On the theory of multispin cross relaxation and dynamic polarization of nuclei in solids

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A formalism is developed that makes it possible to treat multispin transitions in magnetic resonance in a unified manner. Three- and four-spin processes in cross relaxation and dynamic polarization of nuclei are treated. The results obtained are compared with available experimental data.

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Problems of cross relaxation and dynamic polarization of nuclei and electron-spin systems form an important part of the theory of magnetic resonance in solids. The quantum statistical theory of these phenomena is well developed and is applicable to the description of a wide range of experimental data.[1,2] Most of the problems examined up to now, however, have usually been treated only in the lowest order of perturbation theory, although experimental data on the dynamic polarization of nuclei are available[3] that can be explained only in terms of multispin processes that appear in higher orders of perturbation theory. In principle, multispin processes can be taken into account within the framework of any quantum statistical formalism—e.g. using Zubarev's nonequilibrium statistical operator (NSO) method,[4] which is widely employed in the theory of magnetic resonance. However, it is difficult to calculate kinetic coefficients in higher orders of perturbation theory. Moreover, when solving such problems it is not always obvious how to choose the subsystem operators with allowance for higher order corrections.

In this paper we present a formalism that makes it possible to describe a wide range of the problems mentioned above in a unified manner. This formalism is based on an analogy with the so-called uniform convergence method,[5] which is widely used in nonlinear mechanics.

In order to reach the most general mathematical formulation of the problem, we consider a simple model: a system of spins of two types with dipole-dipole (*d–d*) interactions in a static magnetic field H_0. The Hamiltonian for such a system has the form

$$\mathscr{H}=\omega_S S_z+\omega_I I_z+\mathscr{H}_{II}{}^d+\mathscr{H}_{IS}{}^d+\mathscr{H}_{SS}{}^d. \tag{1}$$

Here $\omega_{S,I}=\gamma_{S,I}H_0$, where the $\gamma_{S,I}$ are the gyromagnetic ratios of the spins I and S, and the last three terms in (1) are the Hamiltonians for the *d-d* interactions between the spins I and I, I and S, and S and S, respectively.

We shall use the notation[2]

$$\{I^+S^z\}=\sum_{i,j} c_{ij}I_i^+S_j^z;\qquad \{S^+S^-\}=\sum c_{ij}S_i^+S_j^-$$

and so on. In view of the fact that the Hamiltonian $\mathscr{H}_{IS}^d$ contains the terms $\{I^+S^-\}$ and $\{I^-S^+\}$, simultaneous flips of the spins I and S (flip-flops) may take place. These processes are important when $\omega_S\sim\omega_I$—more accurately, when the difference $\Delta=\omega_I-\omega_S$ is equal to ω_d in order of magnitude (ω_d is the line width due to the interaction), and it is sufficient to use only the first order of perturbation theory in describing them. However, multispin relaxation processes, i.e., processes in which three or more spins flip simultaneously, may take place in the system. The structure of the terms in the *d-d* interaction that give rise to cross relaxation becomes clearly evident when Eq. (1) is transformed to a new coordinate system by the unitary transformation

$$U=\exp\left[it(\omega_S S_z+\omega_I I_z)\right]. \tag{2}$$

In this coordinate system the Hamiltonian takes the form

$$\mathscr{H}_d(t)=\sum_{n,m=0,\pm1,\pm2}\mathscr{H}_{nm}\exp[i(n\omega_I+m\omega_S)t], \tag{3}$$

where the $\mathscr{H}_{nm}$ are defined as follows:

$$\mathscr{H}_{00}=\{I^zI^z\}+\{S^zI^z\}+\{S^zS^z\}+\{I^+I^-\}+\{S^+S^-\},$$
$$\mathscr{H}_{10}=\{I^+I^z\}+\{I^+S^z\}$$

and so on. As is evident from (3), $\mathscr{H}_d(t)$ is a quasiperiodic function of time with the two fundamental frequencies ω_I and ω_S. In the general case we shall have to deal with a system described by the Liouville equation

$$id\rho/dt=[\mathscr{H}(t),\ \rho] \tag{4}$$

with a quasiperiodic Hamiltonian $\mathscr{H}(t)$. It is convenient to rewrite Eq. (4) in dimensionless form:

$$id\rho'/dt'=\varepsilon[\mathscr{H}'(t'),\ \rho'], \tag{5}$$

where $t'=\omega_i$ is the "dimensionless" time and ω_i is one of the fundamental frequencies [for example, one may take either ω_I or ω_s for ω_i in (3)]. We shall assume that the condition $\omega_i\|\mathscr{H}\|\ll 1$ is satisfied, where $\|\mathscr{H}\|$ is the "magnitude" of the spin-spin interaction Hamiltonian in frequency units, i.e.

