

Relaxation equations for multispin systems. II^{a)}

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The Redfield equations are derived quite generally for multispin systems of arbitrary number of spins with arbitrary spin magnitudes. The spin lattice coupling Hamiltonian is assumed to arise from random fluctuations only. The extreme narrowing limit is not taken.

I. INTRODUCTION

Nuclear magnetic relaxation and resonance is a powerful tool in the study of structures and dynamics of molecules.¹⁻³ The instrumentation has developed rapidly over the last few years so that it is now possible to study both selectively and non-selectively pulsed spins of high as well as low natural abundance. Since molecules of interest usually contain groups of different spins which couple together, a proper theoretical understanding of both the spectra and relaxation is required in order to interpret the data. The Redfield^{4,5} theory of relaxation gives the starting point for the study of relaxation in NMR. The validity of the Redfield equations is well established. However, the Redfield equations can involve extremely tedious and error prone calculations when the spin matrix elements are calculated using standard angular momentum algebra for systems containing several spins.^{2,3} This results from the rapid increase in the number of spin states as more spins are included in the system or if their magnitudes are greater than $\frac{1}{2}$.

On the other hand, the Redfield equations are one of the few examples in quantum mechanics which can be solved exactly for a given Hamiltonian. The spin space is finite for a fixed number of spins and therefore a finite set of first order differential equations with constant coefficients can be obtained. The reason that the full Redfield equations have not been derived before lies only in the formidable algebra involved^{3,4,7,9-12} as mentioned above. Solutions do exist for small numbers of spins, and invariably in the extreme narrowing limit. In this paper the relaxation equations are obtained for an arbitrary number of spins of different magnitude without using the extreme narrowing limit. The restriction imposed at this stage is that the coupling Hamiltonian is composed of isotropic spin and lattice terms. Thus, systems with macroscopic anisotropies such as solids, liquid crystals, or systems where the anisotropic chemical shift is a dominant relaxation mechanism are not treated. Hence, coupling mechanisms like the dipole-dipole, quadrupole, spin rotation, and any other single spin or double spin mechanism of tensor rank l are included. The resulting lattice correlation functions are treated phenomenologically.

The central part of this derivation is the construction of a complete set of tensor operators which completely

span the spin space. This is presented in paper I (Ref. 13). Such sets have been known for a long time^{8,9} and applied to spin systems by numerous workers.^{7,10-12} The particularly useful feature taken advantage of here is the orthonormal properties of the basis set of operators.^{13,15} Hence, by expanding the density operator in this basis, a set of differential equations is easily obtained for the Redfield equations. The spin part of the problem is tractable since only a few reduced matrix elements in operator space need be evaluated. These can be obtained quite generally.

A further advantage of the multipole expansion lies in the explicit way in which all possible mixed (cross) polarizations appear.¹³ Solution of the differential equations will give the transverse and longitudinal vector magnetizations. Also contained in the solution is the relaxation and spectrum of not only the vector magnetization but also of *all* the polarizations in the system. Hence, in addition to NMR, nuclear quadrupole relaxation and higher multipole relaxation are explicitly treated.

Recent up-to-date and thorough reviews of nuclear magnetic relaxation show the extent and variety of systems to which the Redfield equations can be applied.¹⁻³ It is not the object of this paper to review this literature nor to make applications to specific systems. Moreover, the differential equations are not solved in this work. Rather, the full set of coupled equations are set up to be the starting point for future numerical studies on specific multispin systems.

After briefly deriving the Redfield equations in Sec. II, the frequency spectrum (Sec. III) and relaxation matrix (Sec. IV) are calculated with emphasis on the spin part. In the discussion (Sec. V) the appropriate initial condition is given which results from a rapid pulse away from equilibrium.

II. THE REDFIELD EQUATIONS

The equations governing the relaxation of nuclear spins are the Redfield equations.⁴ As a consequence of the weak coupling between the spins and the other degrees of freedom of the system (e.g., internal, translation states, orientational observables, and nonpure observables) called the lattice, the spin polarization relaxes slowly in comparison to lattice modes. This makes a weak coupling perturbative treatment possible. In this section a brief account of the derivation of the Redfield equations is given. Numerous detailed derivations exist.^{2,4,5,16}

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The starting point is the Von Neuman equation

$$i\hbar \frac{\partial \rho}{\partial t} = \mathcal{L}\rho, \quad (1)$$

where ρ is the full density operator for both the spins and lattice spaces. The spin operator is projected out from ρ by a projection operator P :

$$\rho_0^L \text{Tr}_L \rho \equiv P\rho = \rho_0^L \sigma, \quad (2)$$

while the lattice density operator is obtained by

$$Q\rho = \sigma_0 \text{Tr}_I \rho = \sigma_0 \rho_L. \quad (3)$$

σ_0 and ρ_0^L are the equilibrium spin and lattice density operators, respectively.

The Liouville operator \mathcal{L} acting on an operator A is

$$\mathcal{L}A = [H, A], \quad (4)$$

and H is the total Hamiltonian for the system. In this treatment H is written

$$H = H_I + H_L + H_c, \quad (5)$$

where H_I accounts for the Zeeman effects, chemical shifts, and scalar hyperfine spin couplings. The lattice Hamiltonian H_L contains effects which arise from the lattice observables. The Hamiltonian H_c couples the spins to the lattice.

