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Redfield–Langevin Equation for Nuclear Spin Relaxation*

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We present a derivation of a Langevin-type equation for the operator $G_{\alpha\alpha}'(t)=\exp(iHt)|\alpha'\rangle\langle\alpha|\exp(-iHt)$, where $|\alpha\rangle$ and $|\alpha'\rangle$ are eigenstates of the subsystem Hamiltonian and H is the full Hamiltonian for subsystem plus bath. For the case in which we consider a spin system weakly coupled to a thermal bath (lattice), the equation of motion is of the form of the Redfield equation with a fluctuating term. This equation may be used to derive the standard Redfield equation for the spin density matrix as well as Bloch equations with fluctuating terms for the components of the magnetization for individual systems in the nonequilibrium ensemble. The latter presents a first principles derivation of the magnetic analog of hydrodynamic fluctuation theory. A calculation of several of the correlation functions which may be constructed from the theory is presented.

I. INTRODUCTION

The relaxation of a nuclear spin in weak interaction with a lattice is described by the Redfield equation for the spin density matrix. Several interesting and diverse derivations of this equation have been presented in the recent past.[1–3] The spin density matrix which is obtained from the Redfield equation is an *averaged* quantity since it is obtained from the complete density matrix of the system by averaging over the lattice degrees of freedom. Furthermore, the spin density matrix obtained from the Redfield equation provides an adequate description of the spin system only on a slow time scale; the rapid, fluctuating, motion of the lattice degrees of freedom are excluded. From this spin density matrix it is possible to obtain equations of motion for the magnetization which we shall refer to as Bloch equations. The Bloch equations are, of course, equations of motion for the *average* magnetization. A corresponding microscopic equation for this dynamical variable is not available.

Our present purpose is to consider a more fundamental equation that simultaneously leads to the ordinary Redfield and Bloch equations upon suitable averaging. The generalized equation of motion we obtain here is for the operator

$$G_{\alpha\alpha'}(t)=\exp(iHt)\,|\,\alpha'\rangle\langle\alpha\,|\,\exp(-iHt), \quad (1.1)$$

where $|\alpha\rangle$ and $|\alpha'\rangle$ denote eigenstates of the spin (Zeeman) system and H is the full Hamiltonian for the system. The equation of motion for $G_{\alpha\alpha'}(t)$ is a microscopic equation that includes the effects of the lattice. We assume that the spin system is in weak interaction with the lattice and obtain an equation which is a valid description of the slow time scale on which the spins relax. On this slow time scale the lattice motion is extremely rapid. We show that $G_{\alpha\alpha'}(t)$ satisfies an equation of motion of the Redfield form with the effects of the lattice appearing in a rapidly fluctuating term. In addition, we obtain a microscopic equation of motion for the magnetization operator directly from the equation of motion for $G_{\alpha\alpha'}(t)$. This equation is similar to the Bloch equation, but an added fluctuating term is present which includes the effects of the lattice. The stochastic properties of the fluctuating terms that appear in the equation for the magnetization and the equation for $G_{\alpha\alpha'}(t)$ are determined.

The analysis presented here is not intended to provide a new practical calculational procedure. Rather, we wish to present a point of view of spin relaxation. The point of view is that the existence of a simple linear relaxation equation for a dynamical variable or its associated density matrix implies that the microscopic equations may also be expressed in a simple way on the slow time scale of the macroscopic variable. This situation will hold for a variety of weakly coupled systems that can be described by a master equation. The same point of view has been adopted recently by Zwanzig and Bixon[4] in their treatment of the Boltzmann–Langevin equation for dilute gases and by Oppenheim and us[5] in our treatment of Brownian motion.

We employ a projection operator technique to obtain an equation of motion for $G_{\alpha\alpha'}(t)$. The projection operator technique differs from that employed by Mori[6] in his generalized theory of Brownian motion. In Mori's approach attention is focused on obtaining equations of the macroscopic variables, e.g., the magnetization—no explicit reference is made to the equation of motion for the distribution function, e.g., the spin density matrix. Here attention is focused on obtaining the microscopic equation for the dynamical variable $G_{\alpha\alpha'}(t)$ which satisfies the same equation of motion as the spin density matrix upon averaging over lattice degrees of freedom. The projection operator employed is qualitatively different from that required in the Mori scheme. The results obtained are richer than those obtained by direct application of Mori's method. Related work has been undertaken by Argyres and Kelley[2] who employ a different projection operator to obtain an equation of motion for the spin density matrix directly. These authors, however, do not arrive at the stochastic equation for $G_{\alpha\alpha'}(t)$ or the stochastic equations for the magnetization. Finally, we note that Englert[7] has presented a very careful analysis of weakly coupled quantum systems without explicit reference to the Brownian motion point of view.

The analogy between the theory of Brownian motion and spin relaxation is most useful. The Fokker–Planck equation for the Brownian particle distribution function corresponds to the Redfield equation. The simple exponential relaxation of the average Brownian particle momentum corresponds to the Bloch equations for the magnetization. The existence of these simple transport equations for the averaged quantities implies simple microscopic equations. For the magnetization, the Bloch equations are augmented by a fluctuating "force" which corresponds to the Langevin equation for the Brownian particle momentum. For spins the microscopic analog of the Redfield equation is the equation of motion for $G_{\alpha\alpha'}(t)$, while in Brownian motion theory the microscopic analog of the Fokker Planck equation is the equation of motion for the phase function[4,5]

$$D(t)=\delta[\mathbf{R}(t)-\hat{\mathbf{R}}]\delta[\mathbf{P}(t)-\hat{\mathbf{P}}], \tag{1.2}$$

where $\mathbf{R}(t)$ and $\mathbf{P}(t)$ are the position and momentum of the Brownian particle at time t. In both the case of spin relaxation and Brownian motion, all the results are succinctly expressed in the fundamental equation for $G_{\alpha\alpha'}(t)$ and $D(t)$, respectively.