$$\|\mathscr{H}\|^2=\operatorname{Sp}\mathscr{H}^2/\operatorname{Sp}1.$$

Further,

$$\varepsilon=\|\mathscr{H}\|/\omega_i,\qquad \mathscr{H}'=\mathscr{H}/\|\mathscr{H}\|.$$

Equations of the form of Eq. (5) occur frequently in nonlinear mechanics, and there are many ways of solving them. The basic purpose of the present work is to find a transformation of Eq. (5) such that the transformed density matrix

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will satisfy a Liouville equation with an effective Hamiltonian that will describe multispin resonance transitions in any order of interest to us.

In analogy with the accelerated-convergence method,[5] we perform a series of canonical transformations on Eq. (5):

$$\rho^{(n)}=\exp\,[\varepsilon^n A_n(t')]\rho^{(n-1)}\exp\,[-\varepsilon^n A_n(t')]; \quad \rho^{(0)}=\rho' \tag{6}$$

(no summation over *n*!).

The present method differs from the usual variants of the averaging method in that we do not improve the transformation of ρ' by including further higher-order terms in order to obtain an approximate expression for ρ', but repeatedly perform a transformation of the same type.

Using the formula

$$\frac{d}{dt'}e^{A(t')}=\left(\frac{e^{c_A}-1}{c_A}\dot{A}(t')\right)e^{A(t')}, \quad c_A\dot{A}=[A,\dot{A}],$$

which was proved in Ref. 6, we obtain

$$\begin{gathered} id\rho^{(n)}/dt'=[\mathscr{H}^{(n)}(t'),\,\rho^{(n)}],\\ \mathscr{H}^{(n)}=i[(e^{c_A}-1)/c_A]\dot{A}+e^A\mathscr{H}^{(n-1)}e^{-A}, \end{gathered} \tag{7}$$

where $A=\varepsilon^n A_n$ and $\mathscr{H}^0=\mathscr{H}'$.

We shall choose the quantities A_n so that in the corresponding order in ε the Hamiltonian $\mathscr{H}^{(n)}$ will not contain rapidly oscillating terms with characteristic frequencies higher than or of the order of unity.

In the general case when $\mathscr{H}'(t')$ is a quasiperiodic function of time with two or more basic frequencies, $\mathscr{H}^{(n)}(t')$ may contain not only rapidly oscillating terms, but also slowly varying terms with frequencies of the order of ε. Such terms must be retained in the effective Hamiltonian, since, as will be shown below, it is just they that are responsible for the multispin cross relaxation processes.

Let us introduce two operations: an averaging operation,

$$\overline{\mathscr{H}}=\lim\frac{1}{T}\int_0^T dt\mathscr{H}(t), \tag{8}$$

and an integration operation

$$\tilde{\mathscr{H}}=i\int^t dt'[\mathscr{H}(t')-\mathscr{H}]. \tag{9}$$

It is understood that in formula (9) the antiderivative is taken only at the upper integration limit.

It is easy to see that the operations (8) and (9) have the properties

$$\overline{\overline{\mathscr{H}}}=0, \quad \overline{\tilde{\mathscr{H}}}=0.$$

Now if we expand (7) in powers of A obtain

$$\begin{aligned} \mathscr{H}^{(n)}&=i\dot{A}+{}^1\!/_2 i[A,\,\dot{A}]+{}^1\!/_6 i[A,\,[A,\,\dot{A}]]+\dots\\ &+\mathscr{H}^{(n-1)}+[A,\,\mathscr{H}^{(n-1)}]+{}^1\!/_2[A,\,[A,\,\mathscr{H}^{(n-1)}]]+\dots\\ &=i\varepsilon^n\dot{A}_n+{}^1\!/_2 i\varepsilon^{2n}[A_n,\,\dot{A}_n]+{}^1\!/_2 i\varepsilon^{3n}[A_n,\,[A_n,\,\mathscr{H}^{(n-1)}]]+\dots\\ &+\mathscr{H}^{(n-1)}+\varepsilon^n[A_n,\,\mathscr{H}^{(n-1)}]+{}^1\!/_2\varepsilon^{2n}[A_n,\,[A_n,\,\mathscr{H}^{(n-1)}]]+\dots. \end{aligned}$$

