A Fokker-Planck Equation for Spin Relaxation*

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A method is developed to describe the quantum mechanical motion of a few simple spin systems, with random time-dependent perturbations, in an exact manner, i.e., without reference to perturbation theory. It leads to a Fokker-Planck type diffusion equation. When applied to a spin influenced by a fluctuating local field (Abragam's model), this gives rise to a (microscopic) Bloch-type equation for the spin operators. An application to a system of two identical spins ($S=1/2$) with modulated dipole interaction produces a very complicated diffusion equation in eight variables, which simplifies, however, in a case of restricted rotation. A model Hamiltonian for quadrupole relaxation for $S=1$ gives a relatively simple result, which reveals an interesting difference between the relaxation in finite and zero external fields.

1. INTRODUCTION

THE theory of spin relaxation is customarily developed by means of quantum mechanical perturbation methods. The general formalism based on this method[1] is, in principle, capable of yielding all observables of the system. The methods of statistical field theory can be adapted to cope with this problem. Most of the applications have, however, dealt with weakly interacting systems for which a perturbation expansion up to second order suffices to calculate the relaxation times. These results can also be obtained with more elementary methods. A notable exception is the work by Caspers[2] on spin-spin relaxation in solids, which clearly illustrates the complications that one is going to encounter. A further case for which at least a partial summation of the perturbation series would be needed is a system of weakly interacting pairs of inequivalent spins for which the spin-spin relaxation between pairs as well as the dipole relaxation of each pair is being considered. A perturbation calculation for this system[3] gives the transition probability in the form of a power series in the ratio of the two interactions, and not in the closed form that one obtains with a semiclassical treatment.[4] Finally, it is difficult to justify the use of a perturbation expansion in weak external fields, as Kubo and Tomita's theory presupposes the existence of a resolved energy spectrum.

With these problems in mind we have tried to find a new approach in which the theory of stochastic processes plays a more central role. Our idea is to treat the interactions in terms of a time-dependent self-consistent field. Allowing this field to be a random variable with unspecified time correlation functions, we would first obtain a solution of the quantum mechanical equations of motion of a single spin (or small subsystem) subjected to this field. Then, with all the subsystems moving in an identical manner, but in first approximation incoherently, we would calculate the effective field as the sum of all interactions on a given subsystem. The requirement that this sum of random variables has the same time characteristics as the input field provides the self-consistency condition.

A similar method was recently introduced by Anderson.[5] The main difference between his theory and ours is that he uses a semiclassical equation of motion. This limits the applicability to the case of inhomogeneous broadening. We found that it is sometimes possible to find a rigorous solution of Schrödinger's equation of a small system exposed to a randomly varying perturbation.

The present paper deals with this part of our program. We will study a few models for which its solution is relatively simple. The main problem is to find a set of independent and real parameters such that, when suitably chosen as a function of time, they can fully account for the quantum mechanical motion of the system. These parameters can be obtained either by studying the transformations between the observables of the system, induced by the Hamiltonian, or by a general parametrization of the unitary transformation that links the Schrödinger to the Heisenberg representation. We will use both methods in the following.

For simplicity we impose the restriction that the perturbation has no "long" correlation times, although this may not hold for the actual self-consistent field. This makes the process Markoffian and leads to an equation of Fokker-Planck type.

We will first treat the case of a spin with arbitrary spin quantum number, perturbed by a randomly fluctuating local magnetic field, in the presence of a constant field (Abragam's model). We will then discuss a system of two identical spins with $S=\frac{1}{2}$, with randomly modulated dipole interaction in a constant external field (Bloembergen's model for H_2O).[6] The complicated form that the Fokker-Planck equation takes for this case makes its practical applicability problematic. We then discuss the case of a two-spin system with restricted

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rotation, and finally we apply our theory to a mathematical model for quadrupole relaxation. An application of our solution of Abragam's model to the system of spin-pairs mentioned above is presented in the paper immediately following this one.

2. DERIVATION OF A FOKKER-PLANCK EQUATION FOR ABRAGAM'S MODEL

The Hamiltonian for a spin S in a fluctuating field $\mathbf{V}(t)$ and a constant field $\mathbf{H}(0,0,H)$ is

$$\mathcal{H}=\gamma HS_z+\gamma\mathbf{S}\cdot\mathbf{V}(t). \tag{1}$$

The equations of motion for the operators $\mathbf{S}(t)$ in the Heisenberg representation are

$$-i\hbar d\mathbf{S}/dt=[\mathcal{H}(t),\mathbf{S}(t)]_-. \tag{2}$$

This gives

$$d\mathbf{S}/dt=\gamma\mathbf{V}(t)\times\mathbf{S}(t)+\gamma\mathbf{H}\times\mathbf{S}(t). \tag{3}$$