The corresponding Liouville operators are

$$\mathcal{L} = \mathcal{L}_I + \mathcal{L}_L + \mathcal{L}_c. \quad (6)$$

In particular, the following is assumed: The Hamiltonian H_I alone effects the pure spin operators

$$P\mathcal{L}P = \mathcal{L}_I; \quad (7)$$

the Zeeman and lattice Hamiltonians give the dominant contributions to the non-pure spin operators

$$Q\mathcal{L}Q = \mathcal{L}_I + \mathcal{L}_L \equiv \mathcal{L}_{IR}; \quad (8)$$

and the interaction between spin and lattice is governed by the coupling Hamiltonian

$$Q\mathcal{L}P = P\mathcal{L}Q = \mathcal{L}_c. \quad (9)$$

With these definitions the Von Neumann equation can be rewritten as¹⁷

$$i\hbar \frac{\partial \sigma}{\partial t} = \mathcal{L}_I \sigma - \frac{i}{\hbar} \int_0^t ds \text{Tr}_L \rho_0^L \mathcal{L}_c \times \exp(-i\mathcal{L}_{IR} s / \hbar) \mathcal{L}_c \sigma(t-s). \quad (10)$$

This form is obtained by assuming that the lattice states are at equilibrium at $t=0$ or equivalently $Q\rho(0) = 0$. The trace is over all lattice variables so that Eq. (10) is still an operator in spin space. The convolution can be removed by use of the Markoffian approximation¹⁶

$$\sigma(t-s) \cong e^{i\mathcal{L}_I s / \hbar} \sigma(t) \quad (11)$$

and by assuming that the trace over the lattice

$$\text{Tr}_L [\rho_0^L \mathcal{L}_c \exp(-i\mathcal{L}_{IR} s / \hbar) \mathcal{L}_c] \quad (12)$$

decays much faster than $\sigma(t)$. Hence, the limit $t \rightarrow \infty$ is taken. The resulting equations

$$i\hbar \frac{\partial \sigma}{\partial t} = \mathcal{L}_I \sigma(t) - \frac{i}{\hbar} \int_0^\infty ds \text{Tr}_L (\rho_0^L \mathcal{L}_c e^{-i\mathcal{L}_{IR} s / \hbar} \mathcal{L}_c) e^{i\mathcal{L}_I s / \hbar} \sigma(t) = (\mathcal{L}_I - iR)\sigma(t) \quad (13)$$

are called the Redfield equations in operator form.

The Redfield equations can be written in terms of matrix elements $\sigma_{\alpha\alpha'}(t)$. This leads to the standard results⁴ appearing in treatises like Slichter⁵ and Abragam.⁶ Their form is not used in this work.

The Redfield equations can also be written in matrix notation using the multipole basis of paper I:

$$i \frac{d\Phi}{dt} = \omega \cdot \Phi - \frac{i}{\hbar} \mathbf{R} \cdot \Phi, \quad (14)$$

where the vector Φ has $[(2I_1 + 1) \cdots (2I_n + 1)]^2$ elements, namely, $\phi_{\{k\}}^{\{k'\}}(k_1 \cdots k_n)^{\{k'\}}$, and the matrices ω and \mathbf{R} have elements

$$\hbar^{-1} \langle \langle T_{\{k\}}^{\{k'\}}(k_1 \cdots k_n)^{\{k'\}} | \mathcal{L}_I | T_{\{k'\}}^{\{k'\}}(k'_1 \cdots k'_n)^{\{k'\}} \rangle \rangle_I \quad (15)$$

and

$$\langle \langle T_{\{k\}}^{\{k'\}}(k_1 \cdots k_n)^{\{k'\}} | \mathbf{R} | T_{\{k'\}}^{\{k'\}}(k'_1 \cdots k'_n)^{\{k'\}} \rangle \rangle = \frac{1}{\hbar} \int_0^\infty ds \langle \langle T_{\{k\}}^{\{k'\}}(k_1 \cdots k_n)^{\{k'\}} | \rho_0^L \mathcal{L}_c \mathcal{L}_c(s) | T_{\{k'\}}^{\{k'\}}(k'_1 \cdots k'_n)^{\{k'\}} \rangle \rangle, \quad (16)$$

respectively, where

$$\mathcal{L}_c(s) = e^{-i\mathcal{L}_{IR} s / \hbar} \mathcal{L}_c e^{i\mathcal{L}_{IR} s / \hbar}. \quad (17)$$

Matrix elements of operators like \mathcal{L}_I , R , etc. and various properties of the commutator type are given in Ref. 18.

III. FREQUENCY SPECTRUM FOR MULTISPIN SYSTEMS

The ω matrix [Eq. (15)] contains the complete spectrum which would be observed in high resolution NMR. The spin Hamiltonian can be written

$$H_I = - \sum_{i=1}^n \hbar \gamma_i (1 - \sigma_i) \mathbf{I}_i \cdot \mathbf{B}_0 + \sum_i \hbar Q_i^0 [\mathbf{I}_i]^{(2)0} + \sum_{i < j} \hbar J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j + H_R. \quad (18)$$

In Eq. (18) the linear Zeeman Hamiltonian, the scalar chemical shift σ_i , possible scalar quadrupole Q_i^0 , and scalar spin-spin J_{ij} couplings are included. Higher order effects are not explicitly included, being represented by H_R . Except for very high fields (≥ 10 T) or anisotropic systems (liquid crystals) Eq. (18) is probably sufficient without H_R included.