In particular, the first step of transformation (6) yields

$$\begin{aligned} \mathscr{H}^{(1)}&=i(\varepsilon\dot{A}_1+{}^1\!/_2\varepsilon^2[A_1,\,\dot{A}_1]+{}^1\!/_6\varepsilon^3[A_1,\,[A_1,\,\dot{A}_1]]+\dots)\\ &+\varepsilon\mathscr{H}'+\varepsilon^2[A_1,\,\mathscr{H}']+{}^1\!/_2\varepsilon^3[A_1,\,[A_1,\,\mathscr{H}']]+\dots. \end{aligned} \tag{10}$$

For clarity we shall take a closer look at the case in which $\mathscr{H}'$ is a quasiperiodic function with two fundamental frequencies ω_1 and ω_2 ($\omega_1/\omega_2\neq k/l$, where k and l are integers) so that $\mathscr{H}'$ can be expressed in the form

$$\mathscr{H}'(t')=\sum_{n,m}\mathscr{H}_{nm}'\exp[i(n\omega_1+m\omega_2)t']. \tag{11}$$

We shall assume that the sum (11) contains a term $\mathscr{H}_{n'm'}$ (in general there may be several such terms) that satisfies the condition

$$n'\omega_1+m'\omega_2\sim\varepsilon.$$

Now we introduce the slowly varying quantity

$$\vartheta_1=\varepsilon\Delta_1 t'=(n'\omega_1+m'\omega_2)t'$$

and perform the averaging operation (8) only at frequencies that satisfy the condition

$$n\omega_1+m\omega_2\gg\varepsilon,$$

so that

$$\overline{\mathscr{H}}(\vartheta_1)=\mathscr{H}_{00}+\mathscr{H}_{n'm'}e^{i\vartheta_1}. \tag{12}$$

If we now choose A_1 in the form

$$\begin{aligned} A_1=\tilde{\mathscr{H}}&=i\int^t dt'[\mathscr{H}(t')-\overline{\mathscr{H}}]\\ &=\sum_{n,m\neq n',m'}\frac{1}{n\omega_1+m\omega_2}\mathscr{H}_{nm}\exp[i(n\omega_1+m\omega_2)t], \end{aligned} \tag{13}$$

all the rapidly oscillating terms in (10) will cancel out to the first order in ε. Actually, it follows from (13) that

$$i\dot{A}_1+(\mathscr{H}-\overline{\mathscr{H}})=0,$$

so that $\mathscr{H}^{(1)}$ takes the form

$$\begin{aligned} \mathscr{H}^{(1)}&=\varepsilon\overline{\mathscr{H}}(\vartheta_1)-{}^1\!/_2\varepsilon^2[\tilde{\mathscr{H}},\,\mathscr{H}-\overline{\mathscr{H}}]+\varepsilon^2[\tilde{\mathscr{H}},\,\overline{\mathscr{H}}]\\ &-{}^1\!/_6\varepsilon^3[\tilde{\mathscr{H}},\,[\tilde{\mathscr{H}},\,\mathscr{H}-\overline{\mathscr{H}}]]+{}^1\!/_2\varepsilon^3[\tilde{\mathscr{H}},\,[\tilde{\mathscr{H}},\,\mathscr{H}]]+\dots. \end{aligned} \tag{14}$$

Equation (14) contains no rapidly oscillating terms in the first order; such terms appear only in the higher orders.

If we are interested only in the first approximation, it is sufficient to retain only $\varepsilon\overline{\mathscr{H}}(\vartheta_l)$ in (14). To obtain the next approximation one must perform the transformation (6) again—this time on Eq. (14). Each time transformation (6) is applied the slowly varying terms must be singled out and the averaging operation (8) must be applied only to the rapidly oscillating terms—otherwise the expression for A_n will contain small denominators. For example, if we take $\overline{\mathscr{H}}=\mathscr{H}_{00}$ in place of (12), A_1 (Eq. (13)) will contain a small denominator $\sim 1/\varepsilon\Delta_1$. Thus, a correctly constructed effective Hamiltonian will depend on slowly varying quantities.

$$\mathscr{H}_{\text{eff}}=\mathscr{H}_{\text{eff}}(\vartheta_1,\,\vartheta_2,\dots).$$

Now we shall give an expression for the effective Hamiltonian accurate up to terms of the order ε^3. In doing this we shall assume that resonance terms arise each time transformation (6) is applied. At the second stage we have

$$\mathcal{H}^{(2)}=i\varepsilon^2 A_2+\mathcal{H}^{(1)}+\varepsilon^3[A_2,\overline{\mathcal{H}}]+\ldots,$$

$$\mathcal{H}^{(2)}_{\text{eff}}={}^1/_2\,\overline{[\tilde{\mathcal{H}},\mathcal{H}]},\qquad A_2={}^1/_2\,[\tilde{\mathcal{H}},\mathcal{H}+\overline{\mathcal{H}}]^{\sim}. \tag{15}$$