These equations can be solved in terms of two time-dependent rotations $\mathbf{A}^0(t)$ and $\mathbf{A}(t)$ by

$$\mathbf{S}(t)=\mathbf{A}^0(t)\mathbf{A}(t)\mathbf{S}. \tag{4}$$

$\mathbf{A}^0(t)$ is the rotation matrix corresponding to the precession in the external field. Therefore, the operators

$$\mathbf{S}^0(t)=\mathbf{A}^0(t)\mathbf{S} \tag{5}$$

satisfy the equation

$$d\mathbf{S}^0/dt=\gamma\mathbf{H}\times\mathbf{S}^0(t). \tag{6}$$

We now perform the unitary transformation

$$S_\pm=(S_x\pm iS_y)/\sqrt{2},\quad S_0=S_z, \tag{7}$$

which diagonalizes $\mathbf{A}^0(t)$ for our choice of $\mathbf{H}$. This gives, writing $\omega=\gamma H$,

$$S_k{}^0(t)=S_k\exp(ik\omega t),\quad k=+,-,0. \tag{8}$$

$\mathbf{A}(t)$ is a general rotation. In terms of Euler angles, and using the operators (7), one has

$$\begin{aligned}
&A_{\pm\pm}=\tfrac{1}{2}(1+\cos\theta)\exp[\pm i(\psi+\varphi)],\\
&A_{\pm\mp}=\tfrac{1}{2}(1-\cos\theta)\exp[\pm i(\psi-\varphi)],\\
&A_{\pm 0}=\mp(i/\sqrt{2})\sin\theta\exp(\pm i\psi),\\
&A_{0\pm}=\mp(i/\sqrt{2})\sin\theta\exp(\pm i\varphi),\\
&A_{00}=\cos\theta.
\end{aligned} \tag{9}$$

Inserting Eq. (9) into Eq. (3), one finds

$$\begin{aligned}
&\cos\psi\,\dot\theta+\sin\psi\sin\theta\,\dot\varphi=\gamma(V_x\cos\omega t+V_y\sin\omega t),\\
&\sin\psi\,\dot\theta-\cos\psi\sin\theta\,\dot\varphi=\gamma(-V_x\sin\omega t+V_y\cos\omega t),\\
&\dot\psi+\cos\theta\,\dot\varphi=\gamma V_z.
\end{aligned} \tag{10}$$

We now assume that the correlation times of $\mathbf{V}(t)$ are short compared with the relaxation times, i.e., that a time Δt exists such that the changes $\Delta\theta$, $\Delta\phi$, and $\Delta\psi$ in the time Δt are, in the average, small, but that $\mathbf{V}(t+\Delta t)$ is not correlated with $\mathbf{V}(t)$. Integrating Eq. (10) between t and $t+\Delta t$, one obtains

$$\begin{aligned}
&L_1\equiv\cos\bar\psi\,\Delta\theta+\sin\bar\psi\sin\bar\theta\,\Delta\varphi=\gamma\bar V_1{}^\Delta(t)\Delta t,\\
&L_2\equiv\sin\bar\psi\,\Delta\theta-\cos\bar\psi\sin\bar\theta\,\Delta\varphi=\gamma\bar V_2{}^\Delta(t)\Delta t,\\
&L_0\equiv\Delta\psi+\cos\bar\theta\,\Delta\varphi\qquad\qquad=\gamma\bar V_0{}^\Delta(t)\Delta t,
\end{aligned} \tag{11}$$

where, e.g.,

$$\bar V_1{}^\Delta(t)\Delta t=\int_t^{t+\Delta t}[V_x(t')\cos\omega t'+V_y(t')\sin\omega t']dt', \tag{12}$$

and

$$\bar\psi=\psi(t)+\tfrac{1}{2}\Delta\psi. \tag{13}$$

The Eqs. (11) define an elementary step in a Markoffian process, because the right-hand members have, by assumption, zero correlations in subsequent intervals Δt. We will assume in addition that the components $\bar V^\Delta$ in three mutually perpendicular directions are statistically independent. The probability $W(\bar\theta,\bar\phi,\bar\psi,\Delta\theta,\Delta\phi,\Delta\psi)\Delta t$ that, in the time Δt, θ changes to $\theta+\Delta\theta$ etc., can then be written as

$$W\Delta t=f_1{}^\Delta(L_1)f_2{}^\Delta(L_2)f_0{}^\Delta(L_0), \tag{14}$$

where $f_i{}^\Delta$ is the normalized probability distribution of $\gamma\Delta t\bar V_i{}^\Delta(t)$. The normalization of W is given by

$$\Delta t\int W\sin\bar\theta d\Delta\theta d\Delta\varphi d\Delta\psi=1, \tag{15}$$

because the Jacobian between L_i and $\Delta\theta$, $\Delta\phi$, $\Delta\psi$ (with constant values of $\bar\theta$, $\bar\phi$, $\bar\psi$) is equal to $\sin\bar\theta$. $\bar\theta$, $\bar\phi$ and $\bar\psi$ are constants in the integration (15).

We can now follow a standard procedure,[7] with only a slight generalization, to obtain an equation for the probability $P(\theta,\phi,\psi,\theta_0,\phi_0,\psi_0,t)$ that, at time t, the values θ,ϕ,ψ are realized when, at time $t=0$, they were θ_0,ϕ_0,ψ_0. Let $x_\alpha=(\theta,\phi,\psi)$, $y_\alpha=(\Delta\theta,\Delta\phi,\Delta\psi)$, $\rho(x_\alpha)=\sin x_1=\sin\theta$. With the above expression for the probability $W(x+\frac{1}{2}y, y)$ the master equation for $P(x,x_0,t)\equiv P(x)$ takes the form

$$\begin{aligned}
\partial P(x)/\partial t=&\int P(x-y)W(x-\tfrac{1}{2}y,y)\rho(x-y)d^3y\\
&-P(x)\int W(x-\tfrac{1}{2}y,-y)\rho(x-y)d^3y.
\end{aligned} \tag{16}$$

The normalization is

$$\int P(x,x_0,t)\rho(x)d^3x=1, \tag{17}$$

which can be satisfied for all times by virtue of Eq. (16). At $t=0$, one has

$$\begin{aligned}
P(x,x_0,0)&=\rho^{-1}(x_0)\delta^3(x-x_0)\\
&=\delta(\cos\theta-\cos\theta_0)\delta(\varphi-\varphi_0)\delta(\psi-\psi_0).
\end{aligned} \tag{18}$$

[7] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943); N. G. van Kampen, Ned. Tijdschr. Natuurk. **26**, 225 (1960).