By use of the notation of paper I and by assuming $\mathbf{B}_0 = B_0 \hat{z}$, Eq. (18) becomes

$$H_I = - \frac{i\hbar}{\sqrt{3}} \sum_{i=1}^n \gamma_i (1 - \sigma_i) B_0 \sqrt{I_i(I_i + 1)} \mathcal{Y}^{(1)0}(\mathbf{I}_i) + \frac{\hbar}{\sqrt{30}} \sum_{i=1}^n Q_i^0 \sqrt{I_i(I_i + 1)(2I_i - 1)(2I_i + 3)} \mathcal{Y}^{(2)0}(\mathbf{I}_i) + \frac{\hbar}{\sqrt{3}} \sum_{i, j=1}^n J_{ij} \sqrt{I_i(I_i + 1)(I_i - 1)(I_i + 1)(I_j - 1)(I_j + 1)} T^{00}(11). \quad (19)$$

This result shows that the Hamiltonian can be written in terms of spin operators alone. Hence, operators of the type

$$\mathcal{L}^{I_i m_i} A \equiv [Y^{(I_i) m_i}(\mathbf{I}_i), A] \quad (20)$$

are the only terms which arise in Eq. (16). The relevant matrix elements of Eq. (15) take the form

$$\begin{aligned} & \langle\langle T^{(k)q}(v) | \mathcal{L}^{I_i m_i} | T^{(k')q'}(v) \rangle\rangle_I \\ &= (-1)^{k-q} \begin{pmatrix} k & l_i & k' \\ -q & m_i & q' \end{pmatrix} \langle\langle T^{(k)}(v) || \mathcal{L}^{I_i} || T^{(k')}(v) \rangle\rangle_I, \end{aligned} \quad (21)$$

where the Wigner-Eckart theorem has been used.¹⁵

If the form of the Hamiltonian (19) is sufficient, then there can be no mixing between q and q' of the basis operators. k and k' can differ only by values to a maximum of 2. The reduced matrix elements of \mathcal{L}^{I_m} are given in Sec. III.

At this stage it is pointed out that the frequency matrix can generate the full unbroadened spectrum. If relaxation due to R is ignored, then the solution of the differential equation (14) is equivalent to finding the eigenvalues and eigenvectors of ω or

$$\det |\omega - \lambda| = 0. \quad (22)$$

Here λ is a diagonal matrix of eigenvalues.

From the properties of $\langle IM | T^{(k)q}(v) | IM' \rangle$, $q = \Delta M$, where M is the magnetic component of the total nuclear spin I . Hence, the $q=1$ block of ω gives the frequency positions and intensities which would be obtained from a vector interaction with the radiation field [i. e., $\boldsymbol{\mu} \cdot \mathbf{B}(t)$].

From the point of view of this work, the relaxation matrix is added to the frequency matrix before diagonalization is carried out. This gives rise to a broadened spectrum for $q=1$ as observed in high resolution NMR.

Also available are the hyperfine spectra of higher multipoles. For example, $k=2$ corresponds to nuclear quadrupole resonance while higher tensor ranks have not been observed experimentally.

$$\begin{aligned} & \langle\langle T^{(k)q}(v) | \mathcal{L}_\eta^{I m \dagger} \mathcal{L}_\mu^{I m}(s) | T^{(k')q'}(v') \rangle\rangle_I = \sum_{\substack{\bar{k} \bar{l} \bar{k}' \\ \bar{q} \bar{q}' \bar{q}'' \\ \bar{m} \bar{m}' \bar{m}''}} (-1)^{\bar{k}-\bar{q}+l-m+k-q} \begin{pmatrix} k & l & \bar{k} \\ -q & -m & \bar{q} \end{pmatrix} \begin{pmatrix} \bar{k} & l & \bar{k}' \\ -\bar{q} & m & \bar{q}' \end{pmatrix} \langle\langle T^{(k)}(v) || \mathcal{L}_\eta^{I m} || T^{(\bar{k})}(\bar{v}) \rangle\rangle_I \\ & \times \langle\langle T^{(\bar{k})}(\bar{v}) || \mathcal{L}_\mu^{I m} || T^{(\bar{k}')}(\bar{v}') \rangle\rangle_I \langle\langle T^{(\bar{k})}(\bar{v}) | e^{-i\mathcal{L}_I s/\hbar} | T^{(\bar{k}')}(\bar{v}') \rangle\rangle_I \langle\langle T^{(\bar{k}')}(\bar{v}') | e^{i\mathcal{L}_I s/\hbar} | T^{(k')q'}(v') \rangle\rangle_I. \end{aligned} \quad (28)$$

The spectral resolution of the identity (4) has been used. Equation (28) is obtained by invoking the Wigner-Eckart theorem (21). Since the most important term in \mathcal{L}_I depends upon the magnetic field strength B_0 which cannot be factored out of the matrix element, $e^{-i\mathcal{L}_I s/\hbar}$ is not an isotropic operator and the Wigner-Eckart theorem cannot be used on the last two terms in Eq. (28).

IV. RELAXATION MATRIX FOR MULTISPIN SYSTEMS

The coupling Hamiltonian for most problems of interest takes the form

$$\begin{aligned} H_c &= \sum_{i < j} \sum_{m=-l}^l T^{(i)}(l_i l_j) F_m^I(ij) \\ &+ \sum_{i=1}^n \sum_{m=-l}^l Y^{(i) m}(\mathbf{I}_i) F_m^I(i), \end{aligned} \quad (23)$$

where the lattice terms $F_m^I(\eta)$ are assumed to be time dependent isotropic tensor components. In particular, they arise from randomly fluctuating lattice modes which are assumed not to depend on the external field or macroscopic anisotropies. The lattice correlation function is therefore

$$\begin{aligned} G_{\eta\mu}^{I m}(0, s) &= \text{Tr} \left\{ \rho_0^L F^{I m}(\eta) e^{-i\mathcal{L}_L s/\hbar} F_{m'}^{I'} e^{i\mathcal{L}_L s/\hbar} \right\} \delta_{I I'} \delta_{m m'} \\ &= \text{Tr} \left\{ \rho_0^L F^{I m}(\eta) F_{m'}^{I'}(\mu)(s) \right\} \delta_{I I'} \delta_{m m'}, \end{aligned} \quad (24)$$

where η denotes the i th and j th spins or a single spin i depending on the form of the Hamiltonian in Eq. (23). Spin commutator operators are written as $\mathcal{L}_\eta^{I m}$.