Similarly, in the third order we obtain

$$\mathcal{H}^{(3)}_{\text{eff}}={}^1/_3\,\overline{[\tilde{\mathcal{H}},[\tilde{\mathcal{H}},\mathcal{H}+\overline{\mathcal{H}}/2]]}. \tag{16}$$

Thus, an effective Hamiltonian accurate to ε^3 has the form

$$\mathcal{H}_{\text{eff}}=\varepsilon\overline{\mathcal{H}}+{}^1/_2\varepsilon^2\,\overline{[\tilde{\mathcal{H}},\mathcal{H}]}+{}^1/_3\varepsilon^3\,\overline{[\tilde{\mathcal{H}},[\tilde{\mathcal{H}},\mathcal{H}+\overline{\mathcal{H}}/2]]}. \tag{17}$$

This expression is formally the same as the expression for the effective Hamiltonian in the classical[7] and quantum[6] cases, but, unlike the expression in Ref. 6, Eq. (17) has a slow time dependence since the averaging in (17) is taken, as in (12), only over the rapidly oscillating variables.

Now let us consider concrete examples.

1. Let us consider cross relaxation between the Zeeman and dipole subsystems in a solid. This problem has been an object of discussion in the liaterature.[8,9] In a rotating coordinate system, the Hamiltonian of the system takes the form

$$\mathcal{H}(t)=\sum_{n=0,\pm1,\pm2}\mathcal{H}_n{}^d e^{in\omega_0 t},$$

where the $\mathcal{H}^d_n$ are the operators for the secular and nonsecular parts of the d-d interaction (see Ref. 1 for the explicit form) and ω_0 is the Zeeman frequency ($\omega_0\gg\omega_d$). Since in this case $\mathcal{H}(t)$ is a periodic function of time, the effective Hamiltonian will be time independent in all orders. Since

$$[I_z,\mathcal{H}_n{}^d]=n\mathcal{H}_n{}^d,$$

while the general structure of the effective Hamiltonian in the αth order will have the form

$$\mathcal{H}^{(\alpha)}_{\text{eff}}=\sum_{n_1+n_2+\ldots+n_\alpha=0}\frac{c^{n_1n_2\ldots n_\alpha}}{\omega_0^{\alpha-1}}[\mathcal{H}_d{}^{n_1},[\mathcal{H}_d{}^{n_2}\ldots[\mathcal{H}_d{}^{n_{\alpha-1}},\mathcal{H}_d{}^{n_\alpha}]],$$

where the $c^{n_1\ldots n_\alpha}$ are certain coefficients, we have

$$[I_z,\mathcal{H}^{(\alpha)}_{\text{eff}}]=0.$$

This means that there are no resonance transitions between the Zeeman and dipole subsystems. Cross relaxation processes can take place only as a result of rapidly oscillating terms in frequencies $n\omega_0$.

The transition probability calculated with such terms contains the exponentially small factor $\exp(-n^2\omega_0^2/\omega_d^2)$.

2. Let us consider cross relaxation in a system described by Hamiltonian (3) for the case in which $\omega_S\sim 2\omega_I$ (i.e., the difference $\Delta=2\omega_I-\omega_S$ is to be of the order of ω_d). In this case resonance terms appear in the effective Hamiltonian (17) in the second order. In fact, on substituting Eq. (3) and

$$\tilde{\mathcal{H}}=\sum_{m,n}\frac{\mathcal{H}_{nm}\exp[i(m\omega_I+n\omega_S)t]}{m\omega_I+n\omega_S} \tag{18}$$

into formula (15), we obtain

$$\mathcal{H}_{\text{eff}}=A+Be^{-i\Delta t}+B^+e^{i\Delta t},$$

where

$$A=\mathcal{H}_{00}+\frac{1}{4\omega_I}[\mathcal{H}_{02},\mathcal{H}_{0-2}]+\frac{1}{2\omega_I}[\mathcal{H}_{01},\mathcal{H}_{0-1}]$$
$$+\frac{1}{2\omega_I}[\mathcal{H}_{20},\mathcal{H}_{-20}]$$
$$+\frac{1}{\omega_I}[\mathcal{H}_{10},\mathcal{H}_{-10}]+\frac{1}{3\omega_I}[\mathcal{H}_{11},\mathcal{H}_{-1-1}]+\frac{1}{\omega_I}[\mathcal{H}_{-11},\mathcal{H}_{1-1}],$$

$$B=\frac{1}{2\omega_I}[\mathcal{H}_{01},\mathcal{H}_{-20}]+\frac{1}{\omega_I}[\mathcal{H}_{-11},\mathcal{H}_{-10}].$$

