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Spin Relaxation: The Multiple-Time-Scale Point of View*

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The linear (Redfield) form of the equation of motion for the density matrix of a spin system immersed in a heat bath is derived. The usual derivations employ perturbation theory which suffers from the presence of secular terms familiar from nonlinear mechanics. We employ the multiple-time-scale technique as developed by Frieman and Sandri to eliminate the secular terms and render the expansions valid for all time. The method introduces explicit time variables to exploit the multiplicity of time scales inherent to the problem.

I. INTRODUCTION

Nuclear magnetic relaxation (NMR) is one example of a general class of relaxation processes which may, to a certain degree of approximation, be described by a master equation. The essential feature of such processes is the existence of a large heat bath or reservoir which is weakly coupled to the subsystem. For these nonequilibrium systems one finds that the equation of motion for the density matrix of the subsystem (spins in the NMR case) has the form of a master equation. The purpose of this paper is to derive the well-known equation of motion for the spin density matrix[1]

$$\partial\sigma^{\alpha\alpha'}/\partial t = -i\omega_{\alpha\alpha'}\sigma^{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\sigma^{\beta\beta'} \qquad (1.1)$$

by use of the multiple-time-scale (MTS) method. In Eq. (1.1) $\sigma^{\alpha\alpha'}$ is the α, α' matrix element of the spin density matrix, $\omega_{\alpha\alpha'} = [(E_\alpha - E_{\alpha'})/\hbar]$, where E_α is energy of the spin state α, and $R_{\alpha\alpha'\beta\beta'}$ is the "relaxation matrix." Our motivation for presenting this alternative derivation is based on the conviction that the MTS method provides considerable advantage in displaying the physics of the relaxation process.

The microscopic description of the relaxation of nuclear spins in a fluid was first formulated by Bloembergen, Purcell, and Pound.[2] Subsequent derivations of the equation of motion for the spin density matrix have been presented by Wangness and Bloch,[3] Bloch,[4] Redfield,[1] Fano,[5] Hubbard,[6] and Abragam.[7] All these methods proceed by a sophisticated version of ordinary time-dependent perturbation theory applied to the density matrix rather than the wavefunction. The restriction of ordinary perturbation theory still applies, namely within the time interval considered the density matrix cannot change substantially. The following assumptions are common to these developments: (a) The bath and spin subsystems are uncorrelated for all times, i.e., the density matrix factors into spin and bath parts[1]; (b) the bath remains in thermodynamic equilibrium for all times[1,7]; (c) the correlation time of the bath τ_c is much shorter than the spin relaxation time τ_R. The first assumption can only be true in the case of vanishing interaction between spins and bath but yields useful results when properly employed. The second assumption implies a random phase condition for all times (actually discrete time points). The last condition insures that the equation of motion for the spin density matrix will refer to one time and not to the system's history. As long as one does not require a description for times short compared to τ_c, the last condition assures that a "Markovian" master equation can be obtained for the spin density matrix.

General techniques have been developed to circumvent these assumptions. The pioneering effort was undertaken by Van Hove[8] who rederived the Pauli equation[9] (a prototype master equation) using the techniques of quantum field theory. Zwanzig[10] demonstrated that the Pauli equation could be derived by more direct methods by using projection operator techniques. Many applications of his formulation have followed.[10a]

In the field of spin relaxation, Zwanzig's techniques were first employed by Argyres and Kelley.[11] The random phase approximation, as manifested in the assumption of thermal equilibrium for the bath, appears only once as an initial condition. Argyres and Kelley remove the restriction $\tau_c < \tau_R$ and derive an equation of motion for the spin density matrix that depends on the history of the system. For the case $\tau_c < \tau_R$ they obtain the standard result Eq. (1.1) by keeping terms to second order in the spin–lattice coupling and taking a weak-coupling limit. This limiting procedure, introduced by Van Hove,[8] consists of

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letting the coupling parameter λ approach zero and the time approach infinity such that the product $(\lambda^2 t)$ remains constant. This procedure has been extensively applied to generate "Markovian" equations of motion for the density matrix of the subsystem.

