

urements<sup>11</sup> on uranium,  $L$  vacancies were produced by irradiating samples with x rays from molybdenum. This method of  $L$  vacancy production results in an appreciable proportion of  $L_I$  vacancies (15–20%), so this result is not directly comparable with the present work.

It may seem surprising that the  $L$  fluorescence yield measurements in this region do not appear to fall on a smoothly rising curve (see Fig. 5). It should be pointed out, however, that Coster-Kronig transitions of the  $L_{II} \rightarrow L_{III}M_V$  type are energetically possible at  $Z=90$  and above, and those of the  $L_{II} \rightarrow L_{III}M_{IV}$  type at  $Z=94$  and above. If the  $L_{II}$  and  $L_{III}$  subshell yields

are different, these Coster-Kronig transitions will introduce discontinuities in a plot of  $\omega_L$  versus  $Z$ .

No theoretical computations of  $L$  fluorescence yields for these elements were found although a program was begun by Rose and Goertzel.<sup>12</sup> Theoretical computations of  $L$  fluorescence yields for elements with lower  $Z$  have been carried out by Pincherle.<sup>13</sup>

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<sup>11</sup> H. Lay, *Z. Physik* **91**, 533 (1934).

<sup>12</sup> M. E. Rose (private communication).

<sup>13</sup> L. Pincherle, *Nuovo Cimento* **12**, 81 (1935).

## Nuclear Spin-Lattice Relaxation in Three-Spin Molecules\*

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The free longitudinal relaxation of the nuclear magnetization of systems of three identical spins  $\frac{1}{2}$  at the corners of an equilateral triangle is investigated using the semiclassical form of the density operator theory. The relaxation mechanism investigated is a fluctuating dipolar interaction between the spins. Assuming only that the symmetry of the thermal motion of the molecules preserves the complete equivalence of the three spins, the general relaxation equation is obtained before adopting models for this thermal motion. The effect of correlations between different pairwise interactions is studied; this effect can be more significant in the case of anisotropic reorientations possible in solids than for isotropic motion. For systems initially describable by a spin temperature, the effect of cross correlations always is to retard the relaxation. In general the relaxation is described by a sum of four exponentials, although three suffice for isotropic motion and two for the limit of long correlation times. An "effective relaxation time" is defined, the calculation of which is far simpler than that of the complete solution.

### 1. INTRODUCTION

THE THERMAL equilibration of nuclear spins with their surroundings often proceeds by means of a fluctuating magnetic dipolar interaction between the spins; the calculation of the longitudinal or spin-lattice relaxation has been much discussed.<sup>1</sup>

It has been realized that the nuclear paramagnetism need not necessarily approach its equilibrium value exponentially—that is, there need not be a single relaxation time  $T_1$ . For two important cases, however, the approach is exponential and  $T_1$  is well defined: the first is an isolated pair of interacting spins; the second is a system of any number of spins with no correlations between the interactions of the various *pairs* of spins.<sup>1,2</sup>

A more precise statement of this latter requirement will be made later.

The assumption of uncorrelated pair interactions is an attractive one, since it not only insures the existence of a single relaxation time  $T_1$  but also facilitates its calculation since different dipolar interactions contribute additively to  $T_1^{-1}$  under this assumption.

Hubbard<sup>3,4</sup> has examined carefully the problem of equivalent three- and four-spin molecules in a liquid with isotropic rotational diffusion of the molecules. He investigated the three-spin molecules at high temperatures and the four-spin molecules at many temperatures, finding two and three decaying exponentials involved in the approach of the nuclear magnetism to its equilibrium value at the "lattice" temperature. However, one of the relaxation times was found to be very close to the uncorrelated-pairs value and the other exponentials were found to be multiplied by small coef-

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<sup>1</sup> See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. VIII.

<sup>2</sup> P. S. Hubbard, *Rev. Mod. Phys.* **33**, 249 (1961).

<sup>3</sup> P. S. Hubbard, *Phys. Rev.* **109**, 1153 (1958); **111**, 1746 (1958).

<sup>4</sup> P. S. Hubbard, *Phys. Rev.* **128**, 650 (1962).

ficients. A similar result has been found for an asymmetric three-spin molecule.<sup>5</sup> This communication and one to appear by Hilt and Hubbard<sup>6</sup> contain the first examples of systems for which cross-correlations have a significant effect on the relaxation.

In order to examine the "many-body" aspects of equivalent three-spin molecules it is necessary to describe the relaxation in somewhat more general terms than previously before adopting models for the thermal motion of the molecules. The equations of motion are obtained in a convenient form in Sec. 2 and the properties of the solution are examined in Sec. 3. In Sec. 4 is introduced a rather simply calculated parameter which measures the significance of the cross-correlations, and some examples are discussed in Sec. 5.

## 2. RELAXATION MATRIX

The calculation will be based on the "semiclassical" approach of Redfield<sup>7</sup>; this method will be outlined briefly since the resulting Eqs. (2.6) differ somewhat from those given by Redfield.