Using the fact that $W(x,y)$ is a smooth function of its first argument and expanding correspondingly, one obtains, to second powers of y_α,

$$\frac{\partial P}{\partial t}=-\sum_\alpha\left[\frac{\partial}{\partial x_\alpha}(P\rho\mu_\alpha)+P\mu_\alpha\frac{\partial\rho}{\partial x_\alpha}\right]+\tfrac{1}{2}\sum_{\alpha,\beta}\left[\rho\mu_{\alpha\beta}\frac{\partial^2 P}{\partial x_\alpha\partial x_\beta}+\frac{\partial P}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}(\rho\mu_{\alpha\beta})+\mu_{\alpha\beta}\frac{\partial P}{\partial x_\alpha}\frac{\partial\rho}{\partial x_\beta}\right], \quad (19)$$

where

$$\mu_\alpha=\int y_\alpha W(x,y)d^3y,$$
$$\mu_{\alpha\beta}=\int y_\alpha y_\beta W(x,y)d^3y. \quad (20)$$

With use of Eq. (14) and with the definition of L_i given in Eq. (11), the quantities μ_α and $\mu_{\alpha\beta}$ can be expressed in terms of the first and second moments of f_i^Δ, i.e., in terms of $\int vf_i^\Delta(v)dv$ and $\int v^2f_i^\Delta(v)dv$. As an important simplification we can take the first moments to be zero, because the constant part of the total field, i.e., H, has been eliminated. Furthermore, the second moments of f_1^Δ and f_2^Δ are equal, because these two quantities refer to two perpendicular components rotating in the plane $\perp\mathbf{H}$.

Defining

$$1/\tau_1=(\Delta t)^{-1}\int v^2f_1^\Delta(v)dv,$$
$$1/\tau_0=(\Delta t)^{-1}\int v^2f_0^\Delta(v)dv, \quad (21)$$

one finds

$$\begin{aligned}&\mu_\alpha=0,\\&\rho\mu_{1\alpha}=\delta_{1\alpha}\tau_1^{-1},\\&\rho\mu_{22}=(\tau_1\sin^2\theta)^{-1},\\&\rho\mu_{23}=-(\tau_1\sin^2\theta)^{-1}\cos\theta,\\&\rho\mu_{33}=(\tau_1\sin^2\theta)^{-1}\cos^2\theta+\tau_0^{-1}.\end{aligned} \quad (22)$$

Inserting this in Eq. (19), we finally obtain

$$\partial P/\partial t=\mathfrak{F}(P), \quad (23)$$

$$\mathfrak{F}=\frac{1}{2\tau_1}\left[\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\theta^2}+\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}-\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\psi}\right)^2\right]+\frac{1}{2\tau_0}\frac{\partial^2}{\partial\psi^2}. \quad (24)$$

An alternative derivation of Eq. (10), and therefore of Eqs. (23) and (24) is obtained by considering the unitary transformation $U(t)$ that connects the Heisenberg with the Schrödinger representation. Writing

$$\Psi(0)=U(t)\Psi(t), \quad (25)$$

we have

$$-i\hbar U^{-1}(t)dU/dt=\mathfrak{IC}(t). \quad (26)$$

Expressing the general unitary transformation of the system in terms of a set of real and independent parameters, $x_1\cdots x_s$: $U(x_1\cdots x_s)$, the Eq. (26) immediately gives rise to a set of linear first order differential equations:

$$L_\alpha\equiv\sum_i F_{\alpha i}(x_j)\dot{x}_i=h_\alpha(t)/\hbar, \quad (27)$$

where $h_\alpha(t)$ is any matrix element of $\mathfrak{IC}(t)$. The existence of linear relations (with constant coefficients) between the elements of $\mathfrak{IC}$ can be used to ensure that the $h_\alpha(t)$ in Eq. (27) are either zero or are one of a set of linearly independent matrix elements of $\mathfrak{IC}$.

The Eqs. (27) can, in principle at least, be used to derive a Fokker-Planck equation, in analogy with the procedure followed above. One merely introduces a factor $\delta(L_\alpha)$ in the expression for $W(x+\frac{1}{2}y,y)$ whenever $h_\alpha(t)\equiv0$. For the case of a spin $S=\frac{1}{2}$ the unitary transformation contains only 3 parameters, and can be written in the well-known form

$$U=\begin{pmatrix}\alpha & \beta\\ -\beta^* & \alpha^*\end{pmatrix}, \quad (28)$$

$$\alpha=\cos\tfrac{1}{2}\theta\exp[\tfrac{1}{2}i(\varphi+\psi+\omega t)],$$
$$\beta=i\sin\tfrac{1}{2}\theta\exp[\tfrac{1}{2}i(\varphi-\psi-\omega t)]. \quad (29)$$

As is easily seen, the Eqs. (27) become identical with the Eqs. (10); the rotation matrix $\mathbf{A}(t)$ of Eq. (9) is obtained from

$$\mathbf{S}(t)=U(t)\mathbf{S}U^{-1}(t). \quad (30)$$

For higher values of the spin quantum number the parametrization of the general unitary transformation is difficult to carry out. As the perturbation $\mathbf{V}(t)$ can only produce a rotation, all but three of the parameters can in this case be eliminated from Eq. (27). This means that those of Eqs. (27) for which $h_\alpha(t)\equiv0$, are integrable, i.e., impose holonomic conditions for this case. For other forms of $\mathfrak{IC}$ these conditions may be anholonomic, as we will show in Sec. 4.