In this article we present an alternative for circumventing the difficulties of the standard techniques for deriving an equation of motion for the spin density matrix, i.e., see Redfield,[1] Slichter,[12] or Abragam.[7] The difficulties of the standard methods are associated with a failure of the perturbation theory. In the usual treatments one encounters secular terms (those which grow linearly in time) which destroy the smallness of the terms in the perturbation expansion. The problem is to find an expansion procedure that avoids the secular behavior. A similar problem occurs in the field of nonlinear mechanics and has been extensively considered by Krylov and Bogoliubov.[13] Their techniques have been modified by Frieman[14] and Sandri[15] who developed the MTS method in order to treat a variety of problems that arise in the kinetic theory of gases. We have used the MTS method to present a microscopic derivation of the Fokker–Planck equation for a heavy, Brownian particle in a classical fluid.[16] The MTS method is applicable to systems whose key feature is the existence of processes occurring on widely separated time scales. This feature is quite general for weakly coupled many-body systems. In the NMR case the bath changes on the fast time scale characterized by τ_c while the spins change on the slow time scale characterized by τ_R. The virtue of the MTS method is that it focuses attention, at the outset, on the existence of different time scales.

In the next section we establish notation and explicitly demonstrate the secular behavior of the NMR problem. The third section contains the derivation of the equation of motion using the MTS method. The final section contains some concluding remarks concerning the MTS method.

II. SECULAR BEHAVIOR IN NMR

The system consists of a spin subsystem plus a heat bath which for concreteness we think of as a liquid. The system Hamiltonian is

$$H = H_s + H_L + \lambda H' = H_0 + \lambda H', \tag{2.1}$$

where H_s is the Hamiltonian of the spin subsystem in a static magnetic field, H_L is the bath Hamiltonian, and H' is the interaction between spins and bath responsible for the relaxation. The parameter λ measures the strength of this interaction. The Liouville equation describing the time evolution of the system density matrix, $\rho(t)$ is

$$i(\partial/\partial t)\rho(t) = \hbar^{-1}[H, \rho] \equiv L\rho. \tag{2.2}$$

The operator L is

$$\hbar^{-1}[H, \Phi] \equiv L\Phi, \tag{2.3}$$

where Φ is an arbitrary function.

We decompose L as

$$L = L_s + L_L + \lambda L' = L_0 + \lambda L'. \tag{2.4}$$

The system is prepared such that initially $(t=0)$ the system density matrix is the product of an equilibrium bath density matrix and an arbitrary spin density matrix:

$$\rho(0) = \rho_L \sigma(0), \tag{2.5}$$

where $\sigma(t)$ is the spin density matrix and ρ_L the bath density matrix,

$$\rho_L = \exp[-\beta H_L]/Z; \qquad Z = \mathrm{Tr}_L[\exp(-\beta H_L)]. \tag{2.6}$$

The arbitrary initial spin state, produced by some constraint introduced in the distant past, will evolve in time toward its equilibrium value σ_{eq} when the constraint is removed at $t=0$. The spin energy term H_s is defined to include the thermal equilibrium average of the interaction term. This implies

$$\mathrm{Tr}_L\{[\lambda H', \rho_{eq}]\} = \mathrm{Tr}_L\{\lambda L' \rho_{eq}\} = 0. \tag{2.7}$$

To obtain the spin density matrix from the system density matrix we must take a trace over the bath variables

$$\mathrm{Tr}_L \rho(t) = \sigma(t) \tag{2.8}$$

so that $\sigma(t)$ satisfies the equation

$$i(\partial\sigma/\partial t) = \mathrm{Tr}_L[L\rho(t)]. \tag{2.9}$$

We proceed to exhibit explicitly the breakdown of perturbation theory in the derivation of the equation of motion for $\sigma(t)$. To facilitate the discussion we cast the Liouville equation in the interaction picture:

$$i[\partial\rho^*(t)/\partial t] = \lambda L'^*(t)\rho^*(t) \tag{2.10}$$

with

$$A^*(t) = \exp[(i/\hbar)H_0 t]A \exp[-(i/\hbar)H_0 t]. \tag{2.10'}$$

We expand $\rho^*(t)$ in powers of λ,

$$\rho^*(t) = \rho_0^*(t) + \lambda\rho_1^*(t) + \lambda^2\rho_2^*(t) + \cdots, \tag{2.11}$$

substitute this in Eq. (2.10) and equate powers of λ to

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obtain

$$i[\partial\rho_0^*(t)/\partial t]=0; \qquad \rho_0^*(0)=\rho_L\sigma(0); \quad (2.12a)$$