For clarity, we explicitly consider here the primitive case of a single spin relaxing via an intramolecular mechanism. It is an easy matter to interpret our results in terms of an N-spin system where intermolecular and/or intramolecular relaxation mechanisms are present. However, when intermolecular relaxation mechanisms prevail, the reduction to a Bloch-type equation for the magnetization is accomplished with greater difficulty.

II. DERIVATION OF THE EQUATION OF MOTION

The Hamiltonian for the spin system and the lattice is

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

where H_s is the Hamiltonian for the spin system in the presence of a static magnetic field (Zeeman Hamiltonian), H_l is the lattice Hamiltonian, and H' is the interaction of the spin system and the lattice characterized by the coupling constant λ. We require that the lattice average of the interaction Hamiltonian vanish, i.e.,

$$\langle H'\rangle\equiv \mathrm{Tr}_l\rho_l H'=0, \tag{2.2}$$

where Tr_l indicates a trace over the eigenstates of the lattice Hamiltonian and ρ_l is the equilibrium density matrix for the lattice

$$\rho_l=\exp(-\beta H_l)/\mathrm{Tr}_l \exp(-\beta H_l). \tag{2.3}$$

If $\langle H'\rangle$ is not zero, we redefine H_s and H' so that (2.2) holds.

The equation of motion for the density matrix of the system, $\rho(t)$, is

$$\dot{\rho}(t)=-i[H,\rho(t)]\equiv -iL\rho(t), \qquad (\hbar=1), \tag{2.4}$$

where L is the Liouville operator for the system. From the form of the Hamiltonian, the Liouville operator may be written as

$$L=L_s+L_l+\lambda L'=L_0+\lambda L', \tag{2.5}$$

where $L_0=[H_0,\cdots]$ is the Liouville operator for the spins and lattice in the absence of any interaction and $L'=[H',\cdots]$ is the interaction Liouville operator.

We seek an equation of motion for the operator defined in Eq. (1.1),

$$G_{\alpha\alpha'}(t)=\exp(iLt)\,|\,\alpha'\rangle\langle\alpha\,|. \tag{2.6}$$

To obtain this equation of motion we introduce a projection operator $\mathcal{P}$ and let the operator identity

$$\exp(iLt)=\exp[i(1-\mathcal{P})Lt]+\int_0^t d\tau\, \exp[iL(t-\tau)]i\mathcal{P}L \times\exp[i(1-\mathcal{P})L\tau] \tag{2.7}$$

act upon

$$(1-\mathcal{P})\dot{G}_{\alpha\alpha'}(0)=(1-\mathcal{P})iLG_{\alpha\alpha'}(0). \tag{2.8}$$

The result is

$$\dot{G}_{\alpha\alpha'}(t)=\exp(iLt)\mathcal{P}iLG_{\alpha\alpha'}(0) +\exp[i(1-\mathcal{P})Lt](1-\mathcal{P})iLG_{\alpha\alpha'}(0) +\int_0^t d\tau\,\exp[iL(t-\tau)]i\mathcal{P}L \times\exp[i(1-\mathcal{P})L\tau](1-\mathcal{P})iLG_{\alpha\alpha'}(0), \tag{2.9}$$

where we have used the fact that for any operator A

$$A(t)\equiv\exp(iLt)A(0)=\exp(iHt)A(0)\,\exp(-iHt). \tag{2.10}$$

The appropriate projection operator for spin relaxation is defined by

$$\mathcal{P}A \equiv \langle A\rangle \equiv \mathrm{Tr}_l \rho_l A. \tag{2.11}$$

From this definition one may easily show

$$\mathcal{P}iL_l(\cdots)=0 \tag{2.12}$$

and

$$\mathcal{P}iL_s G_{\alpha\alpha'}(0) = -i\omega_{\alpha\alpha'}G_{\alpha\alpha'}(0), \tag{2.13}$$

where $\omega_{\alpha\alpha'}=(E_\alpha - E_{\alpha'})$ and E_α is the energy of spin state $|\alpha\rangle$. We may reduce Eq. (2.9) to the form

$$\dot{G}_{\alpha\alpha'}(t) = -i\omega_{\alpha\alpha'}G_{\alpha\alpha'}(t)+K_{\alpha\alpha'}(t) -\lambda^2\int_0^t d\tau \exp[iL(t-\tau)] \times \mathrm{Tr}_l\{\rho_l L' \exp[i(1-\mathcal{P})L]\tau L' G_{\alpha\alpha'}(0)\}, \tag{2.14}$$

where we have defined the random "force" term $K_{\alpha\alpha'}(t)$ as

$$K_{\alpha\alpha'}(t)=\exp[i(1-\mathcal{P})Lt]i\lambda L' G_{\alpha\alpha'}(0). \tag{2.15}$$

In order to obtain Eq. (2.14), we have used Eqs. (2.9), (2.10), and the fact that

$$\mathcal{P}K_{\alpha\alpha'}(t) = \langle K_{\alpha\alpha'}(t)\rangle = 0. \tag{2.16}$$

The operator identity

$$\exp[i(1-\mathcal{P})L\tau] = \exp(iL_0\tau) + \int_0^\tau d\tau' \exp[iL_0(t-\tau)] \times [i(1-\mathcal{P})\lambda L' - iL_s\mathcal{P}] \exp[i(1-\mathcal{P})L\tau'] \tag{2.17}$$

relates $\exp[i(1-\mathcal{P})Lt]$ to $\exp[iL_0t]$. Our basic assumption[3] will be that in the limit of weak spin–lattice interaction and for long times, one is justified in retaining only the lowest-order term in λ in Eq. (2.17) when operating on $K_{\alpha\alpha'}(0)$. With this assumption, Eq. (2.14) becomes

$$\dot{G}_{\alpha\alpha'}(t) = -i\omega_{\alpha\alpha'}G_{\alpha\alpha'}(t)+K_{\alpha\alpha'}(t) -\lambda^2\int_0^t d\tau \exp[iL(t-\tau)] \times \mathrm{Tr}_l[\rho_l L' \exp(iL_0\tau) L' G_{\alpha\alpha'}(0)]. \tag{2.18}$$

