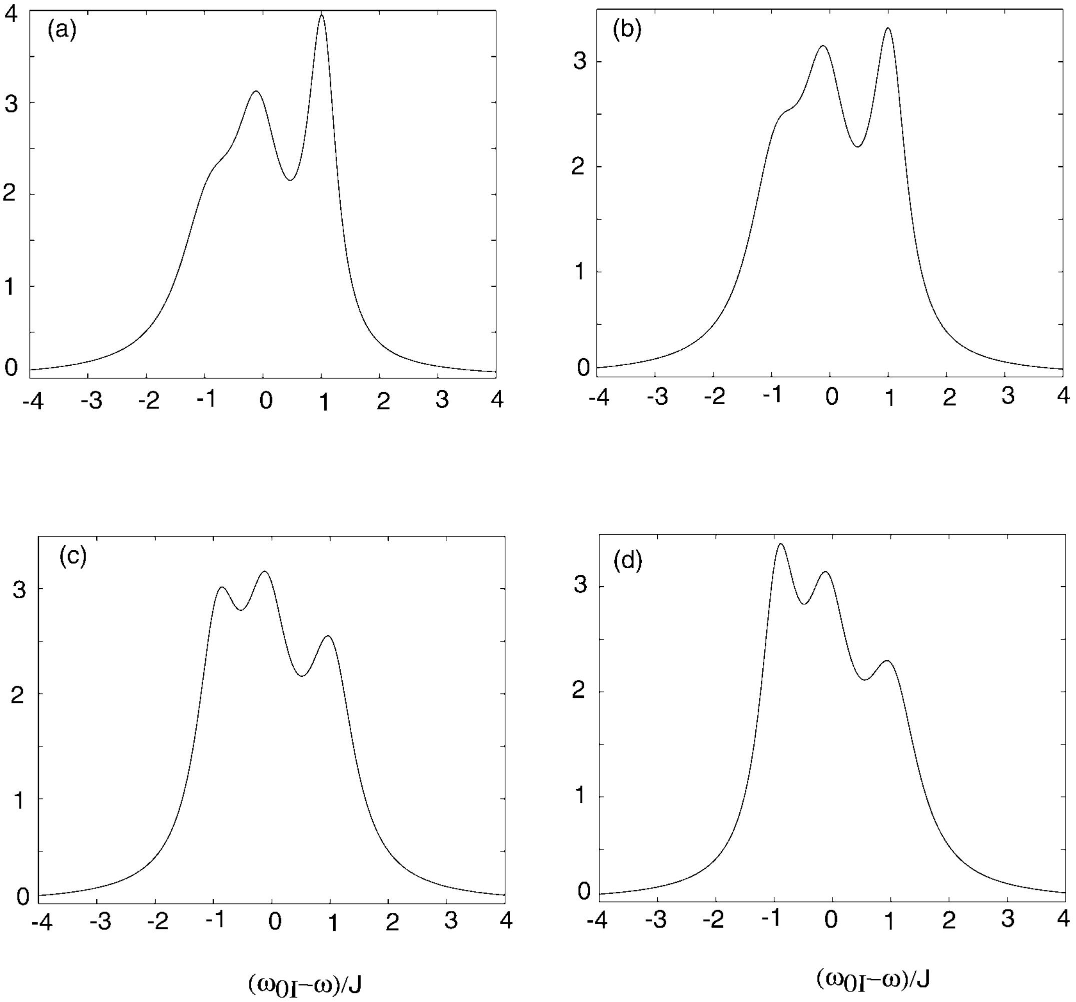

Figure 4 The simulated line shapes for spin *I*. The spectrometer frequency was set at 900 MHz for protons. Other parameters: 170-kHz ^{2}H-quadrupole coupling constant, ^{15}N-CSA = -160 ppm, internuclear distance = 1.025 Å, J_{IS} = 15 Hz. The orientation of the CSA tensor with respect to the dipolar frame was varied by setting the angle to (a) 0°, (b) 30°, (c) 60°, and (d) 90°.