$$i[\partial\rho_1^*(t)/\partial t]=L'^*(t)\rho_0^*(t); \quad (2.12b)$$

$$i[\partial\rho_2^*(t)/\partial t]=L'^*(t)\rho_1^*(t). \quad (2.12c)$$

With the use of Eq. (2.8) and the expansion

$$\sigma^*(t)=\sigma_0^*(t)+\lambda\sigma_1^*(t)+\lambda^2\sigma_2^*(t)+\cdots \quad (2.13)$$

we obtain

$$i[\partial\sigma_0^*(t)/\partial t]=0; \qquad \sigma_0^*(0)=\sigma(0); \quad (2.14a)$$

$$i[\partial\sigma_1^*(t)/\partial t]=\mathrm{Tr}_L\{L'^*(t)\rho_0^*(t)\}; \quad (2.14b)$$

$$i[\partial\sigma_2^*(t)/\partial t]=\mathrm{Tr}_L\{L'^*(t)\rho_1^*(t)\}. \quad (2.14c)$$

Inserting the solution of Eq. (2.12a) into Eq. (2.12b) and introducing the solution of Eq. (2.12b) into Eq. (2.14c) yields

$$\frac{\partial\sigma_2^*(t)}{\partial t}=-\mathrm{Tr}_L\int_0^t L'^*(t)L'^*(t')dt'\rho_{\mathrm{eq}}\sigma(0)\sim\tau_cG\sigma(0), \quad (2.15)$$

where τ_c is some correlation time after which the integrand is negligible and τ_cG the value of the integral (see Ref. 7, p. 276). Solving Eq. (2.15) for $\sigma_2^*(t)$ yields

$$\sigma_2^*(t)\sim t\tau_cG\sigma(0). \quad (2.16)$$

This quantity grows linearly in time (secular behavior) and for times $\sim(1/\tau_cG)$ the supposed correction is of the same size as the zero-order term. The expansion procedure, valid for short times, will break down when we try to describe the long-time behavior of the system. The original derivations were successful because they deal with time intervals Δt satisfying the inequality[1]

$$\tau_r>\Delta t>\tau_c. \quad (2.17)$$

While this procedure yields the proper equations of motion the previously mentioned restrictive assumptions must be imposed. Abragam's iteration scheme[7] requires the replacement of the initial density matrix by its value at time t to avoid secular behavior. Finally, the Zwanzig technique in conjunction with a weak coupling limit circumvents secular behavior by considering the limit of an infinitely slow process. The condition $\lambda^2t=\mathrm{const}$ for all t prevents the secular behavior of the expansion terms.

The MTS method deals explicitly with secular behavior by introducing a set of time variables which permit the construction of a perturbation theory valid for all times. The single time variable of $\rho(t)$ and $\sigma(t)$ is replaced by the set of time variables τ_0, τ_1, $\tau_2\cdots$ each of which is treated as an independent variable. Thus

$$\rho(t)\rightarrow\boldsymbol{\rho}(\tau_0,\tau_1,\cdots,\tau_n) \quad (2.18)$$

and

$$\sigma(t)\rightarrow\boldsymbol{\sigma}(\tau_0,\tau_1,\cdots,\tau_n). \quad (2.19)$$

We shall seek solutions of Eqs. (2.2) and (2.9) of the form

$$\boldsymbol{\rho}=\boldsymbol{\rho}_0+\lambda\boldsymbol{\rho}_1+\lambda^2\boldsymbol{\rho}_2+\cdots \quad (2.20)$$

and

$$\boldsymbol{\sigma}=\boldsymbol{\sigma}_0+\lambda\boldsymbol{\sigma}_1+\lambda^2\boldsymbol{\sigma}_2+\cdots \quad (2.21)$$

with

$$\boldsymbol{\sigma}_n=\mathrm{Tr}_L[\boldsymbol{\rho}_n]. \quad (2.22)$$

Within the framework of the MTS method one asserts that the new time variables $\{\tau_n\}$ are related to the real time by

$$\tau_n=\lambda^nt. \quad (2.23)$$

This enables us to formally expand the time derivative as

$$\partial/\partial t=(\partial/\partial\tau_0)+\lambda(\partial/\partial\tau_1)+\lambda^2(\partial/\partial\tau_2)+\cdots. \quad (2.24)$$

When we restrict the extended functions $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$ to the physical time line according to Eq. (2.24) we recover $\rho(t)$ and $\sigma(t)$.