It is useful to transform to the interaction representation in order to remove the oscillatory Zeeman terms which appear in Eq. (2.18). This transformation is accomplished by means of the definition

$$G_{\alpha\alpha'}^*(t) \equiv \exp(i\omega_{\alpha\alpha'}t)G_{\alpha\alpha'}(t) = \exp(iLt) \times \exp(-iL_0t)G_{\alpha\alpha'}(0). \tag{2.19}$$

In terms of $G_{\alpha\alpha'}^*(t)$, Eq. (2.18) becomes

$$\dot{G}_{\alpha\alpha'}^*(t) = K_{\alpha\alpha'}^*(t) - \lambda^2\int_0^t d\tau \exp[iL(t-\tau)] \times \exp[-iL_0(t-\tau)]\,\mathrm{Tr}_l[\rho_l L^*(t-\tau)L^*(t)G_{\alpha\alpha'}(0)], \tag{2.20}$$

where we have made use of the distributive property of $\exp(iL_0t)$ and defined

$$L^*(t) = \exp(iL_0t)L'. \tag{2.21}$$

The fluctuating "force" in the interaction representation, $K_{\alpha\alpha'}^*(t)$, is

$$K_{\alpha\alpha'}^*(t) = \exp(i\omega_{\alpha\alpha'}t)K_{\alpha\alpha'}(t) = \exp[i(1-\mathcal{P})Lt]i\lambda L' \times \exp(-iL_0t)G_{\alpha\alpha'}(0). \tag{2.22}$$

We now take the ν, ν' spin–space matrix element of Eq. (2.20)

$$\langle\nu|\dot{G}_{\alpha\alpha'}^*(t)|\nu'\rangle = \langle\nu|K_{\alpha\alpha'}^*(t)|\nu'\rangle -\lambda^2\sum_{\beta,\beta'}\int_0^t d\tau \langle\beta'|\mathrm{Tr}_l[\rho_l L^*(t-\tau)L^*(t)G_{\alpha\alpha'}(0)]|\beta\rangle \times\langle\nu|G_{\beta\beta'}^*(t-\tau)|\nu'\rangle. \tag{2.23}$$

If the interaction Hamiltonian has the form

$$H' = \sum_q F_q S_q, \tag{2.24}$$

where F_q is a lattice operator and S_q is a spin operator, it is possible to evaluate the term

$$\langle\beta'|\mathrm{Tr}_l[\rho_l L^*(t-\tau)L^*(t)G_{\alpha\alpha'}(0)]|\beta\rangle$$

in Eq. (2.23). After a great deal of calculation one obtains

$$\langle\nu|\dot{G}_{\alpha\alpha'}^*(t)|\nu'\rangle = \langle\nu|K_{\alpha\alpha'}^*(t)|\nu'\rangle +\lambda^2\sum_{\beta,\beta'}\int_0^t d\tau F_{\alpha\alpha'\beta\beta'}(\tau)\exp(i\Delta t)\langle\nu|G_{\beta\beta'}^*(t-\tau)|\nu'\rangle, \tag{2.25}$$

where

$$\begin{aligned} F_{\alpha\alpha'\beta\beta'}(\tau) = \sum_{q,q'} \{ &\langle\alpha|S_{q'}|\beta\rangle\langle\beta'|S_q|\alpha'\rangle \\ &\times[g_{qq'}(\tau)\exp(i\omega_{\beta\alpha}\tau)+g_{qq'}(-\tau)\exp(-i\omega_{\beta'\alpha'}\tau)] \\ &-\delta_{\alpha'\beta'}\sum_\gamma\langle\alpha|S_q|\gamma\rangle\langle\gamma|S_{q'}|\beta\rangle g_{qq'}(\tau) \\ &\times\exp(i\omega_{\beta\gamma}\tau)-\delta_{\alpha\beta}\sum_\gamma\langle\beta'|S_q|\gamma\rangle\langle\gamma|S_{q'}|\alpha'\rangle \\ &\times g_{qq'}(-\tau)\exp(-i\omega_{\beta'\gamma}\tau)\}, \end{aligned} \tag{2.26}$$

$g_{qq'}(\tau)$ is the lattice correlation function

$$g_{qq'}(\tau) = \langle F_q{}^l(\tau)F_{q'}(0)\rangle, \tag{2.27}$$

with

$$F_q{}^l(\tau) = \exp(iH_l\tau)F_q\exp(-iH_l\tau). \tag{2.28}$$

Finally, Δ is the difference between the frequencies $\omega_{\alpha\alpha'}$ and $\omega_{\beta\beta'}$,

$$\Delta = \omega_{\alpha\alpha'} - \omega_{\beta\beta'} = (E_\alpha - E_{\alpha'} - E_\beta + E_{\beta'}). \tag{2.29}$$

For $t > \tau_c$, where τ_c is the correlation time associated with the lattice, one may extend the upper limit of the integral to infinity. Because of the factor $\exp(i\Delta t)$ the major contribution arises for those terms in the sum for which $\Delta = 0$. Furthermore, it may be shown that