where X is a row vector with elements (*1*, *1*, *1*) equal to the normalized intensities of the lines in the spectrum in the absence of any relaxation. The spectrum is then given by the real part of the Fourier transform of $G(t)$, that is,

$$F(\omega) = \mathrm{Re}\left[\mathbf{X}\cdot\left\{\int_0^\infty e^{(\mathbf{A}-i\omega\mathbf{E})t}dt\right\}\cdot\sigma^*(0)\right]. \qquad [136]$$

In the above, **E** is a unit matrix and Re stands for the real part. Evaluation of the above integration yields

$$F(\omega) = \mathrm{Re}[\mathbf{X}\cdot[\mathbf{A}-i\omega\mathbf{E}]^{-1}\cdot\sigma^*(0)] \qquad [137]$$

In this approach, the calculation of the line shape is reduced to finding the inverse of the **A** matrix. As an example, a spin system comprising ^{15}N (I = 1/2) coupled to ^{2}H (S = 1) is considered for which the ^{15}N spectrum is a triplet. The line shapes are simulated using Eq. [138]. Simple isotropic tumbling with a correlation time of 20 ns is assumed. The spectrometer frequency was set to 900 MHz for protons. The simulated line shapes are shown in Fig. 4. The other parameters used are a 170-kHz ^{2}H-quadrupole coupling constant, ^{15}N − CSA = -160 ppm, an internuclear distance set at 1.025 Å, and J_{IS} = 15 Hz. The orientation of the CSA tensor with respect to the dipolar frame was varied by setting the angle θ_{C_I} to 0°, 30°, 60°, and 90° [Fig. 4(a–d)].

The asymmetry in the line shape is due to the dynamic frequency shift effect arising predominantly from the cross correlation between quadrupole and DD interactions and the differential line broadening is due to the cross correlation between the CSA and DD interactions. The CSA–DD cross-correlation effect also undergoes a sign change with the change in the angle, leading to the differences in the pattern of asymmetry in the top and bottom panels of Fig. 4.

Dynamics from Line Shapes

In this example we will use the cross-correlation functions that include internal motions derived in Eq. [92] to simulate once again the line shapes of a spin-1/2 nucleus ($I = {}^{15}\mathrm{N}$) that is scalar (J) coupled to a spin-1 nucleus ($S = {}^{2}\mathrm{H}$). The simulations are aimed at bringing out the essential features arising from internal motions.

Let us focus on Eqs. [78] and [92]. The real part of the Fourier transform of the function

$$[S^2 e^{-t/\tau_M} + (1 - S^2) e^{-t/\tau}]$$

will yield a spectral density component

$$j(\omega) = (1 - S^2)\frac{\tau}{1 + (\omega\tau)^2} + S^2 \frac{\tau_M}{1 + (\omega\tau_M)^2} \qquad [138]$$

and an imaginary part that gives rise to the dynamic frequency shifts,

$$k(\omega) = (1 - S^2)\frac{\omega\tau^2}{1 + (\omega\tau)^2} + S^2 \frac{\omega\tau_M^2}{1 + (\omega\tau_M)^2}. \qquad [139]$$

For the present case, the relevant spectral density terms are the autocorrelation spectral densities,

$$J^{Q}(\omega) = \frac{3}{160}(e^2qQ)^2\left(1 + \frac{\eta_Q^2}{3}\right) j(\omega) \qquad [140]$$

$$J^{D}(\omega) = \frac{3}{10}\left(\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{IS}^6}\right) j(\omega) \qquad [141]$$

$$J^{C_I}(\omega) = \frac{3}{10}(\omega_I\delta_{zz})^2\left(1 + \frac{\eta_{C_I}^2}{3}\right) j(\omega) \qquad [142]$$

and the cross-correlation spectral densities,

$$J^{QD}(\omega) = \frac{3}{80}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}(e^2qQ) \times [(3\cos^2\theta_{QD} - 1) - \eta_Q \sin^2\theta_{QD}] j(\omega) \qquad [143]$$

and

$$J^{C_ID}(\omega) = \frac{3}{10}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}(\omega_I\delta_{zz}) \times [(3\cos^2\theta_{C_ID} - 1) - \eta_{C_I} \sin^2\theta_{C_ID}] j(\omega). \qquad [144]$$