The heart of the MTS method is the proviso that the increased flexibility which accompanies the extended definition of the functions may be used to eliminate secular behavior whenever it occurs.

A more detailed discussion of the MTS method may be found in Refs. 15 and 14.

III. MTS DERIVATION OF THE EQUATION OF MOTION

We now substitute Eqs. (2.20) and (2.24) in Eq. (2.2) and equate powers of λ. To order λ^2 one obtains

$$i\frac{\partial\rho_0(\tau_0,\tau_1,\cdots,)}{\partial\tau_0}=L_0\rho_0(\tau_0,\tau_1,\cdots,) \quad (3.1)$$

$$i\left[\frac{\partial\rho_1(\tau_0,\tau_1,\cdots,)}{\partial\tau_0}+\frac{\partial\rho_0(\tau_0,\tau_1,\cdots,)}{\partial\tau_1}\right]=L'\rho_0(\tau_0,\tau_1,\cdots,)+L_0\rho_1(\tau_0,\tau_1,\cdots,) \quad (3.2)$$

$$i\left[\frac{\partial\rho_2(\tau_0,\tau_1,\cdots,)}{\partial\tau_0}+\frac{\partial\rho_1(\tau_0,\tau_1,\cdots,)}{\partial\tau_1}+\frac{\partial\rho_0(\tau_0,\tau_1,\cdots,)}{\partial\tau_2}\right]=L'\rho_1(\tau_0,\tau_1,\cdots,)+L_0\rho_2(\tau_0,\tau_1,\cdots,). \quad (3.3)$$

In these equations the dependence of the extended functions on $\{\tau_n\}$ is explicitly indicated; in the following time arguments will only be included where required for clarity. For simplicity we have suppressed the use of boldface for indicating extended function.

If we place the expansion for σ Eq. (2.21) into Eq. (2.9) and employ Eq. (2.24) an analogous set of equations is obtained for the spin density matrix

$$i(\partial\sigma_0/\partial\tau_0)=\mathrm{Tr}_L[L_0\rho_0], \quad (3.4)$$

$$i[(\partial\sigma_1/\partial\tau_0)+(\partial\sigma_0/\partial\tau_1)]=\mathrm{Tr}_L[L'\rho_0+L_0\rho_1], \quad (3.5)$$

$$i[(\partial\sigma_2/\partial\tau_0)+(\partial\sigma_1/\partial\tau_1)+(\partial\sigma_0/\partial\tau_2)]=\mathrm{Tr}_L[L'\rho_1+L_0\rho_2]. \quad (3.6)$$

The solution of Eq. (3.1) is

$$\rho_0(\tau_0,\tau_1,\cdots,)=\exp(-iL_0\tau_0)\rho_0(0,\tau_1,\cdots,). \quad (3.7)$$

In order to proceed we must formulate appropriate initial conditions for the extended functions. In terms of the extended functions the initial condition Eq. (2.5) is

$$\rho(0,\tau_1,\cdots,)=\rho_L\sigma(0,\tau_1,\cdots,). \quad (3.8)$$

The independence of the time scales permits us to adopt the customary initial condition, Eq. (2.5), for arbitrary τ_1, τ_2, $\cdots$ when $\tau_0=0$. A similar assumption about the initial conditions is present in all MTS developments. It is possible to choose

$$\sigma_0(0,\tau_1,\cdots,)=\sigma(0,\tau_1,\cdots,) \quad (3.9)$$

and

$$\rho_0(0,\tau_1,\cdots,)=\rho_L\sigma_0(0,\tau_1,\cdots,). \quad (3.10)$$

Accordingly we have

$$\sigma_n(0,\tau_1,\cdots,)=\rho_n(0,\tau_1,\cdots,)=0 \quad n\geq 1. \quad (3.11)$$

With these initial conditions Eq. (3.7) becomes

$$\rho_0(\tau_0,\tau_1,\cdots,)=\rho_L\exp(-iL_0\tau_0)\sigma_0(0,\tau_1,\cdots,), \quad (3.12)$$

since $L_0\rho_L=0$. The result may be introduced in Eq. (3.4) to yield the equation

$$i(\partial\sigma_0/\partial\tau_0)=L_0\exp(-iL_0\tau_0)\sigma_0(0,\tau_1,\cdots,). \quad (3.13)$$