Here A is the secular part of the d-d interaction and B is responsible for three-spin cross relaxation processes. Starting from the general concepts of spin-temperature theory,[2] it is not difficult to derive equations for the dynamics of cross relaxation. Since $[I_z,A]=0$ and $[S_z,A]=0$, it must be assumed that a quasiequilibrium state with the density matrix

$$\xi=(1-\alpha_I\omega_I I_z-\alpha_S\omega_S S_z-\beta_d A)/\mathrm{Sp}\,1, \tag{19}$$

where α_I, α_S, and β_d are the inverse temperatures of the corresponding subsystems, will be established in the system in a time of the order of ω_d^{-1}.

To derive the equations for the changes of the inverse temperatures we use the equation for the slowly varying part of the density matrix that was obtained earlier[10]:

$$\frac{d\xi}{dt}=-\lim_{T\to\infty,\varepsilon\to0}\sum\frac{1}{\omega_n+i\varepsilon}[V_n[V_{-n},\xi]], \tag{20}$$

where

$$\omega_n=2\pi n/T,\quad n=0,\pm1,\pm2,\ldots,$$

$$V_n=\frac{1}{T}\int_0^T dt\,V(t)e^{-i\omega_n t},\qquad V(t)=\exp(i\mathcal{H}_0 t)\,V\exp(-i\mathcal{H}_0 t).$$

In this case V must be taken as the operator

$$Be^{i\Delta t}+B^+e^{-i\Delta t},$$

and $\mathcal{H}_0$ must be taken as the operator A, in which it is sufficient to retain only $\mathcal{H}_{00}$.

On substituting Eq. (19) into (20), multiplying both sides successively by I_z, S_z, and A, and passing to the limit $T\to\infty$ and $\varepsilon\to0$, we obtain the following set of equations (the details of the calculations are similar to those presented in Ref. 10):

$$d\alpha_I/dt=-(c_S/2\omega_I)\,W(2\alpha_I\omega_I-\alpha_S\omega_S-\beta_d\Delta),$$
$$d\alpha_S/dt=(c_I/\omega_S)\,W(2\alpha_I\omega_I-\alpha_S\omega_S-\beta_d\Delta),$$
$$d\beta_d/dt=(\Delta/D^2)\,W(2\alpha_I\omega_I-\alpha_S\omega_S-\beta_d\Delta),$$

where

$$c_I=\mathrm{Sp}\,I_z{}^2/N,\qquad c_S=\mathrm{Sp}\,S_z{}^2/N,$$
$$N=\mathrm{Sp}\,I_z{}^2+\mathrm{Sp}\,S_z{}^2,\qquad D^2=\mathrm{Sp}\,(\mathcal{H}_{00})^2/c_Ic_SN,$$
$$W(\Delta)=\frac{1}{c_Ic_SN}\int_0^\infty \mathrm{Sp}\{VV(t)\}\cos\Delta t\,dt,$$
$$V=B+B^+,\qquad V(t)=\exp(i\mathcal{H}_{00}t)\,V\exp(-i\mathcal{H}_{00}t).$$

As was mentioned above, W is the probability for three-spin cross relaxation processes.

Now let us consider the case in which the condition $3\omega_I - \omega_S \sim \omega_d$ is satisfied. In this case the resonance terms appear only in the third order. On substituting Eqs. (3) and (18) into (16), we obtain

$$\mathscr{H}_{\text{eff}}^{(3)\,\text{res}} = Ae^{-i\Delta t} + A^+ e^{i\Delta t},$$

where

$$A = \frac{1}{\omega_1^2}[\mathscr{H}_{-10}, [\mathscr{H}_{-10}, \mathscr{H}_{-11}]] + \frac{1}{4\omega_1^2}[\mathscr{H}_{-11}, [\mathscr{H}_{-11}, \mathscr{H}_{-1-1}]]$$
$$+ \frac{1}{4\omega_1^2}[\mathscr{H}_{-20}, [\mathscr{H}_{-20}, \mathscr{H}_{11}]] + \frac{1}{3\omega_1^2}[\mathscr{H}_{-10}, [\mathscr{H}_{-20}, \mathscr{H}_{01}]]$$
$$+ \frac{1}{6\omega_1^2}[\mathscr{H}_{-20}, [\mathscr{H}_{-10}, \mathscr{H}_{01}]] + \frac{1}{12\omega_1^2}[\mathscr{H}_{-20}, [\mathscr{H}_{00}, \mathscr{H}_{-11}]].$$

The equations for the inverse temperatures can now be written down in complete analogy with the first case. In this case four-spin processes will be the most effective in cross relaxation.