Using Eqs. (23) and (24) in Eq. (16) for R gives

$$\begin{aligned} & \langle\langle T^{(k)q}(v) | R | T^{(k')q'}(v') \rangle\rangle = \sum_{\eta\mu} \sum_m \int_0^\infty ds G_{\eta\mu}^{I m}(0, s) \\ & \times \langle\langle T^{(k)q}(v) | \mathcal{L}_\eta^{I m \dagger} \mathcal{L}_\mu^{I m}(s) | T^{(k')q'}(v') \rangle\rangle_I, \end{aligned} \quad (25)$$

where

$$\begin{aligned} & \langle\langle T^{(k)q}(v) | \mathcal{L}_\eta^{I m \dagger} \mathcal{L}_\mu^{I m}(s) | T^{(k')q'}(v') \rangle\rangle_I \\ &= \text{Tr} T^{(k)q}(v) \mathcal{L}_\eta^{I m \dagger} e^{-i\mathcal{L}_I s/\hbar} \mathcal{L}_\mu^{I m} e^{i\mathcal{L}_I s/\hbar} T^{(k')q'}(v'). \end{aligned} \quad (26)$$

The lattice correlation function $G_{\eta\mu}^{I m}(0, s)$ depends upon the lattice dynamics. It can be treated theoretically, or left as a quantity to be obtained from experiment. One approach is to assume it decays exponentially with a correlation time $\tau_{\eta\mu}^I$:

$$G_{\eta\mu}^{I m}(0, s) \approx G_{\eta\mu}^I(0) \exp(i\omega_{\eta\mu}^m s - s/\tau_{\eta\mu}^I), \quad (27)$$

where the lattice frequencies $\omega_{\eta\mu}^m$ may depend upon m .

The focus of this paper, however, is not on the evaluation of $G_{\eta\mu}^{I m}(0, s)$, but rather on the calculation of the spin matrix elements for multispin systems. The spin part of the relaxation matrix (25) is calculated from

By virtue of the assumed random nature of the lattice terms giving $l=l'$ and $m=m'$ in Eq. (24), the spin operators appearing in Eq. (28) are scalars

$$\mathcal{L}_\eta^{I m \dagger} \mathcal{L}_\mu^{I m}(s) = \frac{1}{2I+1} \mathcal{L}_\eta^{I m} \circ \mathcal{L}_\mu^{I m}(s). \quad (29)$$

The immediate consequence is that $q=q'$ in Eq. (28) and

the relaxation matrix is block diagonal in q as is the frequency matrix ω . As an example, for four spins of $\frac{1}{2}$, the relaxation matrix of dimension 256 reduces to dimension 70 for longitudinal ($q=0$) and dimension 56 for transverse ($q=1$) relaxation.

Although the extreme narrowing limit is not taken in this work, it is straightforward at this stage to see the simplification which results from it. The effect of the extreme narrowing limit is to render Eq. (25) independent of time, s , and G^{lm} independent of m . Substitution of Eq. (28) into Eq. (25) and carrying out the sum over m and \bar{q} results in the uncoupling of different multipoles, i.e., $k=k'$. In the example above of four spins of $\frac{1}{2}$, the extreme narrowing limit reduces the relaxation matrix from dimension 70 and 56 for longitudinal and transverse relaxation, respectively, to dimension 28 in both cases. Moreover, since the resulting relaxation matrix is independent of q , the relaxation is equal for different spherical components of the same multipole. In particular, the relaxation matrix for the vector magnetization is the same for transverse and longitudinal relaxation.

Since the extreme narrowing limit is not used in this work, it is necessary to calculate the matrix elements of Eq. (28) with the time s dependence retained. This requires the matrix elements of $e^{-i\mathcal{L}_I s/\hbar}$. Assuming the Zeeman Hamiltonian to be the only term which is important in the exponential inside R , the matrix elements can be evaluated (Appendix) to give

$$\langle\langle T_{\{K\}}^{(k)q}(k_1 \dots k_n)^e | \exp(i\mathcal{L}_I s/\hbar) | T_{\{K'\}}^{(k')q'}(k'_1 \dots k'_n)^e \rangle\rangle_I$$

$$\begin{aligned} \langle\langle T_{\{K\}}^{(k)q}(v) | R | T_{\{K'\}}^{(k')q'}(v') \rangle\rangle &= \sum_{\nu\mu} \sum_{\substack{\bar{k} \bar{k} \bar{k}' \\ \{\bar{K}\} \{\bar{K}'\} \\ \bar{k}_1 \dots \bar{k}_n \bar{q}_1 \dots \bar{q}_n \bar{q} \\ q_1' \dots q_n'}} \left\{ G_{\nu\mu}^I(0) \frac{\tau_{\nu\mu}^I}{1 - i[\omega_L^m + \sum_i \omega_i(q_i' - \bar{q}_i)]\tau_{\nu\mu}^I} \right\} (-1)^{k+i+\bar{k}} \begin{pmatrix} k & l & \bar{k} \\ -q & -m & \bar{q} \end{pmatrix} \begin{pmatrix} \bar{k} & l & \bar{k}' \\ -\bar{q} & m & q \end{pmatrix} \\ &\times \langle\langle T_{\{K\}}^{(k)}(k_1 \dots k_n)^e | \mathcal{L}_I^l | T_{\{\bar{K}\}}^{(\bar{k})}(\bar{k}_1 \dots \bar{k}_n)^e \rangle\rangle_I \langle\langle T_{\{\bar{K}'\}}^{(\bar{k}')}(\bar{k}'_1 \dots \bar{k}'_n)^e | \mathcal{L}_\mu^l | T_{\{\bar{K}'\}}^{(\bar{k}')}(\bar{k}'_1 \dots \bar{k}'_n)^e \rangle\rangle_I \delta_{qq'} \\ &\times \langle k'_1 q'_1 \dots k'_n q'_n | (k'_1 \dots k'_n)^e \{K'\} k' q \rangle \langle k'_1 q'_1 \dots k'_n q'_n | (k'_1 \dots k'_n)^e \{\bar{K}'\} \bar{k}' q \rangle \\ &\times \langle \bar{k}_1 \bar{q}_1 \dots \bar{k}_n \bar{q}_n | (\bar{k}_1 \dots \bar{k}_n)^e \{\bar{K}\} \bar{k} \bar{q} \rangle \langle \bar{k}_1 \bar{q}_1 \dots \bar{k}_n \bar{q}_n | (\bar{k}_1 \dots \bar{k}_n)^e \{\bar{K}\} \bar{k} \bar{q} \rangle. \end{aligned} \quad (31)$$