We consider an ensemble of  $N$  systems of three identical spins  $\frac{1}{2}$ ,  $a$ ,  $b$ ,  $c$ , located at the corners of an equilateral triangle. Each spin system has the Hamiltonian

$$\hbar\mathcal{H} = \hbar\mathcal{H}_0 + \hbar\mathcal{H}_1, \quad (2.1a)$$

where

$$\mathcal{H}_0 = -\gamma H \sum_{j=a,b,c} I_z^{(j)}, \quad (2.1b)$$

with  $\gamma$  the gyromagnetic ratio and  $H$  the magnetic field applied in the  $+z$  direction in laboratory coordinates. The remainder of the Hamiltonian  $\mathcal{H}_1$  is small compared to  $\mathcal{H}_0$  and in the semiclassical treatment is taken to be a random function of time (with zero average) due to the thermal motion of the material particles bearing the spins.

The information necessary to describe a spin system is contained in the spin density operator  $\sigma$  which obeys the equation of motion

$$d\sigma^*/dt = -i[\mathcal{H}_1^*(t), \sigma^*] \quad (2.2a)$$

in the interaction representation,

$$\begin{aligned} \sigma^* &= \exp(i\mathcal{H}_0 t) \sigma \exp(-i\mathcal{H}_0 t), \\ \mathcal{H}_1^* &= \exp(i\mathcal{H}_0 t) \mathcal{H}_1 \exp(-i\mathcal{H}_0 t). \end{aligned} \quad (2.2b)$$

Abraham<sup>1</sup> has discussed the conditions under which Eqs. (2.2) lead to the more tractable form

$$d\sigma^*/dt = - \int_0^\infty \langle [\mathcal{H}_1^*(t), \mathcal{H}_1^*(t-\tau), \sigma^*(t) - \sigma^{(T)*}] \rangle_{av} d\tau. \quad (2.3)$$

Here  $\sigma^*$  now stands for the average value of the density operator over a statistical ensemble of systems subject to random Hamiltonians  $\mathcal{H}_1^*$ ; the angular brackets

stand for a similar ensemble average, and  $\sigma^{(T)*}$  is the equilibrium value of the density operator at temperature  $T$ ,

$$\sigma^{(T)*} = \sigma^{(T)} = \frac{\exp(-\hbar\mathcal{H}_0/kT)}{\text{tr}[\exp(-\hbar\mathcal{H}_0/kT)]}. \quad (2.4)$$

The conditions for the validity of Eq. (2.3) can be expressed in terms of a "correlation time"  $\tau_c$  defined roughly as a time characteristic of the atomic motion producing the fluctuations in  $\mathcal{H}_1$ ; they are that the equation not be used for times  $t < \tau_c$ , that there be no extreme departures of  $\sigma^*$  from  $\sigma^{(T)*}$  and that  $\mathcal{H}_0$  and  $\mathcal{H}_1$  satisfy

$$\hbar|\mathcal{H}_0| \ll kT, \quad \tau_c |\mathcal{H}_1| \ll 1. \quad (2.5)$$

Taking matrix elements of both sides of Eq. (2.3) in a representation with  $\mathcal{H}_0$  diagonal leads to

$$\frac{d\sigma_{\alpha\alpha'}^*}{dt} = \sum_{\beta\beta'} e^{i(\omega_{\alpha\beta} - \omega_{\alpha'\beta'})t} R_{\alpha\alpha'\beta\beta'} (\sigma_{\beta\beta'}^* - \sigma_{\beta\beta'}^{(T)*}); \quad (2.6a)$$

here  $\omega_{\alpha\beta} = (\alpha, \mathcal{H}_0 \alpha) - (\beta, \mathcal{H}_0 \beta)$ , and the constants  $R_{\alpha\alpha'\beta\beta'}$  are given by

$$\begin{aligned} R_{\alpha\alpha'\beta\beta'} &= J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha\beta}) + J_{\alpha\beta\alpha'\beta'}(\omega_{\beta'\alpha'}) \\ &\quad - \delta_{\alpha\beta} \sum_{\gamma} J_{\beta'\gamma\alpha'\gamma}(\omega_{\beta'\gamma}) - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\alpha\gamma\beta\gamma}(\omega_{\gamma\beta}), \end{aligned} \quad (2.6b)$$

where

$$J_{\alpha\beta\alpha'\beta'}(\omega) = \int_0^\infty e^{-i\omega\tau} P_{\alpha\beta\alpha'\beta'}(\tau) d\tau, \quad (2.6c)$$

with

$$P_{\alpha\beta\alpha'\beta'}(\tau) = \langle (\alpha, \mathcal{H}_1(t)\beta) (\beta', \mathcal{H}_1(t+\tau)\alpha') \rangle_{av}. \quad (2.6d)$$

The correlation functions  $P_{\alpha\beta\alpha'\beta'}(\tau)$  are assumed to be stationary (independent of  $t$ ) and even functions of  $\tau$ . The formulas given by Redfield<sup>7</sup> are equivalent to these for  $P_{\alpha\beta\alpha'\beta'}$  real, but we shall deal with cases where this is not true.

