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.

ACKNOWLEDGMENTS

The authors are indebted to Dr. I. Adawi and W. B. Joyce for helpful discussions.

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PHYSICAL REVIEW VOLUME 128, NUMBER 3 NOVEMBER 1, 1962

Theory of Relaxation of a Two-Spin System*

J. KORRINGA AND A. YOSHIMORI†
The Ohio State University, Columbus, Ohio

(Received May 21, 1962)

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

* This work was supported by the AFOSR through a contract with the Ohio State University Research Foundation.

† On leave of absence from University of Osaka Prefecture, Japan.

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correlated transitions of the spins with use of the formalism of Kubo and Tomita[3] has met with only a partial success.[4] This is mainly due to the fact that this application is based on a perturbation expansion. In the presence of two noncommuting interactions, as in the present system, this leads to an expansion of one of the perturbations in terms of the other, unless one succeeds in summing the series.

We will employ a different approach. We take the simpler of the two interactions and treat this in an exact manner in terms of a Fokker-Planck equation.[5] This leads to a new Hamiltonian in which randomly varying spin operators appear. This Hamiltonian is obtained in Sec. 2. In Sec. 3, we use a perturbation expansion with this Hamiltonian and calculate the time-dependent transitions. In Sec. 4, this result is approximately interpreted in terms of relaxation rates, with the help of phenomenological rate equations. A resonance phenomenon is uncovered which, in Sec. 5, is treated with a self-consistency method. The resulting expressions are discussed in Sec. 6.

2. THE INTERMEDIATE REPRESENTATION

We consider the Hamiltonian

$$\begin{aligned}&\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2,\\&\mathcal{H}_0=\gamma_e H S_z+\gamma_N H I_z,\\&\mathcal{H}_1=\gamma_e \mathbf{V}(t)\cdot\mathbf{S},\\&\mathcal{H}_2=\gamma_e\gamma_N \mathbf{I}\cdot\mathbf{\Phi}(t)\cdot\mathbf{S}.\end{aligned}\tag{1}$$

Here, $\mathbf{V}(t)$ is a random field which, in our model, causes the relaxation of the spin S. The tensor $\mathbf{\Phi}(t)$ is the dipole interaction, which has a random time dependence with characteristic time τ_c. We will use the conventional raising and lowering operators:

$$\begin{aligned}&S_\pm=\tfrac{1}{2}(S_x\pm iS_y), \quad S_0=S_z,\\&I_\pm=\tfrac{1}{2}(I_x\pm iI_y), \quad I_0=I_z.\end{aligned}\tag{2}$$

The corresponding components of $\mathbf{V}(t)$ and $\mathbf{\Phi}(t)$ are

$$V_\pm=V_x\mp iV_y, \quad V_0=V_z,\tag{3}$$

$$\begin{aligned}&\Phi_{\pm\pm}=-3r^{-3}\sin^2\vartheta\exp(\mp 2i\zeta),\\&\Phi_{\pm 0}=\Phi_{0\pm}=-3r^{-3}\sin\vartheta\cos\vartheta\exp(\mp i\zeta),\\&\Phi_{00}=-\Phi_{\pm\mp}=r^{-3}(1-3\cos^2\vartheta),\end{aligned}\tag{4}$$

where $r(t)$, $\vartheta(t)$, and $\zeta(t)$ are the polar coordinates of the distance between the spins.

We now transform to the interaction representation, which eliminates $\mathcal{H}_0$. This gives

$$\begin{aligned}\mathcal{H}^i&=\mathcal{H}_1{}^i+\mathcal{H}_2{}^i\\&=\gamma_e\mathbf{V}(t)\cdot\mathbf{S}^0(t)+\gamma_e\gamma_N\mathbf{I}^0(t)\cdot\mathbf{\Phi}\cdot\mathbf{S}^0(t),\end{aligned}\tag{5}$$

where

$$\begin{aligned}&S_k{}^0(t)=S_k\exp(ik\Omega t),\\&I_k{}^0(t)=I_k\exp(ik\omega t),\\&k=+,-,0, \quad \Omega=\gamma_e H, \quad \omega=\gamma_N H.\end{aligned}\tag{6}$$

Next we transform to the "intermediate" representation, in order to eliminate $\mathcal{H}_1{}^i(t)$. Let $u(t)$ be this transformation. It satisfies the equation

$$-i\hbar du/dt=u\mathcal{H}_1{}^i(t).\tag{7}$$

u is the unit operator with respect to the spin I. This transforms the operators $\mathbf{S}^0(t)$ to

$$\mathbf{S}'(t)=u\mathbf{S}^0(t)u^{-1},\tag{8}$$

and leaves $\mathbf{I}^0(t)$ invariant. The Hamiltonian becomes

$$\mathcal{H}'=\mathcal{H}_2'=\gamma_e\gamma_N\mathbf{I}^0(t)\cdot\mathbf{\Phi}(t)\cdot\mathbf{S}'(t).\tag{9}$$

The time dependence of $\mathbf{S}'(t)$, as given by Eq. (8), has been discussed in the preceding paper. It was there shown that, when $u(t)$ of Eq. (7) is written in parameter form as

$$u(t)=\begin{pmatrix}\alpha(t) & \beta(t)\\ -\beta^*(t) & \alpha^*(t)\end{pmatrix},\tag{10}$$

with

$$\begin{aligned}&\alpha=\cos\tfrac{1}{2}\theta\exp[\tfrac{1}{2}i(\varphi+\psi)],\\&\beta=i\sin\tfrac{1}{2}\theta\exp[\tfrac{1}{2}i(\varphi-\psi)],\end{aligned}\tag{11}$$

the variables $\theta(t)$, $\varphi(t)$, and $\psi(t)$ satisfy

$$\begin{aligned}&(\dot\theta-i\sin\theta\,\dot\varphi)\exp(i\psi)=\gamma_e V_+(t)\exp(-i\Omega t),\\&\dot\psi+\cos\theta\,\dot\varphi=\gamma_e V_0(t).\end{aligned}\tag{12}$$

The solution of the stochastic equations (12) was then obtained in terms of a quantity $P(\theta,\varphi,\psi,\theta_0,\varphi_0,\psi_0,t)\equiv P(x,x_0,t)$ which is the probability that the variables change from the values x_0 at $t=0$ to the values x at time t. P is normalized by

$$\int P(x,x_0,t)\sin\theta\,d^3x=1,\tag{13}$$

it obeys the initial condition

$$\sin\theta_0\,P(x,x_0,0)=\delta^3(x-x_0),\tag{14}$$

and satisfies the Fokker-Planck equation

$$\partial P/\partial t=\mathfrak{F}(P),\tag{15}$$

where

$$\mathfrak{F}=(1/4\tau_1)(K^*K+KK^*)+(1/2\tau_0)\partial^2/\partial\psi^2\tag{16}$$

with

$$K=e^{-i\psi}[\partial/\partial\theta-i(\sin\theta)^{-1}(\partial/\partial\varphi-\cos\theta\partial/\partial\psi)].\tag{17}$$

τ_1 and τ_0 are given by

$$\begin{aligned}&1/\tau_1=\sigma_1\gamma_e{}^2\langle V_x{}^2\rangle_t(1+\Omega^2\sigma_1{}^2)^{-1},\\&1/\tau_0=\sigma_0\gamma_e{}^2\langle V_z{}^2\rangle_t,\end{aligned}\tag{18}$$