3. PROPERTIES OF THE FOKKER-PLANCK EQUATION

The Eqs. (23) and (24) can formally be obtained from the Schrödinger equation of a symmetric top by replacing t by it and by replacing the moments of inertia by τ_1 and τ_0. The functions $f_{nlm}(\theta)\exp[i(m\varphi+n\psi)]$ are, therefore, a complete set of eigenfunctions of the $\mathfrak{F}$ operator, with eigenvalues $-\lambda=-\frac{1}{2}\tau_0^{-1}n^2-\frac{1}{2}\tau_1^{-1}[l(l+1)-n^2]$. In particular, the elements of the rotation matrix, as given by Eq. (9), are eigenfunctions of $\mathfrak{F}$:

$$\begin{aligned}&\mathfrak{F}A_{jk}=-\lambda_jA_{jk},\\&\lambda_0\equiv1/T_1=1/\tau_1,\\&\lambda_\pm\equiv1/T_2=\tfrac{1}{2}(1/\tau_0+1/\tau_1).\end{aligned} \quad (31)$$

From this, it follows that the autocorrelation functions

of A_{jk} have exponential time dependence, with characteristic times T_1 or T_2. One has, indeed, for any component

$$\langle A^*(t)A(t+\tau)\rangle_t=\int A^*(x)A(x')P(x',x,\tau)\rho(x')d^3x'. \quad (32)$$

Therefore,

$$\begin{aligned}\frac{\partial}{\partial\tau}\langle A^*(t)A(t+\tau)\rangle_t&=\int A^*(x)A(x')\mathfrak{F}[P(x',x,\tau)]\rho(x')d^3x'\\&=\int A^*(x)\mathfrak{F}[A(x')]P(x',x,\tau)\rho(x')d^3x'\\&=-\lambda\langle A^*(t)A(t+\tau)\rangle_t. \quad (33)\end{aligned}$$

For the time dependence of $\mathbf{S}(t)$ we have, from Eq. (4),

$$\begin{aligned}\mathbf{S}(t+\tau)&=\mathbf{A}^0(t+\tau)\mathbf{A}(t+\tau)\mathbf{S}\\&=\mathbf{A}^0(t+\tau)\mathbf{A}(t+\tau)\mathbf{A}^{-1}(t)\mathbf{A}^{0-1}(t)\mathbf{S}(t). \quad (34)\end{aligned}$$

Using the operators in the representation (7) and taking the average over the ensemble of all spins with the same $\mathbf{S}(t)$, one obtains, for $\tau\ll(T_1,T_2)$,

$$\begin{aligned}\langle dS_\pm/dt\rangle_{\rm av}&=-S_\pm/T_2\pm i\omega S_\pm,\\\langle dS_z/dt\rangle_{\rm av}&=-S_z/T_1.\end{aligned} \quad (35)$$

The analogy of these operator equations with the Bloch equations permits the identification of T_1 and T_2 with the relaxation times of the spin system.

Explicit expressions for T_1 and T_2 in terms of $\mathbf{V}(t)$ can be obtained from Eq. (21). Defining

$$\begin{aligned}V_1^2&=\langle V_x^2\rangle_t=\langle V_y^2\rangle_t,\\V_0^2&=\langle V_z^2\rangle_t,\end{aligned} \quad (36)$$

and assuming, e.g.,

$$\begin{aligned}\langle V_x(t)V_x(t+\tau)\rangle_t&=V_1^2\exp(-|\tau|/\sigma_1),\\\langle V_z(t)V_z(t+\tau)\rangle_t&=V_0^2\exp(-|\tau|/\sigma_0),\end{aligned} \quad (37)$$

one finds

$$\begin{aligned}1/\tau_0&=\sigma_0\gamma^2V_0^2,\\1/\tau_1&=\sigma_1\gamma^2V_1^2/(1+\omega^2\sigma_1^2).\end{aligned} \quad (38)$$

This leads to the familiar expressions for the relaxation times.

4. THE CASE OF TWO INTERACTING IDENTICAL SPINS

A problem which is still relatively simple is that of two identical spins with $S=\frac{1}{2}$, with randomly modulated dipole interaction. The Hamiltonian is

$$\mathfrak{IC}=\gamma H(S_{1_z}+S_{2_z})+\gamma^2r^{-5}[r^2\mathbf{S}_1\cdot\mathbf{S}_2-3(\mathbf{S}_1\cdot\mathbf{r})(\mathbf{S}_2\cdot\mathbf{r})]. \quad (39)$$

Due to the symmetry, the triplet and singlet state do not mix, and we need only to consider the triplet state. We will use the second method discussed above, and will write $\mathfrak{IC}$ as a matrix with respect to the states $\Psi_1=(\Psi_{+-}+\Psi_{-+})/\sqrt{2}$, $\Psi_2=-\Psi_{++}$, $\Psi_3=\Psi_{--}$, in an obvious notation. This gives, in the interaction representation,

$$\mathfrak{IC}\equiv(h_{ik})=\tfrac{3}{4}\gamma^2\hbar^2\begin{pmatrix}2\Phi_0&\sqrt{2}\Phi_1^*&\sqrt{2}\Phi_1\\\sqrt{2}\Phi_1&-\Phi_0&\Phi_2\\\sqrt{2}\Phi_1^*&\Phi_2^*&-\Phi_0\end{pmatrix}, \quad (40)$$

with

$$\begin{aligned}\Phi_0&=r^{-3}(\cos^2\vartheta-\tfrac{1}{3}),\\\Phi_1&=r^{-3}\cos\vartheta\sin\vartheta\exp[-i(\zeta+\omega t)],\\\Phi_2&=r^{-3}\sin^2\vartheta\exp[-2i(\zeta+\omega t)];\end{aligned} \quad (41)$$

ϑ and ζ are the polar angles of $\mathbf{r}$.