The rapidly varying terms of Eq. (2.6a) for which  $|\omega_{\alpha\beta} - \omega_{\alpha'\beta'}| \gg R_{\alpha\alpha'\beta\beta'}$  can be neglected compared to those secular terms for which  $|\omega_{\alpha\beta} - \omega_{\alpha'\beta'}| \ll R_{\alpha\alpha'\beta\beta'}$ . Since the longitudinal magnetization is determined by those matrix elements  $\sigma_{\alpha\alpha'}^* = \sigma_{\alpha\alpha'}$  for which  $\omega_{\alpha\alpha'} = 0$  and these are coupled secularly with only those elements  $\sigma_{\beta\beta'}^*$  satisfying  $\omega_{\alpha\alpha'} - \omega_{\beta\beta'} \ll R_{\alpha\alpha'\beta\beta'}$ , the relaxation is adequately described by the generalized master equation

$$d\sigma_{\alpha\alpha'}^*/dt = \sum'_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \sigma_{\beta\beta'}^*, \quad (2.7)$$

where the prime indicates the restrictions  $\omega_{\alpha\alpha'} = \omega_{\beta\beta'} = 0$ , and  $\sigma_{\beta\beta'}^* = \sigma_{\beta\beta'} - \sigma_{\beta\beta'}^{(T)}$ .

To proceed further it is necessary to choose a basis set and specify the interaction  $\mathcal{H}_1$ . For basic vectors we choose

$$\begin{aligned} |1\rangle &= |+++ \rangle, \\ |2\rangle &= | - + + \rangle, \quad |3\rangle = | + - + \rangle, \quad |4\rangle = | + + - \rangle, \\ |5\rangle &= | - - + \rangle, \quad |6\rangle = | - + - \rangle, \quad |7\rangle = | + - - \rangle, \\ |8\rangle &= | - - - \rangle. \end{aligned} \quad (2.8)$$

<sup>5</sup> G. W. Kattawar and M. Eisner, Phys. Rev. **126**, 1054 (1962).

<sup>6</sup> R. L. Hilt and P. S. Hubbard (private communication).

<sup>7</sup> A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).

For dipolar couplings between the spins  $\mathcal{H}_1$  can be written<sup>8</sup> where

$$\mathcal{H}_1 = \frac{\hbar\gamma^2}{r^3} \sum_{ij=a,b,ac,bc} (A_{ij} + B_{ij} + C_{ij} + D_{ij} + E_{ij} + F_{ij}), \quad (2.9a)$$

where  $r$  is the (constant) distance between any pair of spins, and the operators  $A-F$  are given by

$$\begin{aligned} A_{ij} &= 2\left(\frac{1}{5}\right)^{1/2} I_z^{(i)} I_z^{(j)} Y_{ij}^{(0)}, \\ B_{ij} &= -\frac{1}{2}\left(\frac{1}{5}\right)^{1/2} (I_-^{(i)} I_+^{(j)} + I_-^{(j)} I_+^{(i)}) Y_{ij}^{(0)}, \\ C_{ij} &= -\left(\frac{3}{10}\right)^{1/2} (I_+^{(i)} I_z^{(j)} + I_+^{(j)} I_z^{(i)}) Y_{ij}^{(1)}, \\ D_{ij} &= \left(\frac{3}{10}\right)^{1/2} (I_-^{(i)} I_z^{(j)} + I_-^{(j)} I_z^{(i)}) Y_{ij}^{(-1)}, \\ E_{ij} &= \left(\frac{3}{10}\right)^{1/2} (I_+^{(i)} I_+^{(j)}) Y_{ij}^{(2)}, \\ F_{ij} &= \left(\frac{3}{10}\right)^{1/2} (I_-^{(i)} I_-^{(j)}) Y_{ij}^{(-2)}, \end{aligned} \quad (2.9b)$$

$$\langle Y_{ab}^{(n)}(t) Y_{ab}^{(n)\dagger}(t+\tau) \rangle_{av} = \langle Y_{bc}^{(n)}(t) Y_{bc}^{(n)\dagger}(t+\tau) \rangle_{av} = \langle Y_{ac}^{(n)}(t) Y_{ac}^{(n)\dagger}(t+\tau) \rangle_{av} \quad (2.10a)$$

$$\begin{aligned} \langle Y_{ab}^{(n)}(t) Y_{bc}^{(n)\dagger}(t+\tau) \rangle_{av} &= \langle Y_{bc}^{(n)}(t) Y_{ac}^{(n)\dagger}(t+\tau) \rangle_{av} = \langle Y_{ac}^{(n)}(t) Y_{ab}^{(n)\dagger}(t+\tau) \rangle_{av} \\ &= \langle Y_{bc}^{(n)}(t) Y_{ab}^{(n)\dagger}(t+\tau) \rangle_{av}^\dagger = \langle Y_{ac}^{(n)}(t) Y_{bc}^{(n)\dagger}(t+\tau) \rangle_{av}^\dagger = \langle Y_{ab}^{(n)}(t) Y_{ac}^{(n)\dagger}(t+\tau) \rangle_{av}^\dagger. \end{aligned} \quad (2.10b)$$