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where σ_1 and σ_0 are the correlation times of V_x (and V_y) and V_z, respectively. The familiar relaxation times T_1 and T_2 of the spin S due to the perturbation $\mathbf{V}(t)$ are given by

$$1/T_1=1/\tau_1, \qquad 1/T_2=\tfrac{1}{2}(1/\tau_0+1/\tau_1). \tag{19}$$

The transformation (8) can be expressed more conveniently in the form

$$S_j'(t)=\sum_k A_{jk}(t)S_k \exp(ij\Omega t), \quad j,k=+,-,0. \tag{20}$$

Using Eq. (10), this gives

$$\begin{aligned} A_{\pm\pm}&=\tfrac{1}{2}(1+\cos\theta)\exp[\pm i(\psi+\varphi)],\\ A_{\pm\mp}&=\tfrac{1}{2}(1-\cos\theta)\exp[\pm i(\psi-\varphi)],\\ A_{\pm 0}&=\mp\tfrac{1}{2}i\sin\theta\exp(\pm i\psi),\\ A_{0\pm}&=\mp i\sin\theta\exp(\pm i\varphi),\\ A_{00}&=\cos\theta. \end{aligned} \tag{21}$$

The A_{jk} are eigenfunctions of $\mathfrak{F}$, satisfying

$$\mathfrak{F}A_{jk}=-\lambda^{(j)}A_{jk}, \qquad \lambda^{(0)}=1/T_1, \quad \lambda^{(\pm)}=1/T_2. \tag{22}$$

Substituting Eq. (20) and Eq. (6) in Eq. (9) and putting

$$\omega_{jk}=j\omega+k\Omega, \tag{23}$$

the Hamiltonian becomes

$$\mathfrak{IC}'=\gamma_e\gamma_N\sum\Phi_{jk}(t)\exp(i\omega_{jk}t)A_{kn}(t)I_jS_n. \tag{24}$$

3. PERTURBATION EXPANSION WITH $\mathfrak{IC}'$

Finally, we transform to the Heisenberg representation. If $U(t)$ is this transformation, the states $\Psi(t)$ in the interaction representation and $\Psi(0)$ in the Heisenberg representation are related by

$$\Psi(0)=U(t)u(t)\Psi(t). \tag{25}$$

$U(t)$ satisfies

$$-i\hbar dU/dt=U\mathfrak{IC}'. \tag{26}$$

The Eqs. (24)–(26) will now be used to obtain the changes with time in the population of the four states of the spin pair. We denote these states $\Psi_\mu=(\Psi_1,\cdots\Psi_4)\equiv(\Psi_{++},\Psi_{+-},\Psi_{-+},\Psi_{--})$, respectively, where the first index refers to the eigenvalue of S_z, the second to I_z. Taking $u(0)=U(0)=1$, the probability that, at time t, the system has made a transition from the state Ψ_μ to Ψ_ν is given by

$$D_{\mu\nu}(t)=\langle\langle|(u^{-1}(t)U^{-1}(t))_{\nu\mu}|^2\rangle\rangle, \tag{27}$$

where $\langle\langle\ \ \rangle\rangle$ signifies the average over the ensemble of all spin pairs which are in the same state at $t=0$. It is therefore an average over the two types of random motion in the system, with the restriction that $u(0)=1$, i.e. that $A_{jk}(0)=\delta_{jk}$.

A perturbation expansion of Eq. (26) gives:

$$U(t)=U(0)+(i/\hbar)U(0)\int_0^t\mathfrak{IC}'(t')dt' +(i/\hbar)^2U(0)\int_0^t dt'\,\mathfrak{IC}'(t')\int_0^{t'}dt_0\mathfrak{IC}'(t_0)+\cdots. \tag{28}$$

Inserting this in Eq. (27) gives

$$D_{\mu\nu}=D_{\mu\nu}{}^e+D_{\mu\nu}{}^d+D'_{\mu\nu}{}^d, \tag{29}$$

$$D_{\mu\nu}{}^e=\langle|u_{\mu\nu}{}^{-1}(t)|^2\rangle,$$

$$D_{\mu\nu}{}^d=\hbar^{-2}\left\langle\left\langle\left|\sum_\lambda u_{\nu\lambda}{}^{-1}(t)\int_0^t\mathfrak{IC}'_{\lambda\mu}(t')dt'\right|^2\right\rangle\right\rangle,$$

$$D'_{\mu\nu}{}^d=-\hbar^{-2}\left\langle\left\langle 2\,\mathrm{Re}\sum_{\lambda,\lambda'}u_{\nu\mu}(t)u_{\mu\lambda}{}^{-1}(t)\times\int_0^t dt'\int_0^{t'}dt_0\,\mathfrak{IC}'_{\lambda\lambda'}(t')\mathfrak{IC}'_{\lambda'\nu}(t_0)\right\rangle\right\rangle. \tag{30}$$

The first term in Eq. (29) is due to the motion of S in absence of the dipole interaction. It is described, without approximation, by the Fokker-Planck (F-P) Eq. (15). The second term comes from the square of the first-order term in Eq. (28), while D'^d is the cross term between u and the second-order term of U. The latter contributes only to the transitions $1\leftrightarrow 3$ and $2\leftrightarrow 4$.

D^d will be evaluated for a time satisfying

$$t\gg\sigma, \quad D^d(t)\ll 1. \tag{31}$$

Here σ is the correlation time of the field $\mathbf{V}(t)$; the inequality $t\gg\sigma$ ensures the applicability of the F-P equation. The second inequality is needed in view of the approximation (28). We assume that the inequalities (31) can be satisfied simultaneously. The conditions on the time t relative to the times τ_c, T_1, and T_2 will be discussed presently.

Equation (30) gives

$$D_{\mu\nu}{}^d(t)=2\hbar^{-2}\,\mathrm{Re}\sum_{\eta\lambda}\left\langle\left\langle u_{\eta\nu}(t)u_{\nu\lambda}{}^{-1}(t)\times\int_0^t dt'\int_0^{t'}dt_0\,\mathfrak{IC}'_{\lambda\mu}(t')\mathfrak{IC}'_{\eta\mu}{}^*(t_0)\right\rangle\right\rangle. \tag{32}$$

The integrand contains factors of the form

$$\langle\Phi_{jk}(t')\Phi_{lm}{}^*(t_0)\rangle\exp[i(\omega_{jk}t'-\omega_{lm}t_0)],$$

averaged over the relative positions of the spins. Of these, only the terms with $j=l$, $k=m$ need to be retained. The others, in so far as they are not zero on account of Eq. (41), contain, in the periodic part, t' and t_0 multiplied with different frequencies. This gives, as will become clear in the following, contributions to D which are periodic in time and which are negligible compared to contributions from the other terms.