There are 4 linear relations between the h_{ik}, viz.,

$$\begin{aligned}\hbar L_0&\equiv\textstyle\sum h_{ii}=0,\\\hbar(L_6+iL_7)&\equiv h_{12}-h_{13}{}^*=0,\\\hbar L_8&\equiv h_{22}-h_{33}=0.\end{aligned} \quad (42)$$

The general unitary matrix U of three by three has nine real parameters. These can be introduced by writing

$$U=R\mathcal{T}_1U_0\mathcal{T}_2R^{-1}, \quad (43)$$

$$\begin{aligned}\mathcal{T}_{1_{jk}}&=\delta_{jk}\exp i\xi_j,\\\mathcal{T}_{2_{jk}}&=\delta_{jk}\exp i\eta_j,\quad \eta_1=0,\end{aligned} \quad (44)$$

and

$$U_0=\begin{pmatrix}\cos\theta&\sin\theta\sin\varphi&\sin\theta\cos\varphi\\\sin\theta\sin\psi&-\cos\theta\sin\psi\sin\varphi+\cos\psi\cos\varphi\exp i\chi&-\cos\theta\sin\psi\cos\varphi-\cos\psi\sin\varphi\exp i\chi\\\sin\theta\cos\psi&-\cos\theta\cos\psi\sin\varphi-\sin\psi\cos\varphi\exp i\chi&-\cos\theta\cos\psi\cos\varphi+\sin\psi\sin\varphi\exp i\chi\end{pmatrix}. \quad (45)$$

For $\chi=0$, U_0 becomes a real rotation matrix in Euler angles. R is the transformation

$$R=\begin{pmatrix}1&0&0\\0&1/\sqrt{2}&i/\sqrt{2}\\0&-1/\sqrt{2}&i/\sqrt{2}\end{pmatrix}.$$

Its introduction simplifies the equations of motion. Inserting Eqs. (43)–(45) in Eq. (26), we find

$$\begin{aligned}L_1&=h_{11}/\hbar,\\L_2+iL_5&=h_{23}/\hbar,\\L_3+iL_4&=\tfrac{1}{2}(h_{12}+h_{13}{}^*)/\hbar\sqrt{2}.\end{aligned} \quad (46)$$

The quantities $L_1\cdots L_8$ in Eq. (46) and Eq. (42) are given by

$$\begin{aligned}L_1&\equiv-(\dot\xi_2+\dot\xi_3+\dot\eta_2+\dot\eta_3+\dot\chi)+s^2X_1,\\L_2&\equiv\tfrac{1}{2}(\dot\eta_3-\dot\eta_2)+[\tfrac{1}{2}(c^2+1)X_1-X_2]\cos2\varphi\\&\qquad-cZ_1''\sin2\varphi,\\L_6-iL_3&\equiv(\dot\theta-iscX_1)\cos\varphi\exp i\eta_3+sZ_3\sin\varphi,\\L_7-iL_4&\equiv(\dot\theta-iscX_1)\sin\varphi\exp i\eta_2-sZ_2\cos\varphi,\\L_8-iL_5&\equiv\{\dot\varphi+i[\tfrac{1}{2}(c^2+1)X_1-X_2]\sin2\varphi\\&\qquad+cZ_1'+icZ_1''\cos2\varphi\}\exp i(\eta_3-\eta_2),\end{aligned} \quad (47)$$

where

$$\begin{aligned} &X_1\equiv\tfrac{3}{2}(\dot\xi_2+\dot\xi_3)+\dot\eta_2+\dot\eta_3+\dot\chi+\tfrac{1}{2}(\dot\xi_3-\dot\xi_2)\cos2\psi,\\ &X_2\equiv\tfrac{3}{2}(\dot\xi_2+\dot\xi_3+\dot\chi)+\dot\eta_2+\dot\eta_3,\\ &Z_j\equiv Z_j'+iZ_j''\equiv[\dot\psi+\tfrac{1}{2}i(\dot\xi_3-\dot\xi_2)\sin2\psi]\exp i(\chi+\eta_j),\\ &c\equiv\cos\theta,\quad s\equiv\sin\theta. \end{aligned} \tag{48}$$

The equation

$$L_0\equiv\sum\dot\xi_j+\sum\dot\eta_j+\dot\chi=0 \tag{49}$$

has been used to eliminate ξ_1.

The equation $L_6=L_7=L_8=0$ is apparently anholonomic, so that the Eqs. (47) and (48) can not be further simplified. The Fokker-Planck equation will thus be a partial differential equation in eight variables. It can be obtained as follows: We assume that the matrix elements $h_{jk}(t)$ are characterized by a correlation time τ_c, short compared with the relaxation times of the spins. We then perform a short-time integration, as in Eq. (11). The integrated matrix elements are then statistically independent, and have zero autocorrelation in subsequent time intervals. The probability of a step $x_\alpha\rightarrow x_\alpha+y_\alpha$ in the Markoffian process is then given by

$$W(x+\tfrac{1}{2}y,y)\Delta t=\prod_1^5 f_j^\Delta(L_j)\prod_6^8\delta(L_j), \tag{50}$$