$\langle \nu | G_{\beta\beta'}^*(t-\tau) | \nu' \rangle$ may be replaced by $\langle \nu | G_{\beta\beta'}^*(t) | \nu' \rangle$ incurring an error that is formally of higher order than λ^2. Hence, for $t > \tau_c$, Eq. (2.26) becomes

$$\langle \nu | \dot{G}_{\alpha\alpha'}^*(t) | \nu' \rangle = \langle \nu | K_{\alpha\alpha'}^*(t) | \nu' \rangle + \lambda^2 \sum_{\beta,\beta'}{}' R_{\alpha\alpha'\beta\beta'} \langle \nu | G_{\beta\beta'}^*(t) | \nu' \rangle, \quad (2.30)$$

where the prime on the summation restricts the sum to include only those terms for which $\Delta = 0$ and where $R_{\alpha\alpha'\beta\beta'}$ is the usual Redfield relaxation tetradic defined as

$$R_{\alpha\alpha'\beta\beta'} = \int_0^\infty d\tau F_{\alpha\alpha'\beta\beta'}(\tau). \quad (2.31)$$

Note that in Eq. (2.30) the relaxation tetradic operates only on the spin states which appear as operator labels and not on the spin states which appear as matrix elements. Furthermore, the matrix element $\langle \nu | G_{\alpha\alpha'}^*(t) | \nu' \rangle$ remains an operator in the lattice variables. From Eqs. (2.28) and (2.29) we obtain the equation

$$\langle \nu | \dot{G}_{\alpha\alpha'}(t) | \nu' \rangle = \langle \nu | K_{\alpha\alpha'}(t) | \nu' \rangle - i\omega_{\alpha\alpha'} \langle \nu | G_{\alpha\alpha'}(t) | \nu' \rangle + \lambda^2 \sum_{\beta,\beta'}{}' R_{\alpha\alpha'\beta\beta'} \langle \nu | G_{\beta\beta'}(t) | \nu' \rangle. \quad (2.32)$$

In operator form Eq. (2.32) is an equation of motion for $G_{\alpha\alpha'}(t)$,

$$\dot{G}_{\alpha\alpha'}(t) = -i\omega_{\alpha\alpha'} G_{\alpha\alpha'}(t) + \lambda^2 \sum_{\beta,\beta'}{}' R_{\alpha\alpha'\beta\beta'} G_{\beta\beta'}(t) + K_{\alpha\alpha'}(t). \quad (2.33)$$

This equation is the central result of our analysis. The form of the equation is identical to the Redfield equation, except for the added fluctuating force $K_{\alpha\alpha'}(t)$.

The spin density matrix $\langle \alpha | \sigma(t) | \alpha' \rangle$ is defined by

$$\langle \alpha | \sigma(t) | \alpha' \rangle = \langle \alpha | \mathrm{Tr}_l[\exp(-iLt)\rho(0)] | \alpha' \rangle, \quad (2.34)$$

where $\rho(0)$ is the initial nonequilibrium density matrix of the over-all system. From the definition of $G_{\alpha\alpha'}(t)$, Eq. (1.1), it follows that

$$\langle \alpha | \sigma(t) | \alpha' \rangle = \mathrm{Tr}[G_{\alpha\alpha'}(t)\rho(0)], \quad (2.35)$$

where $\mathrm{Tr}[\cdots]$ denotes a trace over lattice and spin states. Under usual circumstances the initial density $\rho(0)$ may be approximated by $\rho(0) = \rho_l \sigma(0)$ where $\sigma(0)$ is the initial nonequilibrium density matrix for the spin degrees of freedom. In this case, we have

$$\langle \alpha | \sigma(t) | \alpha' \rangle = \mathrm{Tr}_s[\langle G_{\alpha\alpha'}(t) \rangle \sigma(0)], \quad (2.36)$$

so that the equation of motion for the spin density matrix is the same as the equation of motion for $\langle G_{\alpha\alpha'}(t) \rangle$. Note that $\langle G_{\alpha\alpha'}(t) \rangle$ is an operator in spin space. Since $\langle K_{\alpha\alpha'}(t) \rangle = 0$ [see Eq. (2.16)], it follows immediately from Eqs. (2.33) and (2.36) that $\langle G_{\alpha\alpha}'(t) \rangle$ and $\langle \alpha | \sigma(t) | \alpha' \rangle$ satisfy the equation

$$(\partial/\partial t) \langle \alpha | \sigma(t) | \alpha' \rangle = -i\omega_{\alpha\alpha'} \langle \alpha | \sigma(t) | \alpha' \rangle + \lambda^2 \sum_{\beta,\beta}{}' R_{\alpha\alpha'\beta\beta'} \langle \beta | \sigma(t) | \beta' \rangle \quad (2.37)$$

which is the ordinary Redfield equation. From these considerations, in analogy to the theory of Brownian motion, the equation of motion for $G_{\alpha\alpha'}(t)$, Eq. (2.23), may be referred to as the Redfield–Langevin equation.

III. REDUCTION TO THE BLOCH–LANGEVIN EQUATION

The definition of the average macroscopic magnetization is

$$M_r(t) = \gamma\, \mathrm{Tr}_s[S_r \sigma(t)], \qquad r = x, y, z, \quad (3.1)$$

where S_r is the spin operator and γ the gyromagnetic ratio. In the following, we set $\gamma = 1$. If the spin density matrix obeys the Redfield equation, Eq. (2.37), the magnetization will obey the equation of motion

$$\dot{M}_r(t) = -[\mathcal{H}_0 \times \mathbf{M}(t)]_r + \lambda^2 \sum_{\alpha,\alpha',\beta,\beta'} \langle \alpha' | S_r | \alpha \rangle \times R_{\alpha\alpha'\beta\beta'} \langle \beta | \sigma(t) | \beta' \rangle, \quad (3.2)$$

where $\mathcal{H}_0$ is the static Zeeman field. The form of the usual Bloch equations is

$$\dot{M}_r(t) = -[\mathcal{H}_0 \times \mathbf{M}(t)]_r - (1/T_r)[M_r(t) - M_r^0], \qquad r = x, y, z \quad (3.3)$$

where M_r^0 is the equilibrium magnetization

$$M_r^0 = \sum_{\alpha,\alpha'} \langle \alpha' | S_r | \alpha \rangle \langle \alpha | \sigma^0 | \alpha' \rangle, \quad (3.4)$$

and $\langle \alpha | \sigma^0 | \alpha' \rangle$ is the equilibrium spin density matrix

$$\langle \alpha | \sigma^0 | \alpha' \rangle = \delta_{\alpha\alpha'} [\sum_\alpha \exp(-E_\alpha/kT)]^{-1} \exp(-E_\alpha/kT).$$

If the z axis is chosen so that $\mathcal{H}_0 = \mathcal{H}_0 \hat{\mathbf{k}}$, then $T_x = T_y = T_2$, $T_z = T_1$, and $M_x^0 = M_y^0 = 0$.