We can, therefore, write

$$\langle\Phi_{jk}(t')\Phi_{lm}^*(t_0)\rangle \rightarrow f_{jk}\exp[-(t'-t_0)/\tau_c]\delta_{jl}\delta_{km}. \quad (33)$$

The constants f_{jk} follow from Eq. (4):

$$\begin{aligned} f_{\pm\pm}&=\frac{24}{5}\langle r^{-6}\rangle,\\ f_{\pm 0}=f_{0\pm}&=\frac{6}{5}\langle r^{-6}\rangle,\\ f_{\pm\mp}=f_{00}&=\frac{4}{5}\langle r^{-6}\rangle. \end{aligned} \quad (34)$$

With use of Eqs. (10) and (21), the products $u_{\eta\nu}(t)u_{\nu\lambda}^{-1}(t)$ can be expressed in terms of the A_{jk}. Note that u is the unit operator with respect to the spin I. These expressions are linear, but some contain 1 as an additive constant. As a result, $D_{\mu\nu}{}^d$ can be expressed entirely in terms of the A_{jk}. We find

$$D_{\mu\nu}{}^d(t)=\tfrac{1}{8}\hbar^2\gamma_e{}^2\gamma_N{}^2\,\mathrm{Re}\left\langle\int_0^t dt'\int_0^{t'} dt_0\, X_{\mu\nu}(t,t',t_0)\right\rangle, \quad (35)$$

$$\begin{aligned} X_{12}&=\tfrac{1}{2}\textstyle\sum(M_j+N_j)(\varphi_{+j}+\varphi_{-j}),\\ X_{13}&=\textstyle\sum(M_j-N_j)\varphi_{0j},\\ X_{14}&=\textstyle\sum(M_j-N_j)\varphi_{-j},\\ X_{23}&=\textstyle\sum(M_j-N_j)\varphi_{+j}, \end{aligned} \quad (36)$$

$$\begin{aligned} M_j&=\tfrac{1}{2}[A_{j0}(t')A_{j0}{}^*(t_0)+A_{j-}(t')A_{j-}{}^*(t_0)],\\ N_j&=\tfrac{1}{2}[A_{0-}(t)A_{j0}(t')A_{j-}{}^*(t_0)\\ &\qquad +A_{0+}(t)A_{j-}(t')A_{j0}{}^*(t_0)]\\ &\quad+\tfrac{1}{2}A_{00}(t)[A_{j0}(t')A_{j0}{}^*(t_0)\\ &\qquad -A_{j-}(t')A_{j-}{}^*(t_0)], \end{aligned} \quad (37)$$

$$\varphi_{kj}=f_{kj}\exp-w_{kj}(t'-t_0), \quad (38)$$

$$w_{kj}=1/\tau_c-i\omega_{kj}.$$

For $D'_{\mu\nu}{}^d$ one finds an expression similar to Eq. (35), with $X_{12}'=X_{14}'=X_{23}'=0$. The explicit form of X_{13}' is easily obtained, but D'^d will not be needed in the following.

A typical contribution to D^d is proportional to

$$Z_{\alpha\alpha'\alpha_0}(t)=\left\langle A_\alpha(t)\int_0^t dt'\int_0^{t'} dt_0\, A_{\alpha'}(t')A_{\alpha_0}(t_0)\times\exp[-w(t'-t_0)]\right\rangle. \quad (39)$$

The relations between the A's at different times are expressed by the probability P, which satisfies Eq. (15).

Therefore, writing $\rho(x)=\sin\theta$, we have

$$\begin{aligned} Z(t)=&\int\int\int d^3x_0d^3x'd^3x\\ &\times\int_0^t dt'\int_0^{t'} dt_0\,\rho(x_0)P(x_0,0,t_0)A_{\alpha_0}(x_0)\\ &\times\rho(x')P(x',x_0,t'-t_0)A_{\alpha'}(x')\\ &\times\rho(x)P(x,x',t-t')A_\alpha(x)\exp-w(t'-t_0). \end{aligned} \quad (40)$$

In order to carry out the time integration, we introduce the Laplace transform of $P(x,x_0,t)$, defined by

$$P(x,x_0,v)=\int_0^\infty e^{-vt}P(x,x_0,t)dt. \quad (41)$$

From Eq. (15), we have

$$\int_0^\infty e^{-vt}(\partial P/\partial t)dt=-P(0)+vP(v)=\mathfrak{F}[P(v)]. \quad (42)$$

Using the initial condition (14) we obtain the transformed F-P equation

$$\rho(x_0)P(x,x_0,v)=(v-\mathfrak{F})^{-1}\delta^3(x-x_0), \quad (43)$$

where $\mathfrak{F}$ differentiates with respect to the variables x. The inverse of Eq. (42) is

$$P(x,x_0,t)=\frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty}e^{vt}P(x,x_0,v)dv,\quad \epsilon>0. \quad (44)$$

Introducing this in Eq. (40) and integrating over t_0 and t', we obtain

$$\begin{aligned} Z(t)=&(2\pi i)^{-3}\int\int\int dv_0dv'dvL(-v_0,-v',-v,t)\\ &\times\int\int\int dx_0dx'dxA_{\alpha_0}(x_0)A_{\alpha'}(x')A_\alpha(x)\\ &\times[(v_0-\mathfrak{F}_0)^{-1}\delta(x_0)][(v'-\mathfrak{F}')^{-1}\delta(x'-x_0)]\\ &\times[(v-\mathfrak{F})^{-1}\delta(x-x')], \end{aligned} \quad (45)$$

where

$$\begin{aligned} L(v_0,v',v,t)=&\frac{e^{-v_0t}-e^{-vt}}{(w-v_0+v')(v-v_0)}\\ &+\frac{e^{-(v'+w)t}-e^{-vt}}{(w-v_0+v')(w-v+v')}. \end{aligned} \quad (46)$$

The integration over x in Eq. (45) can now be carried out, because the operation $\mathfrak{F}$ is Hermitian and $A_\alpha(x)$ is an eigenfunction of $\mathfrak{F}$:

$$\mathfrak{F}A_\alpha(x)=-\lambda_\alpha A_\alpha(x). \quad (47)$$

The result is obtained by replacing the last factor in Eq. (45) by $(v+\lambda_\alpha)^{-1}$, and by replacing $A_\alpha(x)$ by $A_\alpha(x')$. In order to carry out the x' integration, the product $A_{\alpha'}(x')A_\alpha(x')$ must be decomposed in eigenfunctions of $\mathfrak{F}$. Let

$$A_{\alpha'}(x')A_\alpha(x')=\sum \mathfrak{A}_\beta(x'),$$
$$\mathfrak{F}'\mathfrak{A}_\beta(x')=-\lambda_\beta\mathfrak{A}_\beta(x'). \tag{48}$$

For each term in Eq. (48) the x' integration can be done. Finally, with

$$A_{\alpha_0}(x_0)\mathfrak{A}_\beta(x_0)=\sum \mathfrak{A}_\gamma(x_0),$$
$$\mathfrak{F}_0\mathfrak{A}_\gamma(x_0)=-\lambda_\gamma\mathfrak{A}_\gamma(x_0), \tag{49}$$

we can also do the x_0 integration. This gives

$$Z(t)=(2\pi i)^{-3}\sum_{\beta,\gamma}\mathfrak{A}_\gamma(0)\int\int\int dv_0dv'dv$$
$$\times L(-v_0,-v',-v,t)(v_0+\lambda_\gamma)^{-1}(v'+\lambda_\beta)^{-1}$$
$$\times(v+\lambda_\alpha)^{-1}. \tag{50}$$

The complex integration then gives, when $\lambda_\alpha\neq\lambda_\gamma$:

$$Z(t)=\sum_{\beta,\gamma}\mathfrak{A}_\gamma(0)L(\lambda_\gamma,\lambda_\beta,\lambda_\alpha,t). \tag{51}$$