If the time dependence of the correlation function is not known, the terms in the square brackets are replaced by

$$J_{\nu\mu}^{lm} \left[\sum_i \omega_i(q_i' - \bar{q}_i) \right] = \int_0^\infty ds G_{\nu\mu}^{lm}(0, s) \exp \left[i \sum_i \omega_i(q_i' - \bar{q}_i) s \right] \quad (32)$$

Finally, the relaxation matrix requires the reduced matrix elements for various cases of coupling Hamiltonians. This involves single spin $\mathcal{Y}^{(li)}(I_i)$ and double spin $T^{(li)}(l_i l_j)$ operators. The reduced matrix elements of $\mathcal{Y}^{(li)}(I_i)$ are¹³ (see Appendix)

$$\begin{aligned} &\langle\langle T_{\{K'\}}^{(k')}(k'_1 \dots k'_i \dots k'_n)^e | \mathcal{Y}^{(li)}(I_i) | T_{\{K\}}^{(k)}(k_1 \dots k_i \dots k_n)^e \rangle\rangle \\ &= \prod_{j=1}^n \delta_{k_j k'_j} \prod_{j=1}^{i-2} (\delta_{K_j K'_j}) a_{I_i}^{k_i k'_i} [(k)(k_i)(k')]^{1/2} [(K_{i-1})(K_i) \dots (K_{n-2})]^{1/2} [(K'_{i-1})(K'_i) \dots (K'_{n-2})]^{1/2} (-1)^{\phi_D} \\ &\times \begin{pmatrix} k_i & k'_i & l \\ K'_{i-1} & K_{i-1} & K_{i-2} \end{pmatrix} \begin{pmatrix} K_{i-1} & K'_{i-1} & l \\ K'_i & K_i & k_{i+1} \end{pmatrix} \dots \begin{pmatrix} K_{n-2} & K'_{n-2} & l \\ k' & k & k_n \end{pmatrix}, \end{aligned} \quad (33)$$

where

$$a_{I_i}^{k_i k'_i} = (i)^{k_i+i+k_i} [(l)(k_i)(I_i)]^{1/2} (-1)^{2I_i} \begin{pmatrix} k'_i & l & k_i \\ I_i & I_i & I_i \end{pmatrix} \quad (34)$$

equal to (a) general (see paper I or Ref. 14):

$$= \sum_{q_1' \dots q_n'}^{k_1'} \exp \left(i \sum_{i=1}^n \omega_i q_i' s \right) \langle k'_1 q'_1 \dots k'_n q'_n | (k'_1 \dots k'_n)^e \{K'\} k' q' \rangle \quad (30a)$$

$$\times \prod_{i=1}^n (\delta_{k_i k_i'}) \delta_{q_i q_i'} \langle k'_1 q'_1 \dots k'_n q'_n | (k'_1 \dots k'_n)^e \{K\} k q \rangle;$$

(b) extreme narrowing:

$$= \prod_{i=1}^n (\delta_{k_i k_i'} \delta_{q_i q_i'}) \delta_{\{K'\}, \{K\}} \delta_{k' k} \delta_{q' q}; \quad (30b)$$

(c) isochronous spins:

$$= e^{i\omega_0 q s} \prod_{i=1}^n (\delta_{k_i k_i'} \delta_{q_i q_i'}) \delta_{\{K'\}, \{K\}} \delta_{k' k} \delta_{q' q}. \quad (30c)$$

There are two cases where this term simplifies. Case (b), already discussed, is the extreme narrowing limit where the exponential term vanishes allowing the sum over $q_i' - q_i$ to be performed. In this case the matrix element is completely diagonal and equal to one. The next case (c) is for isochronous spins. In this case $\omega_i = \omega_0$ for all i and the exponential term can be taken out of the sum. Again the matrix element is completely diagonal, and is equal to $e^{i\omega_0 q s}$. An effect of the time dependence in this spin term in the general case (a) is thus seen to be the mixing of multipoles. It is the sole reason for any differences between transverse and longitudinal relaxation.