The dynamic frequency shift terms arising from the cross-correlation functions are given by

$$L^{QD}(\omega) = \frac{3}{80}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}(e^2qQ) \times [(3\cos^2\theta_{QD} - 1) - \eta_Q \sin^2\theta_{QD}] k(\omega) \qquad [145]$$

and

$$L^{C_ID}(\omega) = \frac{3}{10}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}(\omega_I\delta_{zz}) \times [(3\cos^2\theta_{C_ID} - 1) - \eta_{C_I} \sin^2\theta_{C_ID}] k(\omega) \qquad [146]$$

Using Eqs. [140]–[146] and formulating a relaxation matrix and equation of motion as before (Eq. [131]), we can directly simulate the I-spin line shapes. These equations are different from those of Table 5; because we have included internal motion, the shape of the spectral densities are given by $j(\omega)$ and the dynamic frequency shifts are given by $k(\omega)$.

Figure 5(a–f) presents a case wherein a ${}^{15}\mathrm{N}$ triplet arising from its coupling to a ${}^{2}\mathrm{H}$ nucleus is shown for various order parameters S^2 set at 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0. The quadrupole coupling constant was set at 170 kHz with $\theta_{QD} = 0°$, the distance between deuterium and nitrogen was 1.025 Å, an *axially symmetric* CSA tensor for nitrogen was used with $\delta_{zz} = -160$ ppm with $\theta_{CI-D} = 0°$, the overall τ_c was 20 ns, and the ${}^{1}\mathrm{H}$ Larmor frequency was set at 720 MHz. In Fig. 6 all the parameters were the same as in Fig. 2, except $\theta_{C_I-D} = 90°$ was used. It is clear from these simulations that the line shapes are sensitive to the order parameter and, of course, to the relative orientation of the DD and CSA (or quadrupolar) tensors.

CONCLUSION

We have attempted to present the theory of nuclear magnetic relaxation in liquids starting from first principles. The goal was to enunciate every step involved