The value for $\lambda_\alpha=\lambda_\gamma$ can be obtained as the limit $\lambda_\alpha\to\lambda_\gamma$. The result arising from the various terms M_j and N_j in Eqs. (35)–(37) is as follows:

$$Z[M_\pm]=\tfrac{1}{4}L(0,\lambda_2,0,t)\mp L(\lambda_1,\lambda_2,0,t),$$
$$Z[M_0]=\tfrac{1}{2}L(0,\lambda_1,0,t),$$
$$Z[N_\pm]=-\tfrac{1}{4}L(\lambda_1,\lambda_2,\lambda_1,t)\pm\tfrac{1}{12}L(0,\lambda_2,\lambda_1,t)$$
$$\pm\tfrac{1}{6}L(\lambda_3,\lambda_2,\lambda_1,t), \tag{52}$$
$$Z[N_0]=\tfrac{1}{2}L(\lambda_1,0,\lambda_1,t),$$

where

$$\lambda_1=1/T_1,\quad \lambda_2=1/T_2,\quad \lambda_3=3/T_1. \tag{53}$$

The contributions to $D_{\mu\nu}{}^d$ in Eq. (35) are obtained by multiplying Eq. (52) with the proper factors φ_{kj} as shown in Eq. (36). This means that the expressions (52) are to be multiplied with a factor f_{kj}, as indicated by Eq. (38) and as given by Eq. (34), and that the corresponding value of w is substituted in L from Eq. (38). When $\lambda_\alpha=\lambda_\gamma$, the first term in L is proportional to t. All other terms are either constant or exponential in t. Finally, we must take the real part of these expressions.

4. EVALUATION OF THE TRANSITION RATES

Because of the appearance of two types of transitions in the system, viz., the "S" transitions characterized by the rates λ and the transitions due to the dipolar interactions, the interpretation of Eq. (52) in terms of relaxation rates requires a little care. Customarily, one defines transition rates from the values of the time derivative of quantities such as $D_{\mu\nu}$ in a time range where they vary linearly with t. In the present system, however, there are several t ranges where $D_{\mu\nu}$ is approximately linear in time, with different rates. This property is easily understood from the fact that the rates λ cause a rapid equalization of the states 1 and 3, and of 2 and 4, on which the slower transitions are superimposed. If, e.g., $1/\tau_c\gg\lambda$, the first linear range will occur for $\tau_c\ll t\ll 1/\lambda$, a second for $1/\lambda\ll t\ll 1/\lambda'$, where λ' is a quantity of the order of the dipolar rates.

In view of this circumstance, we will present the results of the previous section in two different ways. We will also exclude from our considerations the case that τ_c is very long, i.e., $\tau_c\gg 1/\lambda$, as in a solid. This case is not excluded in our method, but requires the calculation of several terms which were omitted by using Eq. (33). Also, the leading terms for that case are easily obtained by stationary state perturbation theory.[1,6]

In the first presentation, we consider the following linear combinations of the quantities $D_{\mu\nu}{}^d$:

$$a(t)=D_{12}+D_{14}+D_{21}+D_{23},$$
$$b(t)=D_{12}-D_{14}+D_{21}-D_{23}, \tag{54}$$
$$c(t)=D_{14}-D_{23}.$$

$a(t)$ gives the transitions of the spin I regardless of the transitions of S; $b(t)$ and $c(t)$ describe the correlation in the transitions of the two spins. A fourth quantity, giving the transitions of S irrespective of the transitions of I will not be considered, because this is dominated by the rate λ_1—obtained from the term D^e in Eq. (29)—in the interesting applications of our theory.

From Eq. (36) and Eq. (34), one has

$$2X_{12}+X_{14}+X_{23}=2(M_++M_-)(\varphi_{++}+\varphi_{+-})$$
$$+4M_0\varphi_{+0},$$
$$2X_{12}-X_{14}-X_{23}=2(N_++N_-)(\varphi_{++}+\varphi_{+-})$$
$$+4N_0\varphi_{+0}, \tag{55}$$
$$X_{14}-X_{23}=[(N_+-N_-)-(M_+-M_-)]$$
$$\times(\varphi_{++}-\varphi_{+-}).$$

With use of Eq. (51), one obtains

$$a(t)=Q\ \mathrm{Re}[2L_{++}(0,\lambda_20,t)+\tfrac{1}{3}L_{+-}(0,\lambda_2,0,t)$$
$$+L_{+0}(0,\lambda_1,0,t)],$$
$$b(t)=Q\ \mathrm{Re}[-2L_{++}(\lambda_1,\lambda_2,\lambda_1,t)-\tfrac{1}{3}L_{+-}(\lambda_1,\lambda_2,\lambda_1,t)$$
$$+L_{+0}(\lambda_1,0,\lambda_1,t)], \tag{56}$$
$$c(t)=Q\ \mathrm{Re}[L_{++}(\lambda_1,\lambda_2,0,t)-\tfrac{1}{6}L_{+-}(\lambda_1,\lambda_2,0,t)$$
$$+\tfrac{1}{3}L_{++}(0,\lambda_2,\lambda_1,t)-1/18L_{+-}(0,\lambda_2,\lambda_1,t)$$
$$+\tfrac{2}{3}L_{++}(\lambda_3,\lambda_2,\lambda_1,t)-\tfrac{1}{9}L_{+-}(\lambda_3,\lambda_2,\lambda_1,t)],$$

where

$$Q=\tfrac{3}{10}\hbar^2\gamma_e{}^2\gamma_N{}^2\langle r^{-6}\rangle. \tag{57}$$

In L_{jk}, the frequency ω_{jk} is to be used.

The result (56) for $a(t)$ is particularly simple.

[6] A. Abragam and G. Proctor, Compt. rend. **246**, 2253 (1958).

According to Eq. (46) and Eq. (38), one has

$$L_{jk}(0,\lambda,0,t)=\frac{t}{\lambda+1/\tau_c-i\omega_{jk}}+\frac{\exp[-(\lambda+1/\tau_c-i\omega_{jk})t]-1}{(\lambda+1/\tau_c-i\omega_{jk})^2}. \quad (58)$$

This gives a t^2 dependence for $t\ll\tau_c$, while for $t\gg\tau_c$:

$$a(t)=Qt\left[\frac{\rho_1}{1+\omega^2\rho_1^2}+2\frac{\rho_2}{1+(\Omega+\omega)^2\rho_2^2}+\frac{1}{3}\frac{\rho_2}{1+(\Omega-\omega)^2\rho_2^2}\right], \quad (59)$$

$$1/\rho_1=1/\tau_c+1/T_1, \quad 1/\rho_2=1/\tau_c \quad 1/T_2. \quad (60)$$

Equation (59) is an obvious generalization to the case $T_1\neq T_2$ of a result reported by Bloembergen and Morgan,[2] showing that for the motion of the spin I regardless of correlations with the motion of S, a rate $a(t)/t$ can be defined unambiguously. The result for $b(t)$ and $c(t)$ is less simple, because all the L functions therein have exponential time dependence involving $\exp(-\lambda_1 t)$, $\exp(-\lambda_3 t)$, and—in $b(t)$—also $t\exp(-\lambda_1 t)$. When $\tau_c\ll 1/\lambda$ this gives a different "rate" for $\tau_c\ll t\ll 1/\lambda$ as for $1/\lambda\ll t\ll 1/\lambda'$, and when τ_c and $1/\lambda$ are of the same order of magnitude, the treatment of the exponential terms becomes quite ambiguous.