The solution to this equation is

$$\sigma_0(\tau_0,\tau_1,\cdots,)=\exp(-iL_0\tau_0)\sigma_0(0,\tau_1,\cdots,). \quad (3.14)$$

We now turn to Eq. (3.5) and write it in the form

$$i(\partial\sigma_0/\partial\tau_1)=\mathrm{Tr}_L[-i(\partial\rho_1/\partial\tau_0)+L_0\rho_1], \quad (3.15)$$

where we have used Eq. (2.22) and Eq. (2.7). This equation may be rearranged to yield

$$\begin{aligned} i\exp(iL_0\tau_0)[\partial\sigma_0(\tau_0,\tau_1,\cdots,)/\partial\tau_1] &= i[\partial\sigma_0(0,\tau_1\cdots)/\partial\tau_1] \\ &= -i(\partial/\partial\tau_0)\ \mathrm{Tr}_L[\exp(iL_0\tau_0)\rho_1], \end{aligned} \quad (3.16)$$

where we have used the fact

$$\mathrm{Tr}_L\exp(iL_0t)A=\exp(iL_0t)\ \mathrm{Tr}_L[A] \quad (3.17)$$

with A an arbitrary operator depending on bath and spin variables. The solution of Eq. (3.16) is

$$i\tau_0[\partial\sigma_0(0,\tau_1,\cdots,)/\partial\tau_1]=-i\ \mathrm{Tr}_L[\exp(iL_0\tau_0)\rho_1] \quad (3.18)$$

which may be rearranged using Eqs. (2.22), (3.17), and (3.14) to

$$i\sigma_1(\tau_0,\tau_1,\cdots,)=-i\tau_0[\partial\sigma_0(\tau_0,\tau_1,\cdots,)/\partial\tau_1]. \quad (3.19)$$

In order to prevent the secular growth of σ_1 as τ_0 increases we must set

$$(\partial\sigma_0/\partial\tau_1)\tilde{\tau}_0=0 \quad \text{and} \quad \sigma_1(\tau_0,\tau_1,\cdots,)\tilde{\tau}_0=0, \quad (3.20)$$

where the notation $\tilde{\tau}_0$ means asymptotically on the τ_0 scale. We stress that asymptotically on the τ_0 scale means[15] for a few units of a clock that measures time in units of τ_0. The explicit recognition of the existence of many time scales has created sufficient freedom to eliminate the secular behavior which destroys ordinary perturbation theory. If we are willing to forego a description of the relaxation for a few units of τ_0 we may choose $\sigma_1\equiv 0$ and consequently

$$\sigma_0=\sigma_0(\tau_0,\tau_2,\cdots,), \quad (3.21)$$

i.e., σ_0 does not vary on the τ_1 scale.

We now turn to Eq. (3.2) and integrate with respect to τ_0,

$$i\exp(iL_0\tau_0)\rho_1(\tau_0,\tau_1,\cdots,)=-i\int_0^{\tau_0}\exp(iL_0x)\times\left[\frac{\partial\rho_0(x,\tau_1,\cdots,)}{\partial\tau_1}+iL'\rho_0(x,\tau_1,\cdots,)\right]dx. \quad (3.22)$$

The first term on the rhs of Eq. (3.22) is zero by virtue of the fact that

$$\exp(iL_0x)[\partial\rho_0(x,\tau_1,\cdots,)/\partial\tau_1]=[\partial\rho_0(0,\tau_1,\cdots,)/\partial\tau_1] \quad (3.23)$$

and Eqs. (3.10) and (3.21). As a consequence we find

$$i\rho_1(\tau_0,\tau_2,\cdots,)=\int_0^{\tau_0}\exp[iL_0(x-\tau_0)]\times L'\rho_L\sigma_0(x,\tau_2,\cdots,)dx, \quad (3.24)$$

which may be rewritten using Eq. (3.14) and the definition of L' as

$$i\rho_1(\tau_0,\tau_2,\cdots,)=\frac{1}{\hbar}\int_0^{\tau_0}[H'(x-\tau_0),\rho_L\sigma_0(\tau_0,\tau_2,\cdots,)]dx. \quad (3.25)$$

In Eq. (3.25) we have used the notation

$$\begin{aligned} H'(t) &= \exp(iL_0t)H' \\ &= \exp[+(i/\hbar)H_0t]H'\exp[-(i/\hbar)H_0t]. \end{aligned} \quad (3.26)$$

Note that $\sigma_1=\text{Tr}_L\rho_1=0$ directly from Eq. (3.24) by use of Eq. (2.7).