It is well known that the relaxation matrix is not always of a form that permits a reduction of Eq. (3.2) to Eq. (3.3). The situations where $R_{\alpha\alpha'\beta\beta'}$ has a form where the reduction is possible are discussed in great detail in Aleksandrov.[8] Comparison of Eq. (3.2) and Eq. (3.3) shows that a necessary condition for the equality of these two equations is

$$\sum_{\alpha,\alpha'} [\lambda^2 \langle \alpha' | S_r | \alpha \rangle R_{\alpha\alpha'\beta\beta'} + (1/T_r) \langle \alpha' | S_r | \alpha \rangle \delta_{\alpha\beta} \delta_{\alpha'\beta'} - (1/T_r) \langle \alpha' | S_r | \alpha \rangle \langle \alpha | \sigma^0 | \alpha' \rangle \delta_{\beta\beta'}] = 0. \quad (3.5)$$

Here we assume that the form of the spin–lattice interaction, the multiplicity of the spin, and the temperature are such that $R_{\alpha\alpha'\beta\beta'}$ satisfies Eq. (3.5) so that one realizes the simple form of the Bloch equations for the average magnetization. If the relaxation matrix does not satisfy Eq. (3.5), the resulting equation for the average magnetization will not be of the simple form of Eq. (3.3). An example of a case where $R_{\alpha\alpha'\beta\beta'}$ does not satisfy Eq. (3.5) is for a spin $I>1$, with quadrupole interaction and when conditions of extreme narrowing are not met.

To arrive at the Bloch–Langevin equation we consider Eq. (3.1) in the form

$$M_r(t)=\sum_{\alpha,\alpha',\nu,\nu'}\langle\nu\mid\sigma(0)\mid\nu'\rangle\langle\nu'\mid\langle G_{\alpha\alpha'}(t)\rangle\mid\nu\rangle \times\langle\alpha'\mid S_r\mid\alpha\rangle, \quad (3.6)$$

where we have used Eq. (2.36). We define the operator $\mathcal{S}_r(t)$

$$\mathcal{S}_r(t)=\sum_{\alpha,\alpha'}G_{\alpha\alpha'}(t)\langle\alpha'\mid S_r\mid\alpha\rangle \quad (3.7)$$

which permits us to rewrite Eq. (3.6) as

$$M_r(t)=\sum_{\nu,\nu'}\langle\nu\mid\sigma(0)\mid\nu'\rangle\langle\nu'\mid \mathrm{Tr}_l[\rho_l\mathcal{S}_r(t)]\mid\nu\rangle. \quad (3.8)$$

The operator $\mathcal{S}_r(t)$ is constructed so that its trace with the initial nonequilibrium density matrix, $\rho(0)=\rho_l\sigma(0)$, yields the average macroscopic magnetization. Indeed Eq. (3.8) is identical to

$$M_r(t)=\mathrm{Tr}[\rho(0)\mathcal{S}_r(t)]=\mathrm{Tr}_s[\sigma(0)\langle\mathcal{S}_r(t)\rangle]. \quad (3.9)$$

We may arrive at the Bloch equation for $M_r(t)$ by considering the equation of motion for $\mathcal{S}_r(t)$. From Eq. (3.7) and the equation of motion for $G_{\alpha\alpha'}(t)$, Eq. (2.33), we obtain

$$d\mathcal{S}_r(t)/dt=\sum_{\alpha,\alpha'}[-i\omega_{\alpha\alpha'}G_{\alpha\alpha'}(t)\langle\alpha'\mid S_r\mid\alpha\rangle +K_{\alpha\alpha'}(t)\langle\alpha'\mid S_r\mid\alpha\rangle+\lambda^2\sum_{\beta,\beta'}{}'R_{\alpha\alpha'\beta\beta'}G_{\beta\beta'}(t) \times\langle\alpha'\mid S_r\mid\alpha\rangle]. \quad (3.10)$$

This equation may be immediately simplified to

$$d\mathcal{S}_r(t)/dt=-[\mathcal{H}_0\times\mathbf{S}(t)]_r +\lambda^2\sum_{\alpha,\alpha',\beta\beta'}R_{\alpha\alpha'\beta\beta'}G_{\beta\beta'}(t)\langle\alpha'\mid S_r\mid\alpha\rangle+h_r(t), \quad (3.11)$$

where we have defined the random field operator

$$h_r(t)=\sum_{\alpha,\alpha'}K_{\alpha\alpha'}(t)\langle\alpha'\mid S_r\mid\alpha\rangle. \quad (3.12)$$