The resulting rates for the case $\tau_c\ll 1/\lambda$ in the time range $\tau_c\ll t\ll 1/\lambda$ are obtained from Eq. (56) by equating the exponentials involving $1/\tau_c$ to zero and by expanding the other exponentials. Putting, for simplicity, $\Omega\pm\omega\approx\Omega$, we find

$$b(t)=Qt\left[\frac{\rho_3}{1+\omega^2\rho_3^2}-\frac{7}{3}\frac{\rho_4}{1+\Omega^2\rho_4^2}\right],$$
$$c(t)=Qt\left[\frac{10}{9}\frac{\rho_5}{1+\Omega^2\rho_5^2}-\frac{5}{9}\frac{\rho_6}{1+\Omega^2\rho_6^2}\right], \quad (61)$$

where

$$1/\rho_3=1/\tau_c-2T_1,$$
$$1/\rho_4=1/\tau_c+1/T_2-2/T_1,$$
$$1/\rho_5=1/\tau_c+1/T_2-1/T_1,$$
$$1/\rho_6=1/\tau_c+1/T_2-4/T_1. \quad (62)$$

The relations (59) and (61) reduce to Solomon's[7] result in the limit that $\lambda\to 0$.

For a discussion of the behavior in the time range $1/\lambda\ll t\ll 1/\lambda'$ and, in particular, for the case that $1/\tau_c$ and λ are of the same order of magnitude, we turn now to our second presentation.

When the evolution of the system can be described in terms of transition rates, one can introduce these rates phenomenologically by means of rate equations for the population of the four states, as was, e.g., done in reference 1. Let $n_\mu(t)$ be the population of the state Ψ_μ. Assuming the validity of rate equations, we have

$$dn_\mu/dt=\sum_\nu W_{\mu\nu}(n_\nu-n_\mu), \quad (63)$$

where the matrix W is real and positive and, in the high-temperature approximation, symmetric, $W_{\mu\mu}$ can be taken zero. Also, W is invariant when the direction of the magnetic field is reversed. Consequently, the elements of W can be expressed as follows:

$$W_{13}=W_{24}=p,$$
$$W_{12}=W_{34}=q,$$
$$W_{23}=r, \quad W_{14}=s. \quad (64)$$

p is dominated by the relaxation of S; writing $p=p_0+p'$, we therefore have

$$p_0\gg(p',q,r,s). \quad (65)$$

For comparing the solution of Eq. (63) with the results of our quantum mechanical calculation, we define

$$\bar{D}_{\mu\nu}=[n_\nu(t)]_{n_k(0)=\delta_{uk}}, \quad (66)$$

and introduce quantities $\bar{a}(t)$, $\bar{b}(t)$, and $\bar{c}(t)$ in terms of $\bar{D}$ as in Eq. (54). For times satisfying $(p',q,r,s,)t\ll 1$ one has

$$\bar{a}(t)=(2q+r+s)t,$$
$$\bar{b}(t)=(2q-r-s)te^{-2p_0t},$$
$$\bar{c}(t)=\tfrac{1}{2}(s-r)p_0^{-1}(1-e^{-2p_0t}). \quad (67)$$

Comparing with Eq. (56), we clearly must take

$$2p_0=\lambda_1=1/T_1. \quad (68)$$

Then, if $\tau_c\ll T_1$, the time range $\tau_c\ll t\ll T_1$ yields values of q, r, and s which can immediately be read from Eqs. (59) and (61). However, owing to the manner in which the terms in ω occur, an additional limitation is imposed on the value of T_1. Both r and s contain, besides terms in Ω, an additive term

$$Q[\rho_1/(1+\omega^2\rho_1^2)-\rho_3/(1+\omega^2\rho_3^2)]. \quad (69)$$

From Eqs. (60) and (62), one sees that this term is negative if $\omega\tau_c<1$. The requirement that r (and s) are positive gives the condition

$$\tau_c<\tfrac{1}{9}T_1(1+\omega^2\tau_c^2)(1+\Omega^2\tau_c^2)^{-1}. \quad (70)$$

The coefficient of T_1 can take very small values, e.g., when S is an electronic spin and I is a nuclear spin, and when the magnetic field is such that $\omega\tau_c\geq 1$, it is of the order of magnitude 10^{-6}. Thus, the rate equations (63) can, for sufficiently strong fields, lose their physical meaning, even though the condition $\tau_c\ll T_1$ is satisfied.

Considering next, still for the case $\tau_c\ll T_1$, the time range $T_1\ll t\ll 1/\lambda'$, for which Eq. (56) is also valid, one must compare Eq. (67) directly with Eq. (56). The first term of the functions L in $a(t)$, $b(t)$, and $c(t)$

[7] I. Solomon, Phys. Rev. **99**, 559 (1955).

have indeed the time dependence of $\bar{a}(t)$, $\bar{b}(t)$, and $\bar{c}(t)$, respectively. An exception is the term $L_{+,\pm}(\lambda_3,\lambda_2,\lambda_1,t)$, containing $\exp(-\lambda_3 t)$ which does not appear in Eq. (67). The second term in the functions L, for this case, is small compared to the first term, because it is quadratic in the denominators containing $1/\tau_c$. Disregarding the term in λ_3 one obtains, in this time range, values for q, r, and s similar to those obtained from Eqs. (59)–(62) with the difference that ρ_3, ρ_4, and ρ_5 are to be replaced by ρ_3', ρ_4' and ρ_5', given by

$$\begin{aligned} 1/\rho_3' &= 1/\tau_c - 1/T_1, \\ 1/\rho_4' &= 1/\tau_c + 1/T_2 - 1/T_1, \\ 1/\rho_5' &= 1/\tau_c + 1/T_2, \end{aligned} \tag{71}$$

and that, by lack of correspondence, the term in ρ_6 of $c(t)$ is omitted. As before, the danger exists, that r and s are negative.

Finally, when τ_c and T_1 are of the same order of magnitude, rates could possibly only be defined for $T_1 \ll t \ll 1/\lambda'$, by using the above method of identification. Again, the term in $\exp(-\lambda_3 t)$ of $c(t)$ is not reproduced by Eq. (67) and, more seriously, the inequality corresponding to Eq. (70) is in general not satisfied even for weaker fields, giving negative values for r and s. A still more serious defect seems to occur in weak fields, when $\omega\tau_c \ll 1$, in the case that $\tau_c \approx T_1$. With the abbreviation $2\xi = 1/\tau_c - 1/T_1$ we have for the term L_{+0} in $b(t)$

$$L_{+0}(\lambda_1,0,\lambda_1,t) = e^{-\lambda_1 t}\left[\frac{t}{2\xi - i\omega} + \frac{\exp[(i\omega - 2\xi)t] - 1}{(2\xi - i\omega)^2}\right]. \tag{72}$$

For $\omega t \ll 1$ and ξ very small we have $L \approx t^2 \exp(-\lambda_1 t)$, which does not represent relaxation. We take therefore $\omega t \gg 1$, but leave out ω in the exponential in order to retain only the nonperiodic behavior of L. Then, if ξ is of the same order of magnitude as ω, and $\xi > 0$, the first term of L dominates; its real part has a maximum value for $2\xi = \omega$, and this would give a relaxation rate $\sim 1/\omega$ (cf. Eq. (67)). For $\xi < 0$, $|\xi| \approx \omega$, the second term dominates, giving

$$\mathrm{Re}L = [\exp(-t/\tau_c)](4\xi^2 - \omega^2)(4\xi^2 + \omega^2)^{-2},$$

which does not conform to Eq. (67). This result indicates that the term (72) has a singular behavior in weak fields. We will refer to this phenomenon as a "resonance" in the relaxation. The true nature of this term near the resonance condition $\tau_c \approx T_1$ is, of course, not adequately represented by Eq. (72), because this equation is based on a first-order perturbation theory.