By combining the results of this section and taking the correlation function as decaying exponentially [Eq. (27)], the matrix elements of R take the form

and

$$\phi_D = (n - i + 1)l_i + k'_i + k_{i+1} + \dots + k_n + K_i + \dots + K_{n-2} + K'_i + \dots + K'_{n-2}. \quad (35)$$

Special cases of this reduced matrix element are as follows:

two spin systems:

$$\langle\langle T^{(k')} (k'_1 k'_2) \parallel Y^{(l_1)} (\mathbf{I}_1) \parallel T^{(k)} (k_1 k_2) \rangle\rangle = (-1)^{k_1 + k_2 + k} a_{I_1}^{l_1 k_1 k'_1} [(k') (k) (k'_1)]^{1/2} \begin{Bmatrix} k_1 & k'_1 & l_1 \\ k' & k & k_2 \end{Bmatrix} \delta_{k_2 k'_2}, \quad (36)$$

while for $Y^{(l_2)} (\mathbf{I}_2)$, the labels 1 and 2 are interchanged;

three spin systems:

$$\begin{aligned} &\langle\langle T_{K'_1}^{(k')} (k'_1 k'_2 k'_3) \parallel Y^{(l_1)} (\mathbf{I}_1) \parallel T_{K_1}^{(k)} (k_1 k_2 k_3) \rangle\rangle \\ &= (-1)^{k_1 + k_2 + k_3 + K_1 + K'_1 + k + l_1} a_{I_1}^{l_1 k_1 k'_1} [(k) (k') (k_1) (K_1) (K'_1)]^{1/2} \begin{Bmatrix} k_1 & k'_1 & l_1 \\ K'_1 & K_1 & k_2 \end{Bmatrix} \begin{Bmatrix} K_1 & K'_1 & l_1 \\ k' & k & k_3 \end{Bmatrix} \delta_{k_2 k'_2} \delta_{k_3 k'_3}, \end{aligned} \quad (37)$$

$$\begin{aligned} &\langle\langle T_{K'_1}^{(k')} (k'_1 k'_2 k'_3) \parallel Y^{(l_2)} (\mathbf{I}_2) \parallel T_{K_1}^{(k)} (k_1 k_2 k_3) \rangle\rangle \\ &= (-1)^{k_1 + k_2 + k_3 + K_1 + K'_1 + k + l_2} a_{I_2}^{l_2 k_2 k'_2} [(k) (k') (k_2) (K_1) (K'_1)]^{1/2} \begin{Bmatrix} k_2 & k'_2 & l_2 \\ K'_1 & K_1 & k_1 \end{Bmatrix} \begin{Bmatrix} K_1 & K'_1 & l_2 \\ k' & k & k_3 \end{Bmatrix} \delta_{k_1 k'_1} \delta_{k_3 k'_3}, \end{aligned} \quad (38)$$

and

$$\langle\langle T_{K'_1}^{(k')} (k'_1 k'_2 k'_3) \parallel Y^{(l_3)} (\mathbf{I}_3) \parallel T_{K_1}^{(k)} (k_1 k_2 k_3) \rangle\rangle = (-1)^{k_3 + K_1 + k'} [(k) (k') (k_3)]^{1/2} a_{I_3}^{l_3 k_3 k'_3} \begin{Bmatrix} k_3 & k'_3 & l_3 \\ k' & k & K_1 \end{Bmatrix} \delta_{k_1 k'_1} \delta_{k_2 k'_2}. \quad (39)$$

Reduced matrix elements of the commutator of $Y^{(l_i)} (\mathbf{I}_i)$ are

$$\langle\langle T^{(k')} (v') \parallel \mathcal{L}^{l_i} \parallel T^{(k)} (v) \rangle\rangle = 2\phi(l_i k_i k'_i) \langle\langle T^{(k')} (v') \parallel Y^{(l_i)} (\mathbf{I}_i) \parallel T^{(k)} (v) \rangle\rangle, \quad (40)$$

where $\phi(l_i k_i k'_i)$ is equal to 1 if $l_i + k_i + k'_i$ is odd, and zero otherwise.

For interactions that depend on two spins such as for a dipole interaction, the spin operators take the form

$$\mathcal{L}^l (l_i l_j) = [T^{(l)} (l_i l_j)]_-, \quad (41)$$

where $T^{(l)} (l_i l_j)$ is given by Eq. (39). For a dipole interaction, $l=2$ and $l_i = l_j = 1$. The reduced matrix elements of this operator are

$$\begin{aligned} \langle\langle T^{(k)} (\bar{v}) \parallel \mathcal{L}^l (l_i l_j) \parallel T^{(k')} (v') \rangle\rangle &= [(I_i) (I_j)]^{-1/2} (l)^{1/2} \left[\sum_{\bar{k} \bar{v}} (-1)^{l + k' + \bar{k}} \begin{Bmatrix} l & k' & \bar{k} \\ \bar{k} & l_i & l_j \end{Bmatrix} \langle\langle T^{(k)} (\bar{v}) \parallel Y^{(l_i)} \parallel T^{(k')} (\bar{v}) \rangle\rangle \langle\langle T^{(k')} (\bar{v}) \parallel \mathcal{L}^{(l_j)} \parallel T^{(k')} (v') \rangle\rangle \right. \\ &\quad \left. + \sum_{\bar{k} \bar{v}} (-1)^{l + \bar{k} + k' + l_i} \begin{Bmatrix} l & k' & \bar{k} \\ \bar{k} & l_j & l_i \end{Bmatrix} \langle\langle T^{(k')} (\bar{v}) \parallel Y^{(l_j)} \parallel T^{(k)} (\bar{v}) \rangle\rangle \langle\langle T^{(k)} (\bar{v}) \parallel \mathcal{L}^{(l_i)} \parallel T^{(k')} (v') \rangle\rangle \right]. \end{aligned} \quad (42)$$

V. DISCUSSION

The set of differential equations (14) must be solved in order to obtain the time evolution of the various multipoles. This requires input data regarding the spin coupling strengths and the correlation times. In principle, all these parameters are available from experimental high resolution and relaxation studies. The impeding step in the comparison of experimental spectra with theoretically calculated ones has been the complexity of the operator algebra. This algebra is done in this paper for coupling Hamiltonians of the types in Eq. (23) without invoking the extreme narrowing limit. The resulting relaxation matrices are relatively large for multispin systems, but can be set up numerically. Once

this is done a systematic assessment of the importance of different polarizations on magnetic vector relaxations can be undertaken.