(A dagger will be used to indicate the complex conjugate.) These requirements will be satisfied in each example considered later. It is easily seen that the  $j$  value of the first factor must be the same as that of the second for  $\omega_{\alpha\beta} = \omega_{\alpha'\beta'}$  and that the autocorrelation functions  $\langle Y_{ab}^{(n)}(t) Y_{ab}^{(n)\dagger}(t+\tau) \rangle_{av}$  are real; however, the cross-correlation functions  $\langle Y_{ab}^{(n)}(t) Y_{bc}^{(n)\dagger}(t+\tau) \rangle_{av}$  are in general complex.

The elements of the density matrix involved in the spin-lattice relaxation are those between states of equal energy, that is, the elements

$$\begin{array}{cccc} \sigma_{11} & & & \\ \sigma_{22} & \sigma_{23} & \sigma_{24} & \\ \sigma_{32} & \sigma_{33} & \sigma_{34} & \\ \sigma_{42} & \sigma_{43} & \sigma_{44} & \\ & \sigma_{55} & \sigma_{56} & \sigma_{57} \\ & \sigma_{65} & \sigma_{66} & \sigma_{67} \\ & \sigma_{75} & \sigma_{76} & \sigma_{77} \\ & & & \sigma_{88}. \end{array}$$

The calculation of the 400 matrix elements  $R_{\alpha\alpha'\beta\beta'}$  is facilitated by several symmetry conditions which follow from the Hermitian character of  $\mathcal{H}_1$ , the numbering of the basic vectors and the assumption that the correlation functions are stationary and even functions. Thus the following symmetry conditions may be verified:

$$\begin{aligned} P_{\alpha\beta\alpha'\beta'}(\tau) &= P_{\beta\alpha\beta'\alpha'}^\dagger(\tau) = P_{\alpha'\beta'\alpha\beta}^\dagger(\tau) \\ &= P_{9-\beta,9-\alpha,9-\beta',9-\alpha'}(\tau), \end{aligned} \quad (2.11a)$$

$$\begin{aligned} J_{\alpha\beta\alpha'\beta'}(\omega) &= J_{\beta\alpha\beta'\alpha'}^\dagger(-\omega) = J_{\alpha'\beta'\alpha\beta}^\dagger(-\omega) \\ &= J_{9-\beta,9-\alpha,9-\beta',9-\alpha'}(\omega), \end{aligned} \quad (2.11b)$$

<sup>8</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

$$I_{\pm}^{(i)} = I_x^{(i)} \pm i I_y^{(i)}. \quad (2.9c)$$

The functions  $Y_{ij}$  are the second-order spherical harmonics to  $4\pi$  (so that the isotropic mean squares are one) and are defined as follows:

$$\begin{aligned} Y_{ij}^{(0)} &= (5/4)^{1/2} (1 - 3 \cos^2 \theta_{ij}), \\ Y_{ij}^{(\pm 1)} &= \pm (15/2)^{1/2} \sin \theta_{ij} \cos \theta_{ij} e^{\mp i \varphi_{ij}}, \\ Y_{ij}^{(\pm 2)} &= - (15/8)^{1/2} \sin^2 \theta_{ij} e^{\mp 2i \varphi_{ij}}, \end{aligned} \quad (2.9d)$$

where  $\theta_{ij}$  and  $\varphi_{ij}$  are the polar angles of the vector  $\mathbf{r}_{ij}$  in the laboratory coordinate system.

We assume that the random motion of the molecules preserves the complete equivalence of the three spins in the sense of the following equations, necessary for the evaluation of the functions  $P_{\alpha\beta\alpha'\beta'}$ :

$$\begin{aligned} R_{\alpha\alpha'\beta\beta'}(H) &= R_{\alpha'\alpha\beta\beta'}^\dagger(H) = R_{\beta\beta'\alpha\alpha'}^\dagger(-H) \\ &= R_{9-\alpha',9-\alpha,9-\beta',9-\beta}(H). \end{aligned} \quad (2.11c)$$