5. THE RESONANCE

In order to study the resonance, found in the previous section, we will evaluate the transition probabilities more carefully. Quite generally, they are given by Eq. (27). The double average in that equation means an average over the liquid motion and an average over all the possible paths of the motion of S, with the probability $P(x,x_0,t)$. The matrix $u(t)$ is given by Eq. (10) in terms of the Euler angles x. The matrix $U(t)$ satisfies Eq. (26). Using the initial condition $U_{\mu\nu}(0) = \delta_{\mu\nu}$, this equation can be written as an integral equation

$$U(t) = 1 + (i/\hbar)\int_0^t dt'\, U(t')\mathcal{H}'(t'). \tag{73}$$

$\mathcal{H}'$ is given by Eq. (24).

As in Sec. 3, the products of matrix elements of $u(t)$ appearing in Eq. (27) can be expressed linearly in terms of the A_{jk}. $D_{\mu\nu}$ can then be expressed linearly in terms of quantities $G(t,t)$, which we define quite generally as follows:

$$G^{m',m}{}_{\mu'\nu',\mu\nu}(t',t) = \langle\langle \mathfrak{A}_{m'}{}^*(t') U_{\nu'\mu'}{}^*(t') \mathfrak{A}_m(t) U_{\nu\mu}(t)\rangle\rangle. \tag{74}$$

$\mathfrak{A}_m$ and $\mathfrak{A}_{m'}$ are any eigenfunctions of $\mathfrak{F}$. We will refer to $G(t',t)$ as the "Green's functions" for the present problem; this terminology will be justified presently.

The expression for $D_{\mu\nu}$ contains only the equal-times Green's functions with $\mathfrak{A}_{m'} = 1$, i.e., $m' = 0$, and $\mathfrak{A}_m = 1$ or $\mathfrak{A}_m = A_{0j}$, i.e., $m = 0$, (00), or (0±). We have, e.g.,

$$\begin{aligned} D_{21} = \tfrac{1}{2}[&G^{0,0}{}_{12,12} + G^{0,00}{}_{12,12} + G^{0,0}{}_{32,32} - G^{0,00}{}_{32,32} \\ &+ G^{0,0-}{}_{32,12} + G^{0,0+}{}_{12,32}]. \end{aligned} \tag{75}$$

The reason for introducing the more general functions (74) is, that they have to be included in order to get a closed set of coupled integral equations from which $D_{\mu\nu}$ could be calculated. These integral equations can be obtained as follows: In G, we substitute for U the right-hand side of Eq. (73). Of the three types of terms that one gets, one is linear in $U\mathcal{H}'$. In this, we substitute once more from Eq. (73). This gives

$$\begin{aligned} G^{m',m}{}_{\mu'\nu',\mu\nu}(t',t) = {} & \delta_{\mu'\nu'}\delta_{\mu\nu}\langle \mathfrak{A}_{m'}{}^*(t')\mathfrak{A}_m(t)\rangle \\ & - \hbar^{-2}\delta_{\mu\nu}\int_0^{t'} dt_1 \int_0^{t_1} dt_2 \langle\langle \mathfrak{A}_{m'}{}^*(t')\mathfrak{A}_m(t)(U^*(t_2)\mathcal{H}'(t_2)\mathcal{H}'^*(t_1))_{\nu'\mu'}\rangle\rangle \\ & - \hbar^{-2}\delta_{\mu'\nu'}\int_0^{t} dt_1 \int_0^{t_1} dt_2 \langle\langle \mathfrak{A}_{m'}{}^*(t')\mathfrak{A}_m(t)(U(t_2)\mathcal{H}'(t_2)\mathcal{H}'(t_1))_{\nu\mu}\rangle\rangle \\ & + \hbar^{-2}\int_0^{t'} dt_1 \int_0^{t} dt_2 \langle\langle \mathfrak{A}_{m'}{}^*(t')\mathfrak{A}_m(t)(U^*(t_1)\mathcal{H}'^*(t_1))_{\nu'\mu'}(U(t_2)\mathcal{H}'(t_2))_{\nu\mu}\rangle\rangle. \end{aligned} \tag{76}$$

Inserting $\mathcal{H}'$ from Eq. (24), we now make the approximation that the pair of factors Φ appearing in the last three terms of G is averaged separately over the liquid motion, using Eq. (33), which holds for $t'>t_0$, or the corresponding expression valid for $t'<t_0$. In the remaining expression, we consider all the time orders in which the various factors, $\mathfrak{A}_{m'}{}^*$, $\mathfrak{A}_m$, A_{jk}, $A_{jk'}{}^*$, appear, splitting, if necessary, the integration domain. For every time order we can express the average over the spin motion as an integration over x', x, x_1 and x_2, with use of the probability P as was done in Eq. (40). Due to the presence of a factor $U^*(t_2)$ or $U(t_2)$ in the second and third term, respectively [which should now be written as $U(t_2,x_2)$] and of two factors, $U^*(t_1,x_1)$ and $U(t_2,x_2)$ in the fourth term, the integration over x_2 (or, for the fourth term, x_1 and x_2) can not be carried out. Also, with some of the orders of the four times, e.g., $t_2<t<t_1$, one meets expressions of the form

$$\int dx\, P(x_1, x, t_1-t)\mathfrak{A}(x)P(x, x_2, t-t_2),$$

with x not appearing in any other factor. This integration cannot be carried out either. As a reasonable approximation we will replace this integral by

$$\mathfrak{A}(x_2)e^{-\lambda(t-t_2)}P(x_1, x_2, t_1-t_2),$$

where λ is the eigenvalue for $\mathfrak{A}$.

With this approximation one can now carry out the integrations over the variables x not appearing in the factor(s) U, using, as in Eq. (48), (49), a decomposition of products of $\mathfrak{A}$'s in eigenfunctions of $\mathfrak{F}$. The quantities remaining to be averaged have again the form of G functions, but with different indices. In particular, the second and third terms in (76), which contain only one factor U, give rise to $G_{\nu\nu',\lambda\nu}(0,t_2)$ as one sees from the fact that $U_{\nu\mu}(0)=\delta_{\mu\nu}$.

Thus, one finally obtains a set of coupled integral equations for the functions G. They have approximate validity, and are infinite in number, corresponding to the fact that $\mathfrak{F}$ has an infinite number of eigenfunctions. The nomenclature "Green's function" for $G(t',t)$ is based on the property that dG/dt' has a discontinuity at $t'=t$. This is easily verified from Eq. (76) in the approximation that we put $U(t)\rightarrow U(0)$ in the right-hand side.

We have no intentions of finding a general solution of these integral equations. Indeed, the perturbation treatment of the preceding section gave excellent results except for the few terms which are plagued by the resonance phenomenon. We will now show that these "dangerous" terms can completely be separated from the "normal" terms, and can be obtained from a finite and small set of integral equations.