The term involving the relaxation tetradic in Eq. (3.11) may be evaluated by use of Eq. (3.5). The result is an equation of motion for $\mathcal{S}_r(t)$:

$$d\mathcal{S}_r(t)/dt=-[\mathcal{H}_0\times\mathbf{S}(t)]_r-(1/T_r)[\mathcal{S}_r(t)-\mathcal{S}_r^0]+h_r(t), \quad (3.13)$$

where $\mathcal{S}_r^0=M_r^0$. We refer to Eq. (3.13) as the Bloch–Langevin equation. This equation is an operator equation in both spin and lattice variables. If the average is performed over the lattice, we obtain an operator equation that has the form of the Bloch equation

$$\langle d\mathcal{S}_r(t)/dt\rangle=-[\mathcal{H}_0\times\langle\mathbf{S}(t)\rangle]_r-(1/T_r)[\langle\mathcal{S}_r(t)\rangle-\mathcal{S}_r^0], \quad (3.14)$$

where we have used the fact that

$$\langle h_r(t)\rangle=0 \quad (3.15)$$

which follows from Eqs. (3.12) and (2.16). Of course, Eq. (3.14) remains an operator equation in spin space and will clearly lead to the Bloch equations for the magnetization if use is made of Eq. (3.9). Finally, the spin matrix elements of the Bloch–Langevin equation may be taken

$$\langle\nu\mid d\mathcal{S}_r^0(t)/dt\mid\nu'\rangle=-[\mathcal{H}_0\times\langle\nu\mid\mathbf{S}(t)\mid\nu'\rangle]_r +\langle\nu\mid h_r(t)\mid\nu'\rangle-(1/T_r)[\langle\nu\mid\mathcal{S}_r(t)\mid\nu'\rangle-\mathcal{S}_r^0\delta_{\nu\nu'}]. \quad (3.16)$$

What is the significance of the Bloch–Langevin equation? If the spin is described by the Redfield equation on the slow time scale and if this Redfield equation is consistent with the Bloch equation, then it necessarily follows that a magnetization type operator $\mathcal{S}_r(t)$ satisfies the Bloch–Langevin equation. The operator $\mathcal{S}_r(t)$ is a useful description of the slow time scale and includes the effects of the fast lattice motion in a fluctuating term $h_r(t)$ whose average over the equilibrium lattice density matrix is zero. The Bloch–Langevin equation, Eqs. (3.13)–(3.16), is an operator equation. The microscopic analog of the Bloch equation[9] is obtained by averaging Eq. (3.16) over an initial nonequilibrium spin density matrix $\langle\nu'\mid\sigma(0)\mid\nu\rangle$

$$\dot{m}_r(t)=-[\mathcal{H}_0\times\mathbf{m}(t)]_r-(1/T_r)[m_r(t)-m_r^0] +b_r(t). \quad (3.17)$$

Here

$$m_r(t)=\mathrm{Tr}_s[\sigma(0)\mathcal{S}_r(t)], \quad (3.18)$$

$$m_r^0=M_r^0, \quad (3.19)$$

and $b_r(t)$ is a random magnetic field

$$b_r(t)=\mathrm{Tr}_s[\sigma(0)h_r(t)]. \quad (3.20)$$

In this form, the Bloch–Langevin equation is an equation for the microscopic magnetization, $m_r(t)$, which depends upon the lattice configuration. The observable macroscopic magnetization is related to $m_r(t)$ by

$$M_r(t)=\langle m_r(t)\rangle. \quad (3.21)$$

Since $\langle b_r(t)\rangle=0$, when Eq. (3.17) is averaged over the equilibrium lattice density matrix, one recovers the ordinary Bloch equation. The Bloch–Langevin equation in the form of Eq. (3.17) is analogous to the Langevin equation for a heavy particle in Brownian motion theory.

IV. CALCULATION OF THE CORRELATION FUNCTIONS FOR THE REDFIELD–LANGEVIN EQUATION

In this section we compute the time correlation functions of the random quantities appearing in the previous sections. We begin with the Redfield–Langevin equation in the operator form [$\lambda=1$],

$$\delta\dot{G}_{\alpha\alpha'}^*(t)=\sum_{\beta,\beta'}{}' R_{\alpha\alpha'\beta\beta'}\delta G_{\beta\beta'}^*(t)+K_{\alpha\alpha'}^*(t), \quad (4.1)$$

where

$$\delta G_{\alpha\alpha'}^*(t)=G_{\alpha\alpha'}^*(t)-\sigma_{\alpha\alpha'}{}^0, \quad (4.2)$$

and $\sigma_{\alpha\alpha'}{}^0=\sigma_{\alpha\alpha}{}^0\delta_{\alpha\alpha'}$ is the equilibrium spin density matrix. In obtaining Eq. (4.1) we have used Eq. (2.30) and the fact that

$$\sum_{\beta,\beta'}{}' R_{\alpha\alpha'\beta\beta'}\sigma_{\beta\beta'}{}^0=0. \quad (4.3)$$

It follows from Eqs. (2.16) and (2.22) that

$$\langle\delta G_{\alpha\alpha'}^*(t)\rangle=\sum_{\beta,\beta'}[\exp(tR)]_{\alpha\alpha'\beta\beta'}\delta G_{\beta\beta'}^*(0), \quad (4.4)$$

which leads to the time correlation function expression for $G^*(t)$

$$\langle\delta G_{\alpha\alpha'}^*(t)\delta G_{\gamma\gamma'}^*(0)\rangle=\sum_{\beta,\beta'}[\exp(tR)]_{\alpha\alpha'\beta\beta'}\delta G_{\beta\beta'}^*\delta G_{\gamma\gamma'}^*(0). \quad (4.5)$$

This correlation function is an average over the equilibrium lattice density matrix. The *complete* equilibrium average includes a subsequent average over the equilibrium spin density matrix. This complete average is defined by

$$\langle A\rangle_{\mathrm{Av}}=\mathrm{Tr}[\rho_0 A]=\mathrm{Tr}[\rho_l\sigma^0 A]=\mathrm{Tr}_s[\sigma^0\langle A\rangle]. \quad (4.6)$$

From Eq. (4.5) we find

$$\langle G_{\alpha\alpha'}^*(t)G_{\gamma\gamma'}^*(0)\rangle_{\mathrm{Av}}=[\exp(tR)]_{\alpha\alpha'\gamma'\gamma}\sigma_{\gamma\gamma}{}^0, \quad (4.7)$$

where we have made use of Eq. (4.3). Correlation functions of the type presented in Eq. (4.7) may be used to compute correlation functions of dynamical variables. For example,

$$\langle\mathbf{S}(t)\mathbf{S}(0)\rangle_{\mathrm{Av}}=\sum_{\alpha,\alpha',\gamma,\gamma'}[\langle G_{\alpha\alpha'}(t)G_{\gamma\gamma'}(0)\rangle_{\mathrm{Av}}\times\langle\alpha'\mid\mathbf{S}\mid\alpha\rangle\langle\gamma'\mid\mathbf{S}\mid\gamma\rangle]. \quad (4.8)$$