As the final step of our analysis we integrate Eq. (3.6) with respect to τ_0. We find after some manipulation

$$i\sigma_2(\tau_0,\tau_2,\cdots,)=-\tau_0\left(i\frac{\partial\sigma_0(\tau_0,\tau_2,\cdots,)}{\partial\tau_2}-\frac{1}{\tau_0}\int_0^{\tau_0}\text{Tr}_L\{\exp[iL_0(x-\tau_0)]L'\rho_1(x,\tau_2,\cdots,)\}dx\right). \tag{3.27}$$

When we introduce Eq. (3.25) for ρ_1 into the integral term of Eq. (3.27) and employ Eqs. (3.14) and (3.26) we obtain:

$$i\sigma_2(\tau_0,\tau_2,\cdots,)=-i\tau_0\left(\frac{\partial\sigma_0}{\partial\tau_2}(\tau_0,\tau_2,\cdots,)+\frac{1}{\hbar^2\tau_0}\int_0^{\tau_0}dx\int_0^x dy\times\text{Tr}_L[H'(x-\tau_0),[H'(y-\tau_0),\rho_L\sigma_0(\tau_0,\tau_2,\cdots,)]]\right). \tag{3.28}$$

In order to determine the asymptotic time behavior of this operator equation we must examine matrix elements. The $\alpha\alpha'$ matrix element of Eq. (3.28) is

$$i\sigma_2^{\alpha\alpha'}(\tau_0,\tau_2,\cdots,)=-i\tau_0\left(\frac{\partial\sigma_0^{\alpha\alpha'}(\tau_0,\tau_2,\cdots,)}{\partial\tau_2}+\frac{1}{\hbar^2\tau_0}\int_0^{\tau_0}dx\int_0^x dy\langle\alpha\,|\,\text{Tr}_L[H'(x-\tau_0),[H'(y-\tau_0),\rho_L\sigma_0(\tau_0,\tau_2,\cdots,)]]\,|\,\alpha'\rangle\right). \tag{3.29}$$

We shall expand the interaction term H' as

$$H'=\sum_q S_qF_q\hbar, \tag{3.30}$$

where the S_q are spin operators and the F_q are lattice operators.

The structure of the matrix elements of the integral term I in Eq. (3.29) is

$$I=\tau_0^{-1}\sum_{\beta\beta'}\int_0^{\tau_0}dx\int_0^x dyF_{\alpha\alpha'\beta\beta'}(x-y)\,\exp(i\Delta x)\sigma_{\beta\beta'}(\tau_0,\tau_2,\cdots,), \tag{3.31}$$

where we have introduced the intermediate states $|\beta\rangle\,|\beta'\rangle$ and defined

$$\Delta=(E_\alpha-E_{\alpha'}-E_\beta+E_{\beta'})/\hbar. \tag{3.32}$$

In Eq. (3.31) $F_{\alpha\alpha'\beta\beta'}(t)$ is

$$F_{\alpha\alpha'\beta\beta'}(t)=-\sum_{qq'}\{S_{q'}^{\alpha\beta}S_q^{\beta'\alpha'}[g_{qq'}(t)\exp(+i\omega_{\beta\alpha}t)+g_{qq'}(-t)\exp(-i\omega_{\beta'\alpha'}t)]-\delta_{\beta'\alpha'}\sum_\gamma S_q^{\alpha\gamma}S_{q'}^{\gamma\beta}g_{qq'}(t)\exp(i\omega_{\beta\gamma}t)-\delta_{\beta\alpha}\sum_\gamma S_q^{\beta'\gamma}S_{q'}^{\gamma\alpha'}g_{qq'}(-t)\exp(-i\omega_{\beta'\gamma}t)\}, \tag{3.33}$$

with $g_{qq'}(t)$ the lattice correlation function

$$g_{qq'}(t)=\text{Tr}_L\rho_LF_q(t)F_{q'}(0). \tag{3.34}$$

We now invert the order of integration in Eq. (3.31), replace $(x-y)$ by s and express the quantity as the sum of two terms

$$\tau_0^{-1}\sum_{\beta\beta'}\left(\int_0^{\tau_0}ds\int_0^{\tau_0}dx-\int_0^{\tau_0}ds\int_0^s dx\right)F_{\alpha\alpha'\beta\beta'}(s)\,\exp(i\Delta x)\sigma_{\beta\beta'}(\tau_0,\tau_2,\cdots,). \tag{3.35}$$