From the perturbation treatment in Sec. 3, one sees that the dangerous terms arise only from the following combinations of factors A:

$$A_{00}(t)A_{00}(t_1)A_{00}(t_2) \quad \text{and} \quad A_{0\pm}(t)A_{0\mp}(t_1)A_{00}(t_2),$$

where $t>t_1>t_2$. Beginning with the Green's functions involved directly in $D_{\mu\nu}$, we retain in Eq. (76) only those terms which are linked by these combinations, assuming that these terms are dominant. We will first consider D_{21}, given by Eq. (75), and begin with $G^{0,00}{}_{12,12}$. Taking $t'>t$ we find, with the procedure outlined above,

$$\begin{aligned} G^{0,00}{}_{12,12}(t',t)=&\int_0^t dt_1\int_0^{t_1} dt_2[g_{00}(t_1,t_2,t)G^{0,00}{}_{12,12}(t_1,t_2)\\ &+g_{-0}(t_1,t_2,t)G^{0,00}{}_{22,22}(t_1,t_2)]+\text{c.c.},\\ g_{j0}(t_1,t_2,t)=&\tfrac{1}{3}f_{j0'}\exp[-w_{j0}(t_1-t_2)-\lambda_1(t-t_1)],\\ f_{j0'}=&\tfrac{1}{16}\hbar^2\gamma_e{}^2\gamma_N{}^2f_{j0}, \end{aligned} \tag{77}$$

where f_{jk} is defined in Eq. (34). For the new function $G^{0,00}{}_{22,22}(t_1,t_2)$, $t_1>t_2$, we obtain in a similar way

$$\begin{aligned} G^{0,00}{}_{22,22}(t',t)=&\tfrac{1}{2}e^{-\lambda_1 t}-\int_0^t dt_1\int_0^{t_1} dt_2[g_{-0}(t_1,t_2,t)+g_{00}(t_1,t_2,t)]G^{0,00}{}_{22,22}(0,t_2)\\ &+\int_0^t dt_1\int_0^{t_1} dt_2[g_{-0}(t_1,t_2,t)G^{0,00}{}_{12,12}(t_1,t_2)+g_{00}(t_1,t_2,t)G^{0,00}{}_{22,22}(t_1,t_2)]+\text{c.c.} \end{aligned} \tag{78}$$

Finally, the function $G^{0,00}{}_{22,22}(0,t_2)$, which is new because Eq. (78) is valid only for $t'>t$, is obtained from Eq. (76) with $t'=0$

$$\begin{aligned} G^{0,00}{}_{22,22}(0,t)=&e^{-\lambda_1 t}-\int_0^t dt_1\int_0^{t_1} dt_2[g_{-0}(t_1,t_2,t)\\ &+g_{00}(t_1,t_2,t)]G^{0,00}{}_{22,22}(0,t_2). \end{aligned} \tag{79}$$

This closes the set of equations for this contribution to D_{21}. As the right-hand sides of Eqs. (77) and (78) are independent of t', the equal time Green's functions obey, in the present approximation of the relations

$$\begin{aligned} G^{0,00}{}_{12,12}(t',t)=&G^{0,00}{}_{12,12}(t,t), \quad (t'\geq t)\\ G^{0,00}{}_{22,22}(t',t)=&G^{0,00}{}_{22,22}(t,t), \quad (t'\geq t). \end{aligned} \tag{80}$$

Equation (79) can now be solved, using a Laplace transformation. Defining

$$G(0,v)=\int_0^\infty e^{-vt}G(0,t)dt, \tag{81}$$

and

$$g_{j0}(v)=\tfrac{1}{3}f_{j0}'(v+\lambda_1)^{-1}(v+w_{j0})^{-1}, \tag{82}$$

one has

$$G^{0,00}{}_{22,22}(0,v)=[1+g_{00}(v)+g_{-0}(v)]^{-1}(v+\lambda_1)^{-1}. \tag{83}$$

Defining the Laplace transform of the equal time Green's function by

$$G(v)=\int_0^\infty e^{-vt}G(t,t)dt. \tag{84}$$

We obtain from Eq. (77)

$$G^{0,00}{}_{12,12}(v)=2g_{00}G^{0,00}{}_{12,12}(v)+[g_{-0}(v)+g_{-0}{}^*(v)]G^{0,00}{}_{22,22}(v), \tag{85}$$

and from Eqs. (78) and (83)

$$G^{0,00}{}_{22,22}(v)=2\,\mathrm{Re}G^{0,00}{}_{22,22}(0,v)-(v+\lambda_1)^{-1}+2g_{00}(v)G^{0,00}{}_{22,22}(v)+[g_{-0}(v)+g_{-0}{}^*(v)]\times G^{0,00}{}_{12,12}(v). \tag{86}$$

The Eqs. (83), (85), and (86) are readily solved. To find $G(t,t)$, we take the Laplace inversion, as in Eq. (44), which is equal to the sum of the residues of $G(v)\exp vt$ for the poles in the half-plane $\mathrm{Re}v<0$. The poles can be obtained by solving a cubic equation. For simplicity, and because it is the most interesting case, we will only consider weak fields, for which $\omega\approx 0$. $G(v)$ is then given by

$$G^{0,00}{}_{12,12}(v)=\tfrac{2}{3}f_{-0}'(v+1/\tau_c)[(v+\lambda_1)(v+1/\tau_c)+\tfrac{2}{3}(f_{-0}'-f_{00}')]^{-1}[(v+\lambda_1)(v+1/\tau_c)+\tfrac{2}{3}(f_{-0}'+f_{00}')]^{-1}, \tag{87}$$

$$G^{0,00}{}_{22,22}(v)=[(v+\lambda_1)(v+1/\tau_c)-\tfrac{2}{3}f_{00}'](\tfrac{2}{3}f_{-0}')^{-1}G^{0,00}{}_{12,12}(v). \tag{88}$$

The poles are

$$v_\pm'=-(\xi+\lambda_1)\pm[\xi^2-\tfrac{2}{3}(f_{-0}'-f_{00}')]^{\frac{1}{2}},$$
$$v_\pm''=-(\xi+\lambda_1)\pm[\xi^2-\tfrac{2}{3}(f_{-0}'+f_{00}')]^{\frac{1}{2}}, \tag{89}$$

where $\xi=\frac{1}{2}(1/\tau_c-\lambda_1)$, with which $G(t,t)$ can be obtained as indicated above. This gives

$$G^{0,00}{}_{12,12}(t,t)=\tfrac{1}{4}(f_{-0}'/f_{00}')\times\{(1+\xi/\eta')\exp[-(\lambda_1+\xi-\eta')t]+(1-\xi/\eta')\exp[-(1/\tau_c-\xi+\eta')t]-(1+\xi/\eta'')\exp[-(\lambda_1+\xi-\eta'')t]-(1-\xi/\eta'')\exp[-(1/\tau_c-\xi+\eta'')t]\}, \tag{90}$$

where

$$\eta'=[\xi^2-\tfrac{2}{3}(f_{-0}'-f_{00}')]^{1/2},$$
$$\eta''=[\xi^2-\tfrac{2}{3}(f_{-0}'+f_{00}')]^{1/2}, \tag{91}$$

and a similar expression for $G^{0,00}{}_{22,22}(t,t)$.