Once the elements  $R_{\alpha\alpha'\beta\beta'}$  have been calculated, a partial solution is achieved by extracting "normal modes" in a manner originally used by Hubbard. We define

$$\Psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}, \quad (2.12a)$$

where

$$\begin{aligned} \psi_1 &= \frac{1}{2} [3\bar{\sigma}_{11} + \bar{\sigma}_{22} + \bar{\sigma}_{33} + \bar{\sigma}_{44} - \bar{\sigma}_{55} - \bar{\sigma}_{66} - \bar{\sigma}_{77} - 3\bar{\sigma}_{88}], \\ \psi_2 &= \frac{1}{2} [\bar{\sigma}_{11} - \bar{\sigma}_{22} - \bar{\sigma}_{33} - \bar{\sigma}_{44} + \bar{\sigma}_{55} + \bar{\sigma}_{66} + \bar{\sigma}_{77} - \bar{\sigma}_{88}], \\ \psi_3 &= \text{Re}[\bar{\sigma}_{23} + \bar{\sigma}_{34} + \bar{\sigma}_{42} - \bar{\sigma}_{56} - \bar{\sigma}_{67} - \bar{\sigma}_{75}], \\ \psi_4 &= \text{Im}[\bar{\sigma}_{23} + \bar{\sigma}_{34} + \bar{\sigma}_{42} - \bar{\sigma}_{56} - \bar{\sigma}_{67} - \bar{\sigma}_{75}]. \end{aligned} \quad (2.12b)$$

Further defining  $\omega_0 = \gamma H$  and

$$\begin{aligned} j_n &= \int_0^\infty \cos(n\omega_0\tau) \langle Y_{ab}^{(n)}(t) Y_{ab}^{(n)\dagger}(t+\tau) \rangle_{av} d\tau, \\ k_n &= \text{Re} \int_0^\infty \cos(n\omega_0\tau) \langle Y_{ab}^{(n)}(t) Y_{bc}^{(n)\dagger}(t+\tau) \rangle_{av} d\tau, \\ l_n &= \text{Im} \int_0^\infty \cos(n\omega_0\tau) \langle Y_{ab}^{(n)}(t) Y_{bc}^{(n)\dagger}(t+\tau) \rangle_{av} d\tau, \end{aligned} \quad (2.12c)$$

Eq. (2.7) is found to reduce to

$$\frac{d}{dt} \Psi = \kappa \mathbf{S} \Psi, \quad (2.12d)$$

where

$$\kappa = \frac{3}{10} \hbar^2 \gamma^4 / r^6, \quad (2.12e)$$

$$\mathbf{S} = \begin{pmatrix} -2(j_1+4j_2) & -6k_1 & 4(k_1-2k_2) & -4(l_1+2l_2) \\ -2k_1 & -6j_1 & 2(j_1+k_1) & 2l_1 \\ 2(k_1-2k_2) & 3(j_1+k_1) & -[3(j_0-k_0)+2(j_1+k_1)+2(j_2+k_2)] & -2(l_1-l_2) \\ -2(l_1+2l_2) & 3l_1 & -2(l_1-l_2) & -[(j_0-k_0)+2(j_1-k_1)+2(j_2-k_2)] \end{pmatrix}. \quad (2.12f)$$

### 3. PROPERTIES OF THE RELAXATION

1. *General.* The formal solution of (2.12) is given by<sup>9</sup>

$$\Psi(t) = \exp(\kappa \mathbf{S}t) \Psi(0). \quad (3.1)$$

The first normal mode  $\psi_1$  is, apart from a constant factor, the deviation from equilibrium of the nuclear paramagnetism of the  $N$  three-spin systems; defining  $M_z(t)$  to be the instantaneous value of the magnetization and  $M_z^{(T)}$  to be the thermal equilibrium value, the relationship is

$$M_z(t) - M_z^{(T)} = N \hbar \gamma \psi_1(t). \quad (3.2)$$

Throughout this section we shall assume that at time  $t=0$  the spin system was describable by a (high) spin temperature  $T_s$ , so that

$$\bar{\sigma}_{\alpha\alpha'}(0) \propto -E_\alpha \delta_{\alpha\alpha'}, \quad (3.3a)$$

$$\psi_j(0) = 0 \quad \text{for } j \neq 1. \quad (3.3b)$$

Under this assumption, we shall investigate the behavior of the function

$$m(t) = \frac{M_z(t) - M_z^{(T)}}{M_z(0) - M_z^{(T)}} = [\exp(\kappa \mathbf{S}t)]_{11}. \quad (3.4)$$

The standard against which we shall compare  $m(t)$  is the function that would result if there were no correlations between the interactions of the various pairs of nuclei, or if these correlations were neglected.<sup>1,2</sup> This standard is obtained immediately from (2.12) by setting  $l_n$  and  $k_n$  equal to zero:

$$m_0(t) = \exp(-t/T_1), \quad (3.5a)$$

where

$$T_1^{-1} = 2\kappa(j_1+4j_2). \quad (3.5b)$$

Wherever the symbol  $T_1$  occurs it is defined by Eq. (3.5b), using the appropriate values of  $j_1$  and  $j_2$ .