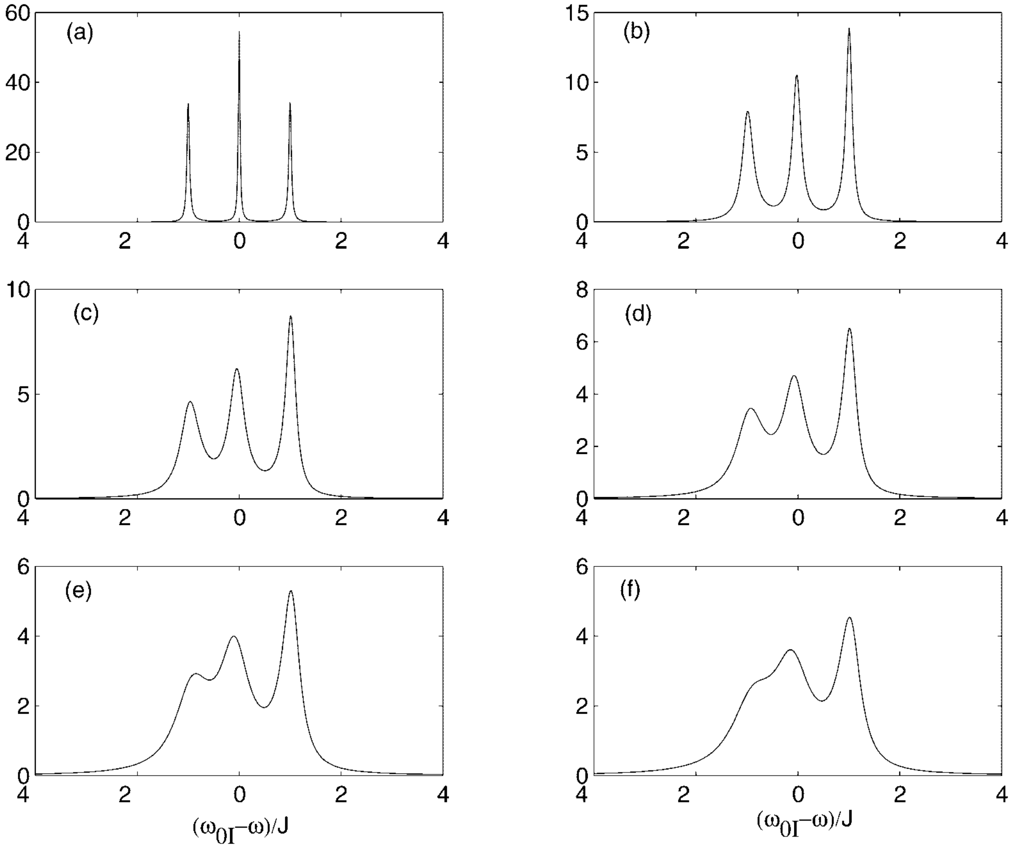

Figure 5 A simulation of ^{15}N triplet line shapes due to their coupling to ^{2}H. The order parameter was varied as (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0. Other parameters: 170-kHz quadrupole coupling constant, with $\theta_{QD} = 0°$; distance between deuterium and nitrogen = 1.025 Å; axially symmetric CSA tensor for nitrogen with $\delta_{zz} = -160$ ppm with $\theta_{C_I D} = 0°$; overall $\tau_c = 20$ ns; $\tau_e = 10^{-12}$ s; $J/2\pi = -15$ Hz; 720-MHz ^{1}H Larmor frequency. In Fig. 2, $\theta_{C_I D} = 90°$ was used.

in the formulation of the theory. The description demonstrates how the equation of motion is derived and highlights important constraints necessary for arriving at the final equations in the density matrix and the operator forms. The detailed derivation of the Hamiltonians gives completeness to the description of the theory. The various coordinate transformations starting from the PAS to the laboratory frame have been explicitly explained so that one can formulate the derivation of the correlation (both auto- and cross correlations) functions for newer contexts. The steps clearly delineate the intricacies and assumptions involved in deriving auto- and cross-correlation functions. The detailed description also allows one to understand the issues relating to internal motions, often termed as dynamics. The examples illustrate the two different approaches to handle relaxation problems, namely, the Redfield matrix and the operator methods.

It is worthwhile to be familiar with both the Redfield and operator approaches in tackling relaxation problems because each of these approaches has its own merits and complexities. When dealing with a problem in the Redfield density matrix approach the dimensionality of the relaxation matrix may appear formidably large and computing all the elements may appear to be a tedious task. It is evident from the examples given here that one can focus on a subset of the whole matrix and simplify the problem. However, one may have to carefully select the subset, otherwise subtle effects may be missed. In the operator approach it is somewhat straightforward to decipher the subset, as the double commutators would lead us to the relevant operators that are to be included. In the example for the operator approach, the evaluation of the double commutator for I_z automatically yielded the dependence on S_z and, thus we arrived at a coupled equation for the longitudinal relaxation of spins I and S. When it comes to solving transverse relaxation or the relaxation of the coherences (single quantum or multiple quantum), both the approaches are similar in complexity but we prefer the Redfield density matrix