where, in L_i of Eq. (47), we have replaced $\dot x_\alpha$ by y_α, and x_α by $x_\alpha+\frac{1}{2}y_\alpha$. f_j^Δ is the distribution function of the matrix elements in Eq. (46) after the short-time integration. The second moments of f_j^Δ can be found from Eqs. (40) and (41) and from the assumption that the motion is characterized by a correlation time τ_c. One has

$$(\Delta t)^{-1}\int v^2 f_j^\Delta(v)dv=1/\tau_j, \tag{51}$$

where

$$\begin{aligned} &1/\tau_1=\tfrac{2}{3}Q\tau_c,\\ &1/\tau_2=1/\tau_5=\tfrac{1}{2}Q\tau_c/(1+4\omega^2\tau_c^2),\\ &1/\tau_3=1/\tau_4=\tfrac{1}{8}Q\tau_c/(1+\omega^2\tau_c^2),\\ &Q=\tfrac{3}{10}\gamma^4\hbar^2\langle r^{-6}\rangle. \end{aligned} \tag{52}$$

The second moments $\mu_{\alpha\beta}$ are then obtained by solving Eq. (47) for $\dot x_\alpha$, which is readily done and which gives, after using Eq. (42), expressions of the form

$$\dot x_\alpha=\sum_{j=1}^5 G_{\alpha j}(x_\beta)L_j. \tag{53}$$

One then has

$$\rho\mu_{\alpha\beta}=\sum_{j=1}^5 G_{\alpha j}(x)G_{\beta j}(x)/\tau_j, \tag{54}$$

where $\rho(x)$ is the Jacobian of the transformation. As the resulting Fokker-Planck equation is rather long, but can be written down without difficulty, we will not give it here explicitly. We were somewhat surprised to find the motion of this system to be so complicated.

It seems that even the case of restricted rotation, considered by Bloembergen,[8] which corresponds to taking $L_1=$ const, does not produce a great simplification. Only when the rotation is restricted in the sense that the angle ϑ is equal to $\pi/2$, does one obtain a simple result. In this case all h_{ij} except h_{23} and h_{32} are zero or constants (time independent), and can therefore be included in the zero-order Hamiltonian which is eliminated in the interaction representation. Using a new basis defined by

$$\Psi_1'=\Psi_1,\ \Psi_2'=(-\Psi_2+i\Psi_3)/\sqrt{2},\text{ and }\Psi_3'=(\Psi_2+i\Psi_3)/\sqrt{2},$$

we find in the interaction representation

$$\begin{aligned} &h_{22}'=-h_{33}'=-\tfrac{3}{4}\gamma^2\hbar^2r^{-3}\sin2(\zeta+\omega t),\\ &h_{23}'=-\tfrac{3}{4}i\gamma^2\hbar^2r^{-3}\cos2(\zeta+\omega t). \end{aligned} \tag{55}$$

All other elements are zero. The number of parameters in U in this case is reduced to only three, namely we can take $\theta=\varphi=0$, $\xi_1=0$, $\xi_2+\xi_3=\pi$, and $\chi+\eta_2+\eta_3=0$. Introducing new variables, ξ, η, and ψ' defined by $\xi=\xi_3-\xi_2$, $\eta=2\eta_3$, $\psi'=2\psi$, Eq. (47) takes the form

$$\begin{aligned} &2L_2\equiv\dot\eta+\dot\xi\cos\psi',\\ &2L_5\equiv\dot\psi'\sin\eta-\dot\xi\sin\psi'\cos\eta,\\ &2L_8\equiv\dot\psi'\cos\eta+\dot\xi\sin\psi'\sin\eta, \end{aligned} \tag{56}$$

while all other L_j are zero. Since Eq. (56) is quite similar to Eq. (10), and since $L_2=\mathrm{Re}h_{23}'=0$, $L_5=\mathrm{Im}h_{23}'$ and $L_8=\frac{1}{2}(h_{22}'-h_{33}')$, it can be verified easily that the Fokker-Planck equation for this case has the same form as that of Eqs. (23) and (24), with θ, ϕ, and ψ of Eq. (24) being replaced by ψ', ξ, and η, respectively. The values of τ_0 and τ_1 in this case are

$$1/\tau_0=0,\quad 1/\tau_1=(15/64)Q\tau_c/(1+4\omega^2\tau_c^2). \tag{57}$$

Here, Q is defined in Eq. (52).

In conclusion of this section, we remark that the results of Sec. 2 for $S=1$ can also be obtained from Eq. (47), namely, by equating the L_j to the matrix elements of $\mathcal{H}=\gamma\mathbf{S}\cdot\mathbf{V}(t)$. One obtains $L_0=L_1=\cdots=L_5=0$, $L_6=\gamma V_x$, $L_7=\gamma V_y$, $L_8=\gamma V_z$. These equations have a solution with $\xi_i=\eta_i=\chi=0$ which reduces to the one found previously, which we know to be valid for arbitrary spin. The fluctuating field $\mathbf{V}(t)$ can also be considered in addition to the dipole interaction. This merely makes the form of $\mu_{\alpha\beta}$ in Eq. (54) still more involved.