From the formal solution (3.1) it is clear that the general form of  $m(t)$  is a sum of four exponentials,

$$m(t) = \sum_{j=1}^4 a_j \exp(\epsilon_j t / T_1). \quad (3.6)$$

Moreover, the coefficients  $a_j$  are non-negative, as results in the following way from the fact that  $\mathbf{S}$  is symmetrizable. The matrix  $\mathbf{M}\mathbf{S}\mathbf{M}^{-1} = \mathbf{S}'$ , where  $\mathbf{M} = \text{diag}[(\frac{1}{3})^{1/2}, 1, (\frac{2}{3})^{1/2}, (\frac{2}{3})^{1/2}]$ , is symmetric and so can

<sup>9</sup> R. Bellman, *Introduction to Matrix Analysis* (McGraw-Hill Book Company, Inc., New York, 1960), Chap. 10.

be diagonalized by an orthogonal matrix  $\mathbf{T}$ :

$$\mathbf{S}' = \mathbf{T}^T \text{diag}(\lambda_1, \lambda_2, \lambda_3, \lambda_4) \mathbf{T}.$$

The equation of motion of  $\Psi' = \mathbf{M}\Psi$  is

$$\frac{d}{dt} \Psi' = \kappa \mathbf{S}' \Psi';$$

consequently  $m(t)$  is given by

$$m(t) = \sqrt{3} \psi_1'(t) = \sqrt{3} \sum_j T_{j1}^2 \exp(\kappa \lambda_j t),$$

which establishes the non-negativity of the coefficients  $a_j$ .

This transformation also shows that the eigenvalues of  $\mathbf{S}$ , being the same as those of  $\mathbf{S}'$ , are real. An important question is the sign of the eigenvalues. It has been stated<sup>7</sup> that the form of Eq. (2.7) is such that the steady-state solution must be  $\sigma(\infty) = \sigma^{(T)}$ . This is equivalent to stating that all eigenvalues of  $\mathbf{S}$  are strictly negative (or at least have strictly negative real parts). This has never been shown, and in fact is not true as will be shown later with a counterexample. It is easily seen that all eigenvalues of  $\mathbf{S}$  are negative when the cross-correlations  $k_m$  and  $l_m$  vanish; hence they are all negative for finite but sufficiently small cross-correlations. Pathological cases can result, then, only when there is a high correlation between the interactions of different pairs; when the motion is restricted to a plane (see Sec. 5.2) indeed a zero eigenvalue can appear. The general problem of how small the cross-correlations must be for reasonably "normal" behavior is unsolved; this problem combines the difficulties of general stability theory<sup>10</sup> with the fact that the various correlation functions are interdependent in a model-sensitive way.

Regardless of the possibility of some non-negative eigenvalues, for times  $t \ll T_1$  the relaxation  $m(t)$  will approximate the exponential decay  $m_0(t)$ ; more precisely, the meaning of this statement is the equality

$$m'(0) = \kappa S_{11} = m_0'(0), \quad (3.7)$$

which follows immediately from (2.12f) and (3.1). This invariance of the initial slope, together with the invariance of the initial value one, would tend to obscure small departures from an exponential decay.

A third general property of the actual relaxation  $m(t)$

<sup>10</sup> R. Bellman, *Introduction to Matrix Analysis* (McGraw-Hill Book Company, Inc., New York, 1960), Chap. 13.

is that it is slower than  $m_0(t)$ ; more exactly,

$$m(t) \geq m_0(t) \quad (3.8)$$

for any positive  $t$ . This is easily seen for short times since  $m(0) = m_0(0)$ ,  $m'(0) = m_0'(0)$  and

$$m''(0) = \kappa(\mathbf{S}^2)_{11} \geq m_0''(0).$$

To prove the assertion for any time  $t$  we proceed as follows. From the previous remarks we have the equations

$$\sum_{j=1}^4 a_j = 1, \quad \sum_{j=1}^4 a_j \epsilon_j = -1. \quad (3.9)$$

Defining  $x = t/T_1$  and

$$f(x) = e^x \sum_j a_j e^{\epsilon_j x} - 1 = \sum_j a_j e^{\mu_j x} - 1,$$

where  $\mu_j = 1 + \epsilon_j$ , it suffices to show that

$$f(x) \geq 0, \quad 0 \leq x < \infty.$$

Now  $f$  has the property that  $f(0) = f'(0) = 0$  and for any such function

$$f(x) = \int_0^x \int_0^y f''(z) dz dy.$$

Since any exponential function of real argument has positive second derivative and the coefficients  $a_j$  are positive, we have the inequality  $f'' \geq 0$  and the assertion follows.

We have thus shown that the effect of the cross-correlations *always* is to retard the relaxation of  $M_z$  from an initial spin temperature.