To solve the Redfield equations, the initial conditions must be supplied. In line with the usual experimental procedures, the initial state is prepared by a pulse. Both selective and nonselective pulses can affect all the multipoles. It is necessary to know how all the $\phi^{(k)}(v)$ respond to a variety of pulses. Recently, this problem has been solved for the case that a pulse occurs on a time scale which is much less than relaxation times and in the absence of coupling processes.¹⁹ Under these conditions, the initial set of polarizations prepared from the ω th Fourier component of a pulse of duration τ of

amplitude H_1 under the assumption that the system was previously at equilibrium in a large static field before the pulse is¹⁹

$$\phi_{(k)}^{(k)q}(k_1 \cdots k_n)^z = \sum_{q_i} \langle k_1 q_1 \cdots k_n q_n | k_1 k_2 \cdots k_n \rangle^z \{K\} kq \times \phi^{(k_1)q_1} \phi^{(k_2)q_2} \cdots \phi^{(k_n)q_n}, \quad (43)$$

where

$$\phi^{(k_i)q_i} = \sqrt{\frac{4\pi}{2k_i + 1}} (+i)^{k_i + q_i} Y_{k_i q_i}^*(\omega_1^i \tau, \omega_i \tau) \quad (44)$$

and

$$\omega_1^i = \gamma_i H_1 \frac{\sin(\omega \tau)}{\omega \tau}. \quad (45)$$

An essential feature of this result is that the effects of pulses on the higher multipoles (i.e., $k > 1$) must be used in addition to the usual effect of pulses on the magnetization ($k = 1$).

APPENDIX

Reduced matrix elements of $\mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i)$ can be obtained using the results of Ref. 13. The basic result is Eq. (I-44) so that the matrix element of $\mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i)$ is

$$\begin{aligned} & \langle \mathcal{Y}^{(k'_i) q'_i}(\mathbf{I}_i) | \mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i) | \mathcal{Y}^{(k_i) q_i}(\mathbf{I}_i) \rangle \\ &= (-1)^{k'_i - q'_i} \begin{pmatrix} k'_i & l_i & k_i \\ -q'_i & m_i & q_i \end{pmatrix} \delta_{ij} (-1)^{l_i - k_i + k'_i} (k'_i)^{1/2} a_{l_i}^{k_i k'_i} \\ &= (-1)^{k'_i - q'_i} \begin{pmatrix} k'_i & l_i & k_i \\ -q'_i & m_i & q_i \end{pmatrix} \\ & \langle \mathcal{Y}^{(k'_i) q'_i}(\mathbf{I}_i) | \mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i) | \mathcal{Y}^{(k_i) q_i}(\mathbf{I}_i) \rangle, \end{aligned} \quad (A1)$$

where [Eq. (I-45)]

$$\begin{aligned} \langle \langle T^{(k') q'}(v') | \mathcal{L}^{(l) m}(l_i l_j) | T^{(k) q}(v) \rangle \rangle &= [(I_i)(I_j)]^{-1/2} (l)^{1/2} \sum_{\substack{m_i m_j \\ \tilde{k} \tilde{q} \tilde{v}}} (-1)^{l - m + k' - q' + \tilde{k} - \tilde{q}} \begin{pmatrix} l & l_i & l_j \\ m & -m_i & -m_j \end{pmatrix} \begin{pmatrix} k' & l_i & \tilde{k} \\ -q' & m_i & \tilde{q} \end{pmatrix} \begin{pmatrix} \tilde{k} & l_j & k \\ -\tilde{q} & m_j & q \end{pmatrix} \\ & \times \langle \langle T^{(k') q'}(v') | \mathcal{Y}^{(l_i)} | T^{(\tilde{k})}(\tilde{v}) \rangle \rangle \langle \langle T^{(\tilde{k})}(\tilde{v}) | \mathcal{L}^{(l_i)} | T^{(k)}(v) \rangle \rangle + \sum_{\substack{m_i m_j \\ \tilde{k} \tilde{v} \tilde{q}}} (-1)^{l - m + k' - q' + \tilde{k} - \tilde{q}} \\ & \times \begin{pmatrix} l & l_i & l_j \\ m & -m_i & -m_j \end{pmatrix} \begin{pmatrix} \tilde{k} & l_j & k' \\ +\tilde{q} & m_j & -q' \end{pmatrix} \begin{pmatrix} \tilde{k} & l_i & k \\ -\tilde{q} & m_i & q \end{pmatrix} \\ & \times \langle \langle T^{(\tilde{k})}(\tilde{v}) | \mathcal{Y}^{(l_j)} | T^{(k')}(\tilde{v}') \rangle \rangle \langle \langle T^{(\tilde{k})}(\tilde{v}) | \mathcal{L}^{(l_j)} | T^{(k)}(v) \rangle \rangle. \end{aligned} \quad (A7)$$

Finally, by using Eq. (6.2.8) of Edmonds,¹⁵ Eq. (42) is obtained.

The matrix elements of $\exp(i\mathcal{L}_r s/\hbar)$ cannot use the Wigner-Eckart theorem. This is because the Zeeman Hamiltonian contains the magnetic field strength which cannot be factored out of the matrix element. It is assumed that only the Zeeman terms are present:

$$H_I \cong -\hbar \sum_i \gamma_i (1 - \sigma_i) I_{i,z} B_0, \quad (A8)$$

which have the property that

$$a_{l_i}^{k_i k'_i} = (i)^{k'_i + i + k_i} [(l_i)(k_i)(l_i)]^{1/2} (-1)^{2l_i} \begin{Bmatrix} k'_i & l_i & k_i \\ l_i & l_i & l_i \end{Bmatrix}. \quad (A2)$$

The second equality in Eq. (A1) defines the reduced matrix elements of $\mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i)$.