5. "QUADRUPOLE RELAXATION" FOR $S=1$

As a final illustration of our theory, we consider the Hamiltonian

$$\mathcal{H}_q=B(t)(\mathbf{S}^2-3S_z^2)+C(t)(S_x^2-S_y^2)+\gamma HS_z. \tag{58}$$

For time-independent B and C, $\mathcal{H}_q$ would be the well-known quadrupole interaction in a solid with orthorhombic symmetry. We will take $B(t)$ and $C(t)$ to be

[8] N. Bloembergen, Phys. Rev. **104**, 1542 (1956).

random functions of time, with $\bar{B}=\bar{C}=0$, as in a cubic crystal, though this is very far removed from a realistic theory of nuclear quadrupole relaxation in solids.[9] For $S=1$, we can use the general formulas of the previous section. Noting the somewhat unconventional basis used there, we find from Eq. (58) that, in the interaction representation, the equations of motion are given by

$$\begin{aligned} &L_0=L_3=L_4=L_6=L_7=L_8=0,\\ &L_1=2\hbar B(t),\\ &-L_2+iL_5=\hbar C(t)\exp 2i\omega t, \end{aligned} \tag{59}$$

where the L_j are defined by the Eqs. (47)–(49). By taking $\theta=0$ one identically satisfies $L_3=L_4=L_6=L_7=0$. There are then three redundant variables. In eliminating these, one must take care not to lose the identical transformation $U=1$. One can indeed take

$$\theta=\eta_2=\eta_3=0, \quad \xi_2=\xi_3. \tag{60}$$

With this choice the Eqs. (47)–(49) take the form:

$$\begin{aligned} &L_0\equiv\dot{\xi}_1+2\dot{\xi}_2+\dot{\chi}=0,\\ &L_1\equiv-2\dot{\xi}_2-\dot{\chi}=2\hbar B(t),\\ &L_2\equiv-\tfrac{1}{2}\dot{\chi}\cos 2\varphi-\dot{\psi}\sin\chi\sin 2\varphi=-\hbar C(t)\cos 2\omega t,\\ &L_5\equiv\tfrac{1}{2}\dot{\chi}\sin 2\varphi-\dot{\psi}\sin\chi\cos 2\varphi=\hbar C(t)\sin 2\omega t,\\ &L_8\equiv\dot{\varphi}+\dot{\psi}\cos\chi=0. \end{aligned} \tag{61}$$

Taking the short-time average of these equations, the question arises whether the right-hand members of the equations for L_2 and L_5 become statistically independent. Statistical independence has been assumed in the foregoing, and was justified in the examples that we treated, independent of the magnetic field. From Eq. (65) it is clear that, in the present case, this condition is only satisfied when $\omega=0$, which gives $L_5=0$, or when ω is sufficiently large, i.e., when the short-time integration can be extended over a time Δt satisfying $\omega\Delta t\gg 1$. This means that the Larmor time is much shorter than the relaxation time.

(a) The case H "large." The Eq. (61) for L_0 can be integrated. In order to retain the unit matrix, the integration constant must be π:

$$\xi_1=-2\xi_2-\chi+\pi. \tag{62}$$

The equation for L_8 is clearly anholonomic, so that the four variables ξ_2, φ, ψ, χ remain in the stochastic equation. Following the procedure described in Sec. 6, we find for the Jacobian $\rho=\sin\chi$. The second moments $\mu_{\alpha\beta}$ are obtained from Eq. (54) in which the times τ_j are given by $\tau_2=\tau_5=\kappa_2$, $\tau_1=\kappa_1$, with

$$\begin{aligned} &1/\kappa_1=\sigma_1\hbar^2\langle B^2(t)\rangle,\\ &1/\kappa_2=\sigma_2\hbar^2\langle C^2(t)\rangle/(1+4\omega^2\sigma_2^2), \end{aligned} \tag{63}$$

where σ_1 and σ_2 are the correlation times of $B(t)$ and $C(t)$, respectively.

This gives a Fokker-Planck equation of the form (23) for the probability $P(\chi,\varphi,\psi,\xi_2,t)$, with the $\mathfrak{F}$ operator:

$$\mathfrak{F}_q=\frac{2}{\kappa_2}\left[\frac{c}{s}\frac{\partial}{\partial\chi}+\frac{\partial^2}{\partial\chi^2}-4\frac{\partial^2}{\partial\chi\partial\xi_2}+\frac{1}{4}\left(\frac{1}{s}\frac{\partial}{\partial\psi}-\frac{c}{s}\frac{\partial}{\partial\varphi}\right)^2\right]+\frac{1}{2}\left(\frac{1}{\kappa_1}+\frac{1}{\kappa_2}\right)\frac{\partial^2}{\partial\xi_2^2}. \tag{64}$$

Here, $c\equiv\cos\chi$, $s\equiv\sin\chi$.

The unitary transformation U is given by

$$\begin{aligned} &U_{12}=U_{13}=U_{21}=U_{31}=0,\\ &U_{11}=-\exp -i(2\xi_2+\chi),\\ &U_{22}=i\sin\tfrac{1}{2}\chi\exp i(\varphi-\psi+\xi_2+\tfrac{1}{2}\chi),\\ &U_{33}=i\sin\tfrac{1}{2}\chi\exp i(-\varphi+\psi+\xi_2+\tfrac{1}{2}\chi),\\ &U_{23}=-\cos\tfrac{1}{2}\chi\exp i(-\varphi-\psi+\xi_2+\tfrac{1}{2}\chi),\\ &U_{32}=-\cos\tfrac{1}{2}\chi\exp i(\varphi+\psi+\xi_2+\tfrac{1}{2}\chi). \end{aligned} \tag{65}$$

The unit matrix is obtained for $\xi_2=\varphi=0$, $\chi=\psi=\pi$, which gives therefore the initial condition.