2. *Special cases.* While the general relaxation involves four exponential functions, for some special cases the number is less. It has already been mentioned that in the event  $k_n = l_n = 0$ , the decay is a single exponential. Here we only add that according to Eqs. (2.12) this is true regardless of the initial condition,  $\Psi(0)$ , as has been pointed out previously.<sup>1</sup>

In the limit of long correlation times (lower temperatures), two exponentials suffice. If  $(j_0 - k_0)$  is not identically zero, the condition  $\omega_0 \tau_c \gg 1$  requires that  $(j_0 - k_0) \gg j_n, k_n, l_n$  for  $n \neq 0$ . [For the validity of the theory Eqs. (2.5) must still be satisfied, however.] A consequence of these inequalities is that  $\psi_3$  and  $\psi_4$  relax independently and rapidly; they can be taken as zero, leaving only the two components  $\psi_1$  and  $\psi_2$ :

$$\frac{d}{dt} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \kappa \mathbf{S}_2 \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad (3.10a)$$

where

$$\mathbf{S}_2 = \begin{pmatrix} -2(j_1 + 4j_2) & -6k_1 \\ -2k_1 & -6j_1 \end{pmatrix}. \quad (3.10b)$$

Diagonalizing  $\mathbf{S}_2$  we have

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{a_- - a_+} \begin{pmatrix} a_+ & a_- \\ 1 & 1 \end{pmatrix} \begin{pmatrix} e^{\lambda_+ t} & 0 \\ 0 & e^{\lambda_- t} \end{pmatrix} \times \begin{pmatrix} -1 & a_- \\ 1 & a_+ \end{pmatrix} \begin{pmatrix} \psi_1(0) \\ \psi_2(0) \end{pmatrix}, \quad (3.11a)$$

where

$$a_{\pm} = -k_1^{-1} \{ j_1 - 2j_2 \pm [(j_1 - 2j_2)^2 + 3k_1^2]^{1/2} \}, \quad (3.11b)$$

$$\lambda_{\pm} = 2\kappa \{ -2(j_1 + j_2) \pm [(j_1 - 2j_2)^2 + 3k_1^2]^{1/2} \}. \quad (3.11c)$$

For a system initially describable by a (high) spin temperature, the relaxation function is given by

$$m(t) = (a_- e^{\lambda_- t} - a_+ e^{\lambda_+ t}) / (a_- - a_+). \quad (3.12)$$

For this limiting case the modest requirement

$$k_1^2 < j_1^2 + 4j_1 j_2 \quad (3.13)$$

suffices to insure that the relaxation involve only decaying exponentials.

A third special case results when the imaginary parts of the cross-correlation functions  $l_n$  vanish. This situation holds when the motion is isotropic and according to (2.12) leads to a relaxation involving at most three exponentials.

#### 4. EFFECTIVE RELAXATION TIME

The calculation of the complete relaxation from Eqs. (2.12) requires considerable effort since it involves finding the eigenvalues and eigenvectors of  $\mathbf{S}$ , a matrix of dimension four. It would be helpful to have a simple test to determine how well the relaxation could be approximated by  $m_0(t)$  without having to calculate the complete result  $m(t)$ .

Assuming an initial spin temperature and also assuming that  $\mathbf{S}$  has no zero or positive eigenvalues, the integral of the relaxation function is given by

$$\int_0^{\infty} m(t) dt = -\kappa^{-1} (\mathbf{S}^{-1})_{11}.$$

This formula is easily verified by diagonalizing  $\mathbf{S}$ , which is always possible since it is symmetrizable. Let us define  $T_e$  by

$$T_e = -\kappa^{-1} (\mathbf{S}^{-1})_{11}; \quad (4.1a)$$

$T_e$  is an effective relaxation time in the sense that

$$\int_0^{\infty} \exp(-t/T_e) dt = \int_0^{\infty} m(t) dt = T_e. \quad (4.1b)$$

We can therefore express the retardation effects of the cross-correlations by the parameter

$$\zeta = \frac{T_1}{T_e} = \frac{|\mathbf{S}|}{2(j_1 + 4j_2) |\mathbf{S}^{11}|}, \quad (4.2)$$

where  $|\mathbf{S}| = \det(S_{ij})$ ,  $i, j \geq 1$ , and  $|\mathbf{S}^{\text{II}}| = \det(S_{ij})$ ,  $i, j \geq 2$ .

From the general properties of the relaxation discussed in the previous section, it is clear that the retardation parameter  $\zeta$  is between 0 and 1. For  $\zeta \approx 1$ , cross-correlations are of little importance and  $m(t) \approx m_0(t)$ ; the smaller  $\zeta$  is, the more important it becomes to calculate the complete relaxation. It should be noticed that, since all coefficients  $a_j$  are positive and  $m(t) \geq m_0(t)$ , the retardation parameter  $\zeta$  cannot "miss" any slowly relaxing components if they are multiplied by significant coefficients. It is well worthwhile then, to calculate  $\zeta$  before investing considerable effort in the calculation of  $m(t)$ .