With this result, we now return to the full integral equation for $G^{0,00}{}_{12,12}(t,t)$, as obtained from Eq. (75). In its right-hand side, we substitute for $G^{0,00}{}_{12,12}$ the result (90), and the corresponding expression for $G^{0,00}{}_{22,22}$, while for the other Green's functions which appear in it, viz., $G^{m,m'}{}_{\xi 2,\xi' 2}(t_1,t_2)$, we substitute:

$$G^{m,m'}{}_{\xi 2,\xi' 2}(t_1,t_2)=\delta_{\xi 2}\delta_{\xi' 2}\exp[-\lambda_m(t_1-t_2)-\lambda_{m'}t_2]. \tag{92}$$

This is the "free" Green's Function, obtained from the definition (74) by replacing $U(t)$ with $U(0)$. We can expect results with this substitution to be valid for times satisfying $\lambda' t\ll 1$, where λ' is a normal part of a rate due to the dipole interaction. An evaluation of the integrals then shows that, if $\lambda_1\gg\lambda'$ (which we have assumed throughout this section) the resulting expression for G is obtained from the result of our perturbation calculation by replacing only the dangerous term, which is

$$\mathrm{Re}\tfrac{2}{3}f_{-0}'e^{-\lambda_1 t}\left[\frac{t}{w_{-0}-\lambda_1}-\frac{1-\exp(\lambda_1-w_{-0})t}{(w_{-0}-\lambda_1)^2}\right]$$

[see Eq. (72)] by the whole right-hand side of Eq. (90). This shows that our procedure, to select in first instance only terms connected by dangerous combinations, is consistent, because a normal part of G is not affected by this treatment of the dangerous terms and remains small compared with them when $\xi\approx 0$.

Turning now to the other Green's functions which according to Eq. (71), contribute directly to D_{21}, and looking for dangerous connections only, one finds that $G^{0,00}{}_{32,32}(t',t)$ and $G^{0,00}{}_{42,42}(t',t)$, with $t'\geq t$, form a closed set. However, the corresponding integral equations lack the inhomogeneous term which we previously found in Eq. (78). As a consequence, these Green's functions remain small. Another contribution to D_{21} comes from $G^{0,0+}{}_{32,12}$, which is linked by the dangerous combination $A_{0+}(t)A_{0-}(t_1)A_{00}(t_2)$ to $G^{0,00}{}_{12,12}$ and $G^{0,00}{}_{22,22}$. A close inspection shows, that

$$G^{0,0+}{}_{32,12}=2G^{0,00}{}_{12,12} \tag{93}$$

as far as dangerous terms are concerned. Finally, $G^{0,0-}{}_{12,12}$ is connected through $A_{0-}(t)A_{0+}(t_1)A_{00}(t)$ with $G^{0,00}{}_{32,32}$ and $G^{0,00}{}_{42,42}$, but remains small because the latter remain small.

In an entirely similar manner we find, for Green's functions contributing to the transitions D_{12}, D_{14} and D_{23}, sets of coupled equations for $G^{0,00}{}_{21,21}(t',t)$, $G^{0,00}{}_{11,11}(t',t)$, $G^{0,00}{}_{11,11}(0,t)$; for $G^{0,00}{}_{34,34}(t',t)$, $G^{0,00}{}_{44,44}(t't)$, $G^{0,00}{}_{44,44}(0,t)$, and for $G^{0,00}{}_{43,43}(t',t)$, $G^{0,00}{}_{33,33}(t',t)$, $G^{0,00}{}_{33,33}(0,t)$. We find that, except for

normal parts, all the relevant functions are proportional to $G^{0,00}{}_{12,12}$:

$$G^{0,00}{}_{21,21}=G^{0,00}{}_{34,34}=G^{0,00}{}_{43,43}=G^{0,00}{}_{12,12}, \quad (94)$$

while

$$G^{0,0+}{}_{41,21}=-G^{0,0-}{}_{14,34}=-G^{0,0-}{}_{23,43}=2G^{0,00}{}_{12,12}. \quad (95)$$

Finally, inserting these results in the transition function $b(t)$, defined by Eq. (54) [$a(t)$ and $c(t)$ being normal throughout], we have

$$b(t)=Q\,\mathrm{Re}[-2L_{++}(\lambda_1,\lambda_2,\lambda_1,t)-\tfrac{1}{3}L_{+-}(\lambda_1,\lambda_2,\lambda_1,t)] +6G^{0,00}{}_{12,12}(t,t), \quad (96)$$

which is obtained from the perturbation expansion, Eq. (56), for $b(t)$ by replacing the term $Q\,\mathrm{Re}L_{+0}(\lambda_1,0,\lambda_1,t)$ with $6G$ from Eq. (90).

Equation (96) is valid for all ω, but the Eq. (90) for G is valid only for $\omega\approx 0$. It reduces to Eq. (56), when $\xi^2\gg f_{-0}'$, i.e., when the resonance condition is not satisfied. One sees this by expanding Eq. (90) with respect to $(f_{-0}'\pm f_{00}')/\xi^2$; the second and fourth terms of Eq. (90) are negligible in this case. The resonance appears as follows: When $\xi^2=\frac{2}{3}(f_{-0}'+f_{00}')$, the third and fourth terms in Eq. (90) become infinite, but their sum remains finite. When $\xi^2=\frac{2}{3}(f_{-0}'-f_{00}')$, the first and second terms show a similar behavior. When ξ^2 is close to one of these values, one has for the contribution of the two singular terms, in good approximation, writing $f'=\frac{2}{3}(f_{-0}'\pm f_{00}')$:

$$G^{0,00}{}_{12,12}(t,t) \sim 2\{\cosh[t(\xi^2-f')^{1/2}]+[\xi/(\xi^2-f')^{1/2}] \times\sinh[t(\xi^2-f')^{1/2}]\}\exp[-(\lambda_1+\xi)t] \sim 2[1+t(f')^{1/2}]\exp\{-[\lambda_1+(f')^{1/2}]t\}. \quad (97)$$

This equation is valid for all times with $\lambda' t\ll 1$. Because of the fact that $(f')^{\frac{1}{2}}\approx(\lambda_1\lambda')^{\frac{1}{2}}\gg\lambda'$, this range of validity includes times with $t(f')^{\frac{1}{2}}\gg 1$. For these times, the rate of change of (97) is therefore $(f')^{\frac{1}{2}}$, which is much larger than λ'. For $t(f')^{\frac{1}{2}}\ll 1$, (97) is proportional to t^2.

6. CONCLUSIONS

The system analyzed in this paper has as a characteristic feature that there are two noncommuting and statistically independent random perturbations. This severely limits the usefulness of a straightforward perturbation expansion. We have employed a new technique, based in part on a description of Schrödinger's equation for a random Hamiltonian in terms of a Fokker-Planck equation. This enabled us to give a complete evaluation of the time-dependence of the diagonal elements of the density matrix. Two results which are perhaps of more general interest are (1) that this time dependence cannot be described in terms of rate equations and (2) that under certain conditions—which we termed resonance—the interference between the two perturbations leads to a considerable enhancement of the rates of change of these matrix elements. The nonexistence of rate equations spells trouble for a semiclassical analysis of magnetic resonance and related phenomena. Indeed, it seems of interest to see what becomes of the F-P equation and its applications to the present systems in the presence of an oscillating field. We hope to report on this problem at a future occasion. The explicit treatment in the case of resonance necessitated another nonperturbative device, which we found in a formulation of the equations for the density matrix by means of integral equations, and by treating selected terms in these equations in an exact manner. The resonance condition is simply that the motional correlation time is approximately equal to the electronics relaxation time. While this could perhaps be produced in a suitably chosen system by a variation of the temperature, it will not be easy to observe this effect in a free precession experiment (in weak fields), to which our calculations apply. We think, however, that this effect could be detected by studying the Overhauser effect.