Let us employ the formalism developed above to describe experiments on the dynamic polarization of nuclei.[3] In this paper we have investigated a system having spins of three types: proton and deuteron spins with the Zeeman frequencies ω_I and ω_M, and paramagnetic impurities with the frequency $\omega \approx \omega_S + p\omega_I + a\omega_M$, where p takes the value ± 1 and ± 2, and d takes the values ± 1 and 0. To describe the dynamic polarization of nuclei under these conditions one must resort to higher orders of perturbation theory. Our formalism substantially simplifies the calculations. Let us first consider the case in which $p, d = \pm 1$. We shall write down the part of the dipole-dipole interaction Hamiltonian that can contribute to the effective Hamiltonian in a rotating coordinate system; it has the form

$$\mathscr{H}(t) = \sum_{n,i} S_n^z (e^{i\omega_I t} v_{ni}^{(1)} I_i^+ + e^{-i\omega_I t} v_{ni}^{(-1)} I_i^-)$$
$$+ \sum_{n,j} S_n^z (e^{i\omega_M t} u_{nj}^{(1)} M_j^+ + e^{-i\omega_M t} u_{nj}^{(-1)} M_j^-)$$
$$+ \sum_{i,j} I_i^z (e^{i\omega_M t} a_{ij}^{(1)} M_j^+ + e^{-i\omega_M t} a_{ij}^{(-1)} M_j^-)$$
$$+ \sum_{i,j} M_j^z (e^{i\omega_I t} b_{ij}^{(1)} I_i^+ + e^{-i\omega_I t} b_{ij}^{(-1)} I_i^-)$$
$$+ \sum_{i,j} e^{i(\omega_I+\omega_M)t} c_{ij}^{(2)} I_i^+ M_j^+ + \sum_{i,j} e^{-i(\omega_I+\omega_M)t} c_{ij}^{-2)} I_i^- M_j^-$$
$$+ \sum_{i,j} c_{ij}^{(0)} (e^{i(\omega_I-\omega_M)t} I_i^+ M_j^- + e^{-i(\omega_I-\omega_M)t} I_i^- M_j^+)$$
$$+ \sum_{n,i} g_{ni} S_n^z I_i^z + \sum_{n,j} l_{nj} S_n^z M_j^z + {}^1/_4\omega_1 (e^{i(\omega_S-\omega)t} S^+ + e^{-i(\omega_S-\omega)t} S^-). \tag{21}$$

Here S, I, and M are the electron, proton, and deuteron spin operators, respectively.

In this case the resonance terms appear in the effective Hamiltinian in the third order. On substituting (21) into (16) we obtain

$$\mathscr{H}_{\text{eff}}^{(3)\,\text{res}} = \sum_{p,d} \{A_{p;d} \exp[i(\omega-\omega_S+p\omega_I+d\omega_M)t]$$
$$+ A_{p;d} \exp[-i(\omega-\omega_S+p\omega_I+d\omega_M)t]\},$$

$$A_{p;d} = \sum_{i,j,n} \left(pd \frac{\omega_1 a_{ij}^{(M)} v_{nj}^{(I)}}{4\omega_M(\omega-\omega_S)} + pd \frac{\omega_1 a_{ij}^{I)} u_{nj}^{(M)}}{4\omega_I(\omega-\omega_S)} \right.$$
$$\left. - \frac{\omega_1 c_{ij}^{(I+M)} (g_{ni}+l_{nj})}{12(\omega-\omega_S)^2} \right) S_n^- I_i^p M_j^d.$$

There are also time-independent secular terms, but because of their complexity we shall not give them here.

It follows from the general principles of nonequilibrium thermodynamics that a quasiequilibrium with the density matrix

$$\xi = \{1 - \alpha_S(\omega_S-\omega) S_z - \alpha_I \omega_I I_z - \alpha_M \omega_M M_z - \beta \mathscr{H}_d'\}/\text{Sp}\, 1.$$

will be established in the system in a time of the order of ω_d^{-1}. In analogy with the case treated earlier we can easily obtain a set of equations for the reciprocal temperatures:

$$\frac{d\alpha_S}{dt} = -\sum_{p,d} \frac{c_I c_M}{\omega - \omega} W_{p;d}[\alpha_S(\omega_S-\omega) - \alpha_I p\omega_I - \alpha_M d\omega_M + \beta\Delta_{p;d}]$$
$$- \frac{1}{T_S}(\alpha_S - \alpha_S^L),$$