The correlation functions of the random "force" $K_{\alpha\alpha'}^*(t)$ may also be calculated. First we integrate Eq. (4.1) to obtain

$$\delta G_{\alpha\alpha'}^*(t)=\sum_{\beta,\beta'}[\exp(tR)]_{\alpha\alpha'\beta\beta'}\delta G_{\beta\beta'}^*(0)+\sum_{\beta,\beta'}\int_0^t d\tau[\exp((t-\tau)R)]_{\alpha\alpha'\beta\beta'}K_{\beta\beta'}^*(\tau). \quad (4.9)$$

Next, we square this expression and take the average over the equilibrium lattice density matrix,

$$\langle\delta G_{\alpha\alpha'}^*(t)\delta G_{\beta\beta'}^*(t)\rangle=T+\lim_{t\to\infty}\int_0^t d\tau_1\times\int_0^t d\tau_2\sum_{\gamma,\gamma',\nu,\nu'}[\exp((t-\tau_1)R)]_{\alpha\alpha'\gamma\gamma'}\times[\exp((t-\tau_2)R)]_{\beta\beta'\nu\nu'}\langle K_{\gamma\gamma'}^*(\tau_1)K_{\nu\nu'}^*(\tau_2)\rangle, \quad (4.10)$$

where

$$T=\lim_{t\to\infty}\langle\delta G_{\alpha\alpha'}^*(t)\rangle\langle\delta G_{\beta\beta'}^*(t)\rangle \quad (4.11)$$

and use has been made of Eq. (2.16). We shall *assume* that

$$\lim_{t\to\infty}\langle\delta G_{\alpha\alpha'}^*(t)\rangle=0, \quad (4.12)$$

so that T may be taken to be zero. If $G_{\beta\beta'}^*(0)$ were a well-behaved matrix, this property could be established from Eq. (4.4) since $\sigma_{\beta\beta}{}^0$, the sole eigenmatrix of R with zero eigenvalue, is subtracted from $G_{\beta\beta'}^*(0)$. Strictly speaking, it is not possible to deduce Eq. (4.5) without an examination of the subsequent spin averages with which $\langle\delta G_{\alpha\alpha'}(t)\rangle$ is eventually to be associated. We may however take $T=0$ provided that we assume that the fluctuation formula will be employed only to compute a restricted class of averages for which Eq. (4.12) can be explicitly justified.

Since $K_{\alpha\alpha'}^*(t)$ is linear in the lattice coordinates, as can be seen from the definition in Eq. (2.15), the random force correlation function has a time variation characteristic of the fast lattice motion. Accordingly, we assume this correlation function to have the form

$$\langle K_{\gamma\gamma'}^*(\tau_1)K_{\nu\nu'}^*(\tau_2)\rangle=B(\gamma,\gamma',\nu,\nu')\delta(\tau_1-\tau_2). \quad (4.13)$$

On the slow time scale where Eq. (4.9) is valid, the random force correlation function appears to be a delta function in time. When Eq. (4.13) is substituted into Eq. (4.10), one obtains

$$\langle\delta G_{\alpha\alpha'}^*(t)\delta G_{\beta\beta'}^*(t)\rangle=\lim_{t\to\infty}\int_0^t d\tau\times\sum_{\gamma,\gamma',\nu,\nu'}[\exp(R(t-\tau))]_{\alpha\alpha'\gamma\gamma'}[\exp(R(t-\tau))]_{\beta\beta'\nu\nu'}\times B(\gamma,\gamma',\nu,\nu'). \quad (4.14)$$

It is an easy, but somewhat lengthy, matter to verify the identity

$$-\sum_{\lambda,\lambda',\eta,\eta'}[R_{\alpha\alpha'\lambda\lambda'}I_{\beta\beta'\eta\eta'}+I_{\alpha\alpha'\lambda\lambda'}R_{\beta\beta'\eta\eta'}]\times\langle\delta G_{\lambda\lambda'}^*(t)\delta G_{\eta\eta'}^*(t)\rangle=\lim_{t\to\infty}\int_0^t d\tau\frac{\partial}{\partial\tau}\times\sum_{\gamma,\gamma',\nu,\nu'}[\exp(R(t-\tau))]_{\alpha\alpha'\gamma\gamma'}[\exp(R(t-\tau))]_{\beta\beta'\nu\nu'}\times B(\gamma,\gamma',\nu,\nu'), \quad (4.15)$$

where I is the unit tetradic

$$I_{\alpha\alpha'\beta\beta'}=\delta_{\alpha\beta}\delta_{\alpha'\beta'}. \quad (4.16)$$

The integration may be formally accomplished, and one finds that

$$B(\alpha,\alpha',\beta,\beta')=-\sum_{\lambda,\lambda',\eta,\eta'}[R_{\alpha\alpha'\lambda\lambda'}I_{\beta\beta'\eta\eta'}+I_{\alpha\alpha'\lambda\lambda'}R_{\beta\beta'\eta\eta'}]\times\langle\delta G_{\lambda\lambda'}{}^*(t)\delta G_{\eta\eta'}{}^*(t)\rangle. \quad (4.17)$$