In obtaining reduced matrix elements of the commutator of $\mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i)$, namely,

$$\langle \langle \mathcal{Y}^{(k'_i) q'_i}(\mathbf{I}_i) | \mathcal{L}^{l_i m_i} | \mathcal{Y}^{(k_i) q_i}(\mathbf{I}_i) \rangle \rangle, \quad (A3)$$

it is seen from Eq. (I-40) that the only difference between Eq. (A1) and the commutator is in the factor $2\phi(k_i l_i k'_i)$ [see Eq. (40)]. This arises in working out $\mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i) \mathcal{Y}^{(k_i) q_i}(\mathbf{I}_i)$ and $\mathcal{Y}^{(k_i) q_i}(\mathbf{I}_i) \mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i)$ in the commutator expression and using the symmetry property of 3j coefficients, namely,

$$\begin{pmatrix} k'_i & l_i & k_i \\ -q_i & m_i & q_i \end{pmatrix} = (-1)^{k'_i + l_i + k_i} \begin{pmatrix} k'_i & k_i & l_i \\ -q_i & q_i & m_i \end{pmatrix}. \quad (A4)$$

To obtain reduced matrix elements of $\mathcal{Y}^{(l_i) m_i}(\mathbf{I}_i)$ with $T^{(k) q}(v)$, the expression (28) is used, followed by Eq. (A1). The 6-j symbols arise from recoupling the $\mathcal{Y}^{(k_i) q_i}(\mathbf{I}_i)$'s back to $T^{(k) q}(v)$'s. Equations (I-46)-(I-54) give matrix elements of the $\mathcal{L}^{l_i q_i}$ which lead to Eqs. (33)-(41) in the text.

To calculate matrix elements of $T^{l_i}(l_i l_j)$ [Eq. (42)], the definition of $T^{l_i}(l_i l_j)$ [Eq. (39)] is first substituted to give

$$\begin{aligned} & \langle \langle T^{(k') q'}(v') | \mathcal{L}^{(l) m}(l_i l_j) | T^{(k) q}(v) \rangle \rangle \\ &= [(I_i)(I_j)]^{-1/2} (l)^{1/2} \sum_{m_i m_j} (-1)^{l_i - l_j + l} (-1)^{l - m} \begin{pmatrix} l & l_i & l_j \\ -m & m_i & m_j \end{pmatrix} \\ & \times \langle \langle T^{(k') q'}(v') | [\mathcal{Y}^{(l_i) m_i} \mathcal{Y}^{(l_j) m_j}, T^{(k) q}(v)]_- \rangle \rangle. \end{aligned} \quad (A5)$$

Then using the property

$$[AB, C]_- = A[B, C]_- + [A, C]_- B \quad (A6)$$

and Eq. (21), it is found that

$$\exp[i\mathcal{L}_{I_i} s/\hbar \mathcal{Y}(l_i)q_i](I_i) = \exp[i\omega_i q_i s \mathcal{Y}(l_i)q_i](I_i) . \quad (\text{A9})$$

The matrix elements of $\exp(i\mathcal{L}_{I_i} s/\hbar)$ are found by substituting Eq. (28) and applying Eq. (A9) on all the n spins. The spin trace gives $\delta_{k_i k'_i} \delta_{q_i q'_i}$ [Eq. (9)] and $\delta_{qq'}$, but does not require $k = k'$. Equation (30a) follows directly while Eqs. (30b) and (30c) use the orthogonality of njm coefficients, namely,

$$\sum_{q_i} \langle k_1 q_1 \cdots k_n q_n | (k_1 \cdots k_n)^{\{K'\}} k' q' \rangle \langle k_1 q_1 \cdots k_n q_n | (k_1 \cdots k_n)^{\{K\}} k q \rangle = \delta(\{K\}, \{K'\}) \delta_{kk'} \delta_{qq'} ; \quad (\text{A10})$$

see Yutsis¹⁴ [Eq. (7.7a)].

¹M. Holz and M. D. Zeidler, "Nuclear Spin Relaxation in Fluids," in *Nuclear Magnetic Resonance* (The Chemical Society, London, 1977), Vol. 6, p. 92.

²L. G. Werbelow and D. M. Grant, *Adv. Magn. Reson.* **9**, 189 (1977).

³R. L. Vold and R. R. Vold, *Prog. NMR Spectrosc.* **12**, 79 (1978).

⁴A. G. Redfield, *IBM J. Res. Dev.* **1**, 19 (1957).

⁵C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

⁶A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, Oxford, 1961).

⁷A. Bain and R. M. Lynden-Bell, *Mol. Phys.* **30**, 325 (1975).

⁸E. P. Wigner, *Group Theory and Its Applications to the Quantum Mechanics of Atomic Spectra* (Academic, New York, 1959).

⁹C. N. Banwell and H. Primas, *Mol. Phys.* **6**, 225 (1963).

¹⁰N. C. Pyper, *Mol. Phys.* **21**, 1 (1971).

¹¹N. C. Pyper, *Mol. Phys.* **22**, 433 (1971).

¹²L. G. Werbelow and D. M. Grant, *J. Chem. Phys.* **63**, 544 (1975).

¹³B. C. Sanctuary, *J. Chem. Phys.* **64**, 4352 (1976), referred to as paper I.

¹⁴A. P. Yutsis, I. B. Levinson, and V. V. Vanagas, *The Theory of Angular Momentum* (Israel Programs for Scientific Translations, Washington, D.C., 1962).

¹⁵A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1960).

¹⁶O. Platz, *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972).

¹⁷R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960).

¹⁸R. F. Snider and B. C. Sanctuary, *J. Chem. Phys.* **55**, 1555 (1971).

¹⁹B. C. Sanctuary, *J. Chem. Phys.* **73**, 1048 (1980).