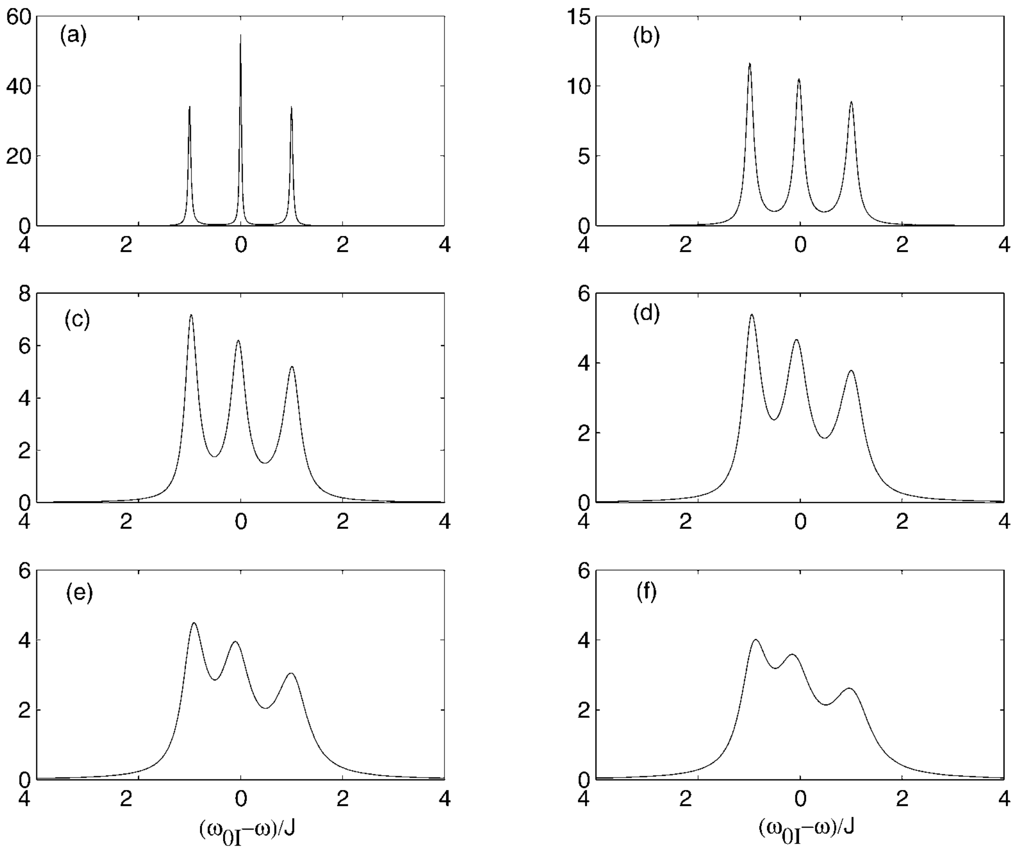

Figure 6 The same simulation as in Fig. 5 but with $\theta_{C,D} = 90°$ and showing the line shape dependence on the tensor orientation (in Fig. 5 $\theta_{C,D} = 0°$).

formulation. For some applications, it is convenient to calculate the elements of the Redfield matrix and later convert them into an operator representation (*82*). The relaxation matrix itself assumes a block form because coherences of different order or spins do not mix during free evolution and it simplifies calculations. For example, we focused only on the subset of the three *I*-spin transitions.

While our description is correct and follows the traditional approach, it is imperative to state that there are other descriptions and different formulations in the literature (*26*, *83*, *84*). This article is mainly intended to serve as a basis for a newcomer to understand relaxation in detail and then move on to further in-depth studies. Although some aspects of relaxation in solids can also be explained based on the theory developed so far, a complete description of the same is beyond the scope of this article. We do not pretend to have covered all aspects of the theory, even for liquids within this framework of description. For example, we have not included relaxation in the presence of an externally applied RF field or chemical exchange. Although in the weak RF limit (also known as nonviscous liquid limit) in which the RF strength is much weaker than the strength of the relaxation interaction, the relaxation part is essentially unaffected and the extension of the theory is straightforward and amounts to adding just one more term in the coherent part of the Hamiltonian. For a complete description, we refer the readers to several research articles (*12*, *40*, *85*). Almost all the cases that we encounter in liquids, in which relaxation is in the presence of RF, come under this category. The strong RF or the viscous liquid limit (RF strength is larger than the relaxation interaction strength) is rather uncommon and a detailed description can be found in Abragam's classic text (*30*).

ACKNOWLEDGMENTS

Acknowledgments are due to the National High Magnetic Field Laboratory, Tallahassee, FL, where the first author (N.M.) gave a series of lectures in the NMR program, which formed the basis for this article. The example for the Redfield method was part of research work performed in the laboratory of Prof. B.D. Nageswara Rao, and the authors have greatly benefited from his insight in relaxation theory. The first author (N.M.) thanks Dr. Steve Smallcombe and Varian Inc. for support during the preparation of this manuscript. The second author (V.V.K.) acknowledges the support of the U.S. Department of Energy under the auspices of the University of California, Lawrence Livermore National Laboratory, and a Laboratory Wide Director's Initiative grant.

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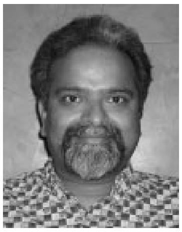
BIOGRAPHIES



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