Since B is proportional to R, to be consistent with our prior approximations, the equal time correlation function appearing in Eq. (4.17) need only be computed to lowest order in the spin–lattice coupling. Thus,

$$\delta G_{\lambda\lambda'}{}^*(t)=\exp(iHt)\exp(-iH_0t)\delta G_{\lambda\lambda'}(0)\times\exp(iH_0t)\exp(-iHt) \quad (4.18)$$

may be approximated by $\delta G_{\lambda\lambda'}(0)$ in the correlation function on the right-hand side of Eq. (4.17) since to lowest order H may be replaced by H_0. It follows that

$$B(\alpha,\alpha',\beta,\beta')=-\sum_{\lambda,\lambda',\eta,\eta'}[R_{\alpha\alpha'\lambda\lambda'}I_{\beta\beta'\eta\eta'}+I_{\alpha\alpha'\lambda\lambda'}R_{\beta\beta'\eta\eta'}]\delta G_{\lambda\lambda'}(0)\delta G_{\eta\eta'}(0). \quad (4.19)$$

The complete equilibrium average is easily found from Eqs. (4.13), (4.19), and (4.6):

$$\langle K_{\alpha\alpha'}{}^*(t)K_{\beta\beta'}{}^*(0)\rangle_{\text{Av}}=-\delta(t)[R_{\alpha\alpha'\beta'\beta}\sigma_{\beta\beta}{}^0+R_{\beta\beta'\alpha'\alpha}\sigma_{\alpha'\alpha'}{}^0]. \quad (4.20)$$

This result for the correlation function of $K^*(t)$ can be obtained by the alternative procedure of direct calculation from the definition of K^*, Eq. (2.22), if only lowest-order terms in the spin–lattice interaction are retained. From Eq. (2.22) and the condition that nonvanishing elements of R satisfy $\Delta=0$ [see Eq. (2.29)], it follows that

$$\langle K_{\alpha\alpha'}(t)K_{\beta\beta'}(0)\rangle_{\text{Av}}=-\delta(t)[R_{\alpha\alpha'\beta'\beta}\sigma_{\beta\beta}{}^0+R_{\beta\beta'\alpha'\alpha}\sigma_{\alpha'\alpha'}{}^0]. \quad (4.21)$$

The correlation functions of interest for the Redfield–Langevin equation are given in Eqs. (4.5), (4.7), (4.13), and (4.21).

V. CALCULATION OF THE CORRELATION FUNCTIONS FOR THE BLOCH–LANGEVIN EQUATION

Calculation of the correlation functions for the random terms appearing in the Bloch–Langevin equation may be obtained in an analogous manner. The Bloch–Langevin equation may be written as

$$\delta d\mathbb{S}_q(t)/dt=+i\omega_q\delta\mathbb{S}_q(t)-(1/T_q)\delta\mathbb{S}_q(t)+h_q(t) \quad (q=0,\pm1), \quad (5.1)$$

where the components of the vector $\delta\mathbf{S}$ are

$$\delta\mathbb{S}_0=\delta\mathbb{S}_z, \qquad \delta\mathbb{S}_{\pm1}=\delta\mathbb{S}_x\pm i\delta\mathbb{S}_y, \quad (5.2)$$

and the vector $\mathbf{h}$ is similarly defined. In Eq. (5.1)

$$\omega_q=-q\mathcal{H}_0 \quad\text{and}\quad T_{\pm1}=T_2,\ T_0=T_1. \quad (5.3)$$

It follows immediately that

$$\langle\delta\mathbb{S}_q(t)\delta\mathbb{S}_p(0)\rangle=\exp[-L_qt]\delta\mathbb{S}_q(0)\delta\mathbb{S}_p(0), \quad (5.4)$$

where $p=0, \pm1$, and $L_q=T_q{}^{-1}+i\omega_q$. The complete average of this correlation function is

$$\langle\delta\mathbb{S}_q(t)\delta\mathbb{S}_p(0)\rangle_{\text{Av}}=\exp[-L_qt]\langle\delta S_q\delta S_p\rangle_{\text{Av}}, \quad (5.5)$$

and it is an easy matter to show that

$$\langle\delta S_q\delta S_p\rangle_{\text{Av}}=\delta_{p-q}C(|q|), \quad (5.6)$$

where $C(|q|)$ denotes the simple spin average. One may easily show from the definition of $\delta\mathbb{S}_q(t)$, Eqs. (5.2), and (3.7), that

$$\langle\delta\mathbb{S}_q(t)\delta\mathbb{S}_p(0)\rangle_{\text{Av}}=\langle\delta S_q(t)\delta S_p(0)\rangle_{\text{Av}}. \quad (5.7)$$

Thus, Eq. (5.5) is a statement of Onsager's assumption for the decay of equilibrium fluctuations on the slow spin relaxation time scale.

Finally, we shall compute the correlation function of the random field $h_q(t)$. From the definition of $h_q(t)$, Eq. (3.12),

$$\langle h_q(t)h_p(0)\rangle_{\text{Av}}=\sum_{\alpha,\alpha',\beta,\beta'}\langle K_{\alpha\alpha'}(t)K_{\beta\beta'}(0)\rangle_{\text{Av}}\times\langle\alpha'|S_q|\alpha'\rangle\langle B'|S_p|B\rangle. \quad (5.8)$$

It follows by direct calculation from Eqs. (4.21) and (3.5) that

$$\langle h_q(t)h_p(0)\rangle_{\text{Av}}=\delta(t)[(1/T_q)\langle\delta S_q\delta S_p\rangle_{\text{Av}}+(1/T_p)\langle\delta S_p\delta S_q\rangle_{\text{Av}}], \quad (5.9)$$

and using Eqs. (5.6) and (5.3)

$$\langle h_q(t)h_{-q}(0)\rangle_{\text{Av}}=2\delta(t)C(|q|)T_q{}^{-1}. \quad (5.10)$$

Thus the correlation function of the random force is simply related to the macroscopic relaxation times

$$T_q{}^{-1}=[1/C(|q|)]\int_0^\infty dt\langle h_q(t)h_{-q}(0)\rangle_{\text{Av}}, \quad (5.11)$$

which is a manifestation of the fluctuation–dissipation theorem.

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