$$\frac{d\alpha_I}{dt} = \sum_{p,d} \frac{c_S c_M}{n\omega_I} W_{p;d}[\alpha_S(\omega_S-\omega) - \alpha_I p\omega_I - \alpha_M d\omega_M + \beta\Delta_{p;d}]$$
$$- \frac{1}{T}(\alpha_I - \beta_L),$$

$$\frac{d\alpha_M}{dt} = \sum_{p,d} \frac{c_S c_I}{d\omega_M} W_{p;d}[\alpha_S(\omega_S-\omega) - \alpha_I p\omega_I - \alpha_M d\omega_M + \beta\Delta_{p;d}]$$
$$- \frac{1}{T}(\alpha_M - \beta_L),$$

$$\frac{d\beta}{dt} = -\sum_{p,d} \frac{\Delta_{p;d}}{D^2} W_{p;d}[\alpha_S(\omega_S-\omega) - \alpha_I p\omega_I - \alpha_M d\omega_M + \beta\Delta_{p;d}]$$
$$- \frac{1}{T}(\beta - \beta_L),$$

where α_S, α_I, and α_M are the reciprocal temperatures of the electron, and deuteron Zeeman subsystems, respectively; β is the reciprocal temperature of the *d-d* pool;

$$\Delta_{p;d} = \omega - \omega_S + p\omega_I + d\omega_M; \qquad \alpha_S^L = \beta_L \omega_S/(\omega_S - \omega);$$
$$W_{p;d} = \frac{1}{c_I c_S c_M N} \int_{-\infty}^{\infty} dt \cos\Delta t\, \text{Sp}(V_{p;d} V_{p;d}(t));$$
$$V_{p,d}(t) = \exp(i\mathscr{H}_d' t)\, V_{p;d} \exp(-i\mathscr{H}_d' t);$$
$$V_{p,d} = A_{p,d} + A_{p;d}^+; \qquad D^2 = \text{Sp}(\mathscr{H}_d')^2 / c_S c_I c_M N;$$

T_S, T_I, T_M, and T_β are the spin-lattice relaxation times of the corresponding subsystems; and

$$c_S = \text{Sp}\, S_z^2/N; \qquad c_I = \text{Sp}\, I_z^2/N; \qquad c_M = \text{Sp}\, M_z^2/N;$$
$$N = \text{Sp}\, S_z^2 + \text{Sp}\, I_z^2 + \text{Sp}\, M_z^2.$$

These equations do not include the effect of the alternating field in the lowest order since experimentally[3] the frequency mismatch greatly exceeds the electron line width, i.e., $|\omega - \omega_S| \gg \delta\omega$. Assuming that the electron width $\delta\omega$ is considerably greater than the nuclear width, we can obtain the following estimate[2] for $W_{p;d}$:

$$W_{p;d}(0) \sim \mathrm{Sp}(V_{p,d})/\delta\omega c_I c_S c_M N.$$

For simplicity we shall consider the case in which there is no bottleneck effect. Then, since $W_{p;d}$ is small, we can put $\alpha = \alpha_S^L$ and $\beta = \beta_L$ in Eqs. (21). On solving the second and third of Eqs. (21) for the steady-state case under the assumption that $\omega_I; \omega_M \gg \delta\omega$, we obtain

$$\Delta_I = \beta_L \frac{\omega_S}{p\omega_I} \frac{c_S c_M T_I W_{p;d}}{1 + W_{p;d} c_S (c_I T_M + c_M T_I)}, \tag{22}$$

$$\alpha_M = \beta_L \frac{\omega_S}{d\omega_M} \frac{c_I c_S T_M W_{p;d}}{1 + W_{p;d} c_S (c_I T_M + c_M T_I)}. \tag{23}$$

Now we shall consider various limiting cases. Assume that $W_{p,d} c_S c_I T_M \gg 1$ and $W_{p,d} c_S c_M T_I \gg 1$. Then

$$\alpha_I = \beta_L \frac{\omega_S}{p\omega_I} \frac{1}{1 + c_I T_M / c_M T_I}, \quad \alpha_M = \beta_L \frac{\omega_S}{d\omega_M} \frac{1}{1 + c_M T_I / c_I T_M}.$$

Here two limiting cases are possible: a) $c_I T_M / c_M T_I \gg 1$, and b) $c_I T_M / c_M T_I \ll 1$.