(b) The case $H=0$. For $\omega=0$, Eq. (61) can be solved with $\varphi=0$, $\psi=$ const. This makes $L_5=L_8=0$. This case is therefore singular in the sense, that the condition $L_8=0$ becomes holonomic. Only the variables χ and ξ_2 remain in the stochastic equation. Instead of Eq. (64), we get

$$\frac{\partial}{\partial t}P(\chi,\xi_2,t)=\left[\frac{2}{\kappa_2^0}\frac{\partial^2}{\partial\chi^2}+\frac{1}{2}\left(\frac{1}{\kappa_2^0}+\frac{1}{\kappa_1}\right)\frac{\partial^2}{\partial\xi_2^2}\right]P(\chi,\xi_2,t), \tag{66}$$

where $\kappa_2^0=\kappa_2(\omega=0)$. The unitary transformation is obtained from Eq. (65) by taking $\varphi=0$, $\psi=\pi$.

In the transition region between case a and b the short time averages of $C(t)\cos 2\omega t$ and $C(t)\sin 2\omega t$ will be correlated. Our method can be extended to this case. One expects a Fokker-Planck equation in which the coefficients depend explicitly on the frequency ω.

An interesting difference in the results obtained from Eq. (66) and Eq. (64) is, that the relaxation time for transitions is twice as long for $H=0$ as it is for finite H. This follows from the long-range time dependence of $|U_{23}|^2$, which gives the occupation of the state Ψ_3 at time t when the spin is in the state Ψ_2 at $t=0$. We have

$$|U_{23}(t)|^2=\int\cos^2(\tfrac{1}{2}\chi)P(\chi,\varphi,\psi,\xi_2,t)\sin\chi d\chi d\varphi d\psi d\xi_2. \tag{67}$$

Writing $\cos^2\frac{1}{2}\chi=\frac{1}{2}(1+\cos\chi)$, noting that $\cos\chi$ is an eigenfunction of $\mathfrak{F}_q$ with eigenvalue $-4/\kappa_2$ and using the fact that at $t=0$, $\chi(0)=\pi$, one finds

$$|U_{23}(t)|^2=\tfrac{1}{2}[1-\exp(-4t/\kappa_2)]. \tag{68}$$

The relaxation time is, therefore, $\kappa_2/4$. For $H=0$ one finds similarly, from Eq. (66) the relaxation time $\kappa_2^0/2$. So, even when $4\sigma_2^2\omega^2\ll 1$, they differ by a factor 2.

[9] J. van Kranendonk, Physica **20**, 781 (1954).

Perhaps this could be observed in a case where our model might have some applicability, such as, e.g., quadrupole relaxation of a nucleus in a liquid.

6. DISCUSSION

In the foregoing, we have shown how some simple quantum mechanical problems involving random Hamiltonians can be solved without reference to perturbation theory. As is apparent from the example of the two-spin system, the limitation of simplicity is very severe: Reasonable equations can be expected only if the unitary transformation, generated by the Hamiltonian, depends on a small number of independent parameters.

A possible application of our method for more complicated systems is its use in combination with perturbation theory. We have not belabored this point here, because the system analyzed in the following paper illustrates it sufficiently.

We have confined the discussion to Markoffian systems, but a generalization to include non-Markoffian stochastic variables could be obtained in analogy with the classical theory of non-Markoffian processes.[10] Such a generalization would be more realistic than our present models. From this point of view it would also be desirable to extend our method to include a coupling of the small system to a large but random system, such as the phonons.[11] This would presumably allow one to include the temperature as a parameter in the stochastic equations. We hope to return to this point in a later publication. In conclusion we want to point out that the classical counterpart of our Fokker-Planck equation can be obtained readily. For the model treated in Sec. 2, e.g., we consider to this end the equations of motion of the expectation values $\langle \mathbf{S}(t) \rangle$. From Eq. (4) and from the fact that in our representation $\langle S_x(0) \rangle = \langle S_y(0) \rangle = 0$, one obtains

$$\langle S_j(t) \rangle = A_{j0}(t) \langle S_z(0) \rangle .$$

As A_{j0} is independent of φ, this motion can be described by the distribution function $p(\theta,\psi,t) = \int P(\theta,\varphi,\psi,t) d\varphi$. p satisfies a Fokker-Planck equation obtained from Eq. (24) by dropping the terms in $\partial/\partial\varphi$.

This classical equation describes fully the time dependence of observables in a free-precession experiment, but should not be used to calculate dynamical effects connected with other interactions.

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Theory of Relaxation of a Two-Spin System*

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The relaxation of a system of two inequivalent spins ($S=\frac{1}{2}$, $I=\frac{1}{2}$) with two noncommuting time-dependent interactions, i.e., a randomly modulated dipole interaction, and a fluctuating local field acting on one of the spins (S), is discussed. The influence of the fluctuating field is treated exactly in terms of a Fokker-Planck equation, which is described in the previous paper. The dipole interaction is then treated with perturbation theory. This gives, in all detail, the time-dependent transitions between the levels established in a constant external field. It is shown that rate equations are insufficient to describe the transitions, and that in weak fields a resonance phenomenon can occur. This resonance is studied in some detail with Green's function methods.

1. INTRODUCTION

IN the following, we discuss the relaxation of a system of two inequivalent spins, $S=1/2$ and $I=1/2$, with randomly modulated dipole interaction, in which one of the spins, S, also takes part in an independent relaxation process. In a recent paper,[1] the Overhauser effect in such a system was analyzed from a phenomenological point of view. Such a treatment assumes the validity of rate equations, which describe the time dependence of the population of the states, established in a constant magnetic field, due to spontaneous transitions. It also presupposes a knowledge of the rates in these equations. These are not easy to come by, with the exception of one special combination which describes the rate of transitions of the spin I regardless of the transition of spin S.[2] An attempt to evaluate the

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