Provided that $F_{\alpha\alpha'\beta\beta'}(t)$ decays on the fast time scale the second term on the right-hand side of Eq. (3.35) may be neglected. This second term is a small correction that describes the short-time behavior of the system. In the limit $\tau_0\to\infty$ it is the first term that must be considered.

For the first term of Eq. (3.35) there are two cases of interest. The first case is when $\Delta\neq0$. Under these circumstances as $\tau_0\to\infty$ (i.e. for times long compared to $1/\Delta$) the x integration approaches zero. Consequently the terms with $\Delta\neq0$ asymptotically do not give rise to secular behavior on the rhs of Eq. (3.29).

In the case when $\Delta=0$, the x integration may be performed and we obtain for the integral term asymptotically as $\tau_0\to\infty$

$$I=-\sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}\sigma_{\beta\beta'}(\tau_0,\tau_2,\cdots), \tag{3.36}$$

where $R_{\alpha\alpha'\beta\beta'}$ is the relaxation matrix defined by

$$R_{\alpha\alpha'\beta\beta'}=-\int_0^\infty F_{\alpha\alpha'\beta\beta'}(t)\,dt. \tag{3.37}$$

After a great deal of manipulation we find, from Eq. (3.33), that $R_{\alpha\alpha'\beta\beta'}$ may be expressed as

$$\begin{aligned}R_{\alpha\alpha'\beta\beta'}=\sum_{qq'}\{&S_q^{\alpha\beta}S_{q'}^{\beta'\alpha'}[j_{qq'}(\omega_{\alpha\beta})+j_{qq'}(\omega_{\alpha'\beta'})]\\&-\delta_{\beta'\alpha'}\sum_\gamma S_q^{\alpha\gamma}S_{q'}^{\gamma\beta}j_{qq'}(\omega_{\beta\gamma})\exp(\hbar\omega_{\beta\gamma}/kT)\\&-\delta_{\beta\alpha}\sum_\gamma S_q^{\beta'\gamma}S_{q'}^{\gamma\alpha'}j_{qq'}(\omega_{\beta'\gamma})\exp(\hbar\omega_{\beta'\gamma}/kT)\},\end{aligned} \tag{3.38}$$

where

$$j_{qq'}(\omega)=\frac{\exp(-\hbar\omega/kT)}{2}\int_{-\infty}^{+\infty}\exp(-i\omega t)\langle F_qF_{q'}(t)\rangle dt. \tag{3.39}$$

Small terms corresponding to the static second-order shift in the spin eigenfunctions have been omitted[1,7] from Eq. (3.38); we will ignore these terms here.

Thus if we include only the terms that have secular growth in Eq. (3.29) we have

$$\begin{aligned}i\sigma_2^{\alpha\alpha'}(\tau_0,\tau_2,\cdots,)=-i\tau_0\{&[\partial\sigma_0^{\alpha\alpha'}(\tau_0,\tau_2,\cdots,)/\partial\tau_2]\\&-\sum_{\beta\beta'}{}' R_{\alpha\alpha'\beta\beta'}\sigma_0^{\beta\beta'}(\tau_0,\tau_2,\cdots,)\},\end{aligned} \tag{3.40}$$

where the prime restricts the summation to those terms for which $\Delta=0$. The terms with $\Delta=0$ result in secular behavior on the right-hand side of Eq. (3.40). These terms correspond to processes in which the spin energy is conserved during a transition, i.e., $\omega_{\alpha\beta}=\omega_{\alpha'\beta'}$.