In case a) we have

$$\alpha_I = \beta_L \frac{\omega_S}{p\omega_I} \frac{c_M T_I}{c_I T_M}, \quad \alpha_M = \beta_L \frac{\omega_S}{d\omega_M}.$$

If further,

$$c_I T_M / c_M T_I > \omega_I / \omega_M,$$

the proton inverse temperature will be smaller than the deuteron inverse temperature (i.e. $\alpha_M > \alpha_I$).

In case b) we have

$$\alpha_I = \beta_L \frac{\omega_S}{p\omega_I}, \quad \alpha_M = \beta_L \frac{\omega_S}{d\omega_M} \frac{c_I T_M}{c_M T_I},$$

$$\alpha_I > \alpha_M \text{ when } c_I T_M / c_M T_I < \omega_M / \omega_I.$$

We can also treat other limiting cases in a similar way, staring with Eqs. (22) and (23).

The experimental values[3] of α_I and α_M are much smaller than their maximum values. This may be attributed to the fact that saturation was not achieved in the experiment, i.e., the conditions

$$c_S c_I T_M W_{p;d}, \; c_S c_M T_I W_{p;d} \ll 1.$$

were satisfied. If we also take account of the fact that the experimental conditions were such that the condition $\omega_M < \delta\omega_S$ was satisfied, we obtain

$$\alpha_I = \beta_L (\omega_S / p\omega_I) c_S c_M T_I (W_{p;+1} + W_{p;-1}),$$

$$\alpha_M = \beta_L (\omega_S / \omega_M) c_S c_I T_M (W_{p;+1} - W_{p;-1}).$$

It follows from this that

$$\frac{\alpha_I}{\alpha_M} = \frac{\omega_M c_M T_I (W_{p;+1} + W_{p;-1})}{p\omega_I c_I T_M (W_{p;+1} - W_{p;-1})}.$$

On substituting the experimental values[3] of ω_I, ω_M, c_M, and c_I into this equation we obtain

$$T_I / T_M \sim 10^2.$$

Such a large difference between T_I and T_M may be attributed to the fact that ω_I is approximately five times larger than $\delta\omega$, while the Fourier transform of the electron-spin-relaxation function falls off more rapidly at high frequencies than the usually assumed Lorentz curve.

Now we shall consider the case in which $\omega \approx \omega_S \pm 2\omega_I$. In this case the part of the d-d interaction Hamiltonian of interest to us has the form

$$\mathscr{H}' = \sum_{i,k} b_{ik}^{(+)} e^{i2\omega_I t} I_i^+ I_k^+ + \sum_{i,k} b_{ik}^{(-)} e^{-i2\omega_I t} I_i^- I_k^- - \frac{\omega_1}{4} (e^{i(\omega_S - \omega)t} S^+ + e^{-i(\omega_S - \omega)t} S^-).$$

In analogy with the previous case we obtain

$$\mathscr{H}_{\text{eff}}^{(3)\,\text{res}} = A \exp[i(\omega - \omega_S \pm 2\omega_I)t] + A^+ \exp[-i(\omega - \omega_S \pm 2\omega_I)t],$$

where

$$A = \mp {}^1/_6 \omega_1 b_{ik}^{(+)} g_{ni} (\omega - \omega_S)^{-2} S_n^- I_i^\pm I_k^\pm.$$

Without writing out the entire set of equations for the inverse temperatures, we note that, as in the preceding case, the conditions $\alpha = \alpha_S^L$ and $\beta_d = \beta_L$ are satisfied. It is therefore sufficient to write down only the equation for α_I:

$$\frac{d\alpha_I}{dt} = \pm \frac{c_S}{\omega_I} W[\alpha_S^L (\omega_S - \omega) \mp \alpha_I \omega_I + \beta_L \Delta] - \frac{1}{T_I} (\alpha_I - \beta_L),$$

$$\Delta = \omega - \omega_S \pm 2\omega_I, \qquad V = A + A^+,$$

$$\alpha_S^L = \beta_L \omega_S / (\omega_S - \omega), \qquad W(0) \sim \mathrm{Sp}\,(V^2)/\delta\omega c_I c_S N.$$

On solving this equation for the steady state case we obtain

$$\alpha_I = \pm \beta_L \frac{\omega_S}{\omega_I} \frac{c_S T_I W}{1 + c_S T_I W}.$$

Since the experimental increase in the proton polarization is very small,[3] it must be assumed that the condition $c_S T_I W \ll 1$ is satisfied, so that

$$\alpha_I = \pm \beta_L (\omega_S / \omega_I) c_S T_I W.$$

In conclusion, we note that nuclear polarization due to multispin processes has also been observed in recent experiments involving β active nuclei.[11] To explain these experiments, the authors of Ref. 11 used ideas similar to those developed on Refs. 6 and 12.

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