The elimination of the secular behavior in Eq. (3.40) yields the equation of motion that determines the variation of σ_0 on the slow time scale:

$$[\partial\sigma_0^{\alpha\alpha'}(\tau_0,\tau_2,\cdots,)/\partial\tau_2]=\sum_{\beta\beta'}{}' R_{\alpha\alpha'\beta\beta'}\sigma_0^{\beta\beta'}(\tau_0,\tau_2,\cdots,). \tag{3.41}$$

In operator form Eq. (3.41) is

$$[\partial\sigma_0(\tau_0,\tau_2,\cdots,)/\partial\tau_2]=R\sigma_0(\tau_0,\tau_2,\cdots,), \tag{3.42}$$

where R is a tetradic operator with elements $R_{\alpha\alpha'\beta\beta'}$. It follows from Eq. (3.41) that (except for short times) $\sigma_2=0$.

When we add $\partial\sigma_0/\partial\tau_0$ [Eq. (3.13)] to $\partial\sigma_0/\partial\tau_2$ [Eq. (3.42)] according to Eq. (2.24) we find

$$\begin{aligned}\partial\sigma_0/\partial t&=(\partial\sigma_0/\partial\tau_0)+\lambda^2(\partial\sigma_0/\partial\tau_2)+0(\lambda^3)\\&=-i[H_z,\sigma_0(\tau_0,\tau_2,\cdots,)]+\lambda^2R\sigma_0(\tau_0,\tau_2,\cdots,).\end{aligned} \tag{3.43}$$

The restriction of σ_0 to the real time t yields

$$\partial\sigma_0(t)/\partial t=-i[H_z,\sigma_0(t)]+\lambda^2R\sigma_0(t). \tag{3.44}$$

When we take matrix elements of this operator equation Eq. (1.1) results. This result is identical to that of Redfield.[1]

We remark in passing that the equilibrium spin density matrix

$$\sigma_{\mathrm{eq}}^{\beta\beta'}=\frac{\delta_{\beta\beta'}\exp(-E_\beta/kT)}{\sum_\beta\exp(-E_\beta/kT)} \tag{3.45}$$

results in

$$\sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}\sigma_{\mathrm{eq}}^{\beta\beta'}=0 \tag{3.46}$$

which means that the system will approach the proper equilibrium state. It is easy to show that in the high-temperature "semiclassical" limit when $\hbar\omega/kT\ll1$ that

$$\begin{aligned}R=R^{\mathrm{Cl}}=\sum_{qq'}\{&S_q^{\alpha\beta}S_{q'}^{\beta'\alpha'}[J_{qq'}(\omega_{\alpha\beta})+J_{qq'}(\omega_{\alpha'\beta'})]\\&-\delta_{\beta'\alpha'}\sum_\gamma S_q^{\alpha\gamma}S_{q'}^{\gamma\beta}J_{qq'}(\omega_{\beta\gamma})\\&-\delta_{\beta\alpha}\sum_\gamma S_q^{\beta'\gamma}S_{q'}^{\gamma\alpha'}J_{qq'}(\omega_{\beta'\gamma})\},\end{aligned} \tag{3.47}$$

where we have taken $\hbar\omega/kT=0$ and defined

$$J_{qq'}(\omega)=\exp(\hbar\omega/kT)j_{qq'}(\omega). \tag{3.48}$$

IV. CONCLUDING REMARKS

The MTS method has provided a compact derivation of the NMR equation of motion. The recognition of the existence of time scales has permitted us to perform the derivation under more general conditions and explicitly demonstrate some key features of previous work. The restriction to a factored density matrix for all time has been removed and appears only as an initial condition. Eq. (2.5).

The initial condition has been chosen to facilitate comparison with existing equations. We feel that our analysis can be generalized to include some initial correlation between spins and lattice. However there is no assurance that in the presence of some initial correlation the same transport equation will be valid for long times. In accord with the general theories[17] of weakly coupled systems we find that the behavior on the macroscopic time scale τ_2 is determined by events occurring on the fast τ_0 time scale. In addition, the processes which contribute strongly to the long-time behavior of the system are explicitly shown to be the secular (energy conserving) terms while the non-secular terms are averaged to zero for these times.

The MTS method suggests a systematic procedure for obtaining higher order corrections to Eq. (1.1). This would entail studying the behavior of σ_0 on time scales slower than τ_2 and the calculation of σ_2, $\sigma_3\cdots$ etc. These corrections will be valid for all macroscopic times since the method eliminates secular behavior in each order of λ. We are currently considering this problem.

[17] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962), and Ref. 10.