The long correlation time limit of Eq. (4.2) is easily found to be

$$\lim_{\omega_0\tau_c \rightarrow \infty} \zeta = 1 - \frac{k_1^2}{j_1(j_1 + 4j_2)}. \quad (4.3)$$

[Compare with Eq. (3.13).]

$$\Psi^* = \frac{2}{15(61)^{1/2}} \begin{pmatrix} 0 & \alpha & \beta & 0 \\ 1 & 1 & 1 & 0 \\ -\frac{3}{2} & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} e^{-a_1 t/T_1} & 0 & 0 & 0 \\ 0 & e^{-a_2 t/T_1} & 0 & 0 \\ 0 & 0 & e^{-a_3 t/T_1} & 0 \\ 0 & 0 & 0 & e^{-a_4 t/T_1} \end{pmatrix} \begin{pmatrix} 0 & 3(61)^{1/2} & -3(61)^{1/2} & 0 \\ \frac{5}{2} & -\frac{3}{2}\beta & -\beta & 0 \\ -\frac{5}{2} & \frac{3}{2}\alpha & \alpha & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \Psi(0),$$

where

$$\begin{aligned} \alpha &= \frac{1}{2}(-23 + 3(61)^{1/2}), & \beta &= \frac{1}{2}(-23 - 3(61)^{1/2}), \\ a_1 &= 69/80, & a_2 &= (3/80)(19 - (61)^{1/2}), \\ & & a_3 &= (3/80)(19 + (61)^{1/2}), & a_4 &= 9/16, \end{aligned}$$

and

$$T_1^{-1} = 3\hbar^2\gamma^4 r^{-6}\tau_c. \quad (5.1a)$$

Assuming an initial spin temperature, it follows that

$$\begin{aligned} m(t) &= 0.009 \exp(-0.420t/T_1) \\ &+ 0.991 \exp(-1.005t/T_1), \end{aligned} \quad (5.1b)$$

the result found by Hubbard.<sup>3</sup>

In the long correlation time limit ( $\omega_0\tau_c \gg 1$ ) the necessary correlation functions are given by

$$j_1 = 4j_2 = -8k_1 = \omega_0^{-2}\tau_c^{-1}.$$

Using Eqs. (3.11) we find

$$a_{\pm} = 4 \pm (19)^{1/2}, \quad \lambda_{\pm} = -(4\omega_0^2\tau_c)^{-1}(20 \mp (19)^{1/2})\kappa,$$

so that

$$\begin{aligned} m(t) &= 0.041 \exp(-1.521t/T_1) \\ &+ 0.959 \exp(-0.978t/T_1), \end{aligned} \quad (5.2a)$$

where

$$T_1^{-1} = (6/5)\hbar^2\gamma^4 r^{-6}\omega_0^{-2}\tau_c^{-1}. \quad (5.2b)$$

This represents a larger departure from a single expon-

## 5. EXAMPLES

*1. Isotropic rotational diffusion.* According to Hubbard,<sup>3</sup> the various correlation functions for a spherical molecule of radius  $a$  are given by

$$\begin{aligned} j_n &= -8k_n = \tau_c [1 + (n\omega_0\tau_c)^2]^{-1}, \\ l_n &= 0, \end{aligned}$$

where  $\tau_c = (6D)^{-1}$  and  $D$  is an isotropic rotational diffusion constant often related<sup>11</sup> to the liquid viscosity  $\eta$  by  $8\pi\eta a^3 D = kT$ .

In the limit of short correlation time ( $\omega_0\tau_c \ll 1$ ) we have

$$j_n = -8k_n = \tau_c.$$

The procedure is to substitute these values of the correlation functions into Eqs. (2.12) and then diagonalize  $\mathbf{S}$ . This leads to

ential decay than in the short correlation time limit, but still of relatively minor importance.

The short and long correlation time limits of the retardation parameter  $\zeta$  are

$$\lim_{\omega_0\tau_c \rightarrow 0} \zeta = 135/136,$$

$$\lim_{\omega_0\tau_c \rightarrow \infty} \zeta = 127/128.$$

For intermediate values of  $\omega_0\tau_c$ , (4.2) was evaluated numerically, giving the results in Table I. It is seen

TABLE I. Three-spin molecules with isotropic rotational diffusion.

$(\omega_0\tau_c)^2$	$\zeta = T_1/T_c$
0	0.9926
0.001	0.9927
0.01	0.9928
0.03	0.9931
0.06	0.9934
0.1	0.9937
0.3	0.9942
0.6	0.9941
1	0.9938
3	0.9929
6	0.9926
10	0.9925
100	0.9922
$\gg 1$	0.9922

<sup>11</sup> See, however, W. A. Steele, J. Chem. Phys. **38**, 2418 (1963).

that for all temperatures cross correlations have a very small effect.

Hubbard<sup>4</sup> has found the analog of the matrix **S** for a tetrahedral arrangement of four identical spins for the special case of isotropic rotational diffusion. A similar expression for  $\zeta$  can be formulated, bearing in mind that according to Hubbard's definitions  $m(i)$  is a sum of components of the matrix exponential. Simple numerical calculations then lead to the results in Table II. These results amount to nothing new; they can be obtained from Hubbard's complete solutions. Again cross-correlations are of minor importance for all temperatures.

**2. Methyl group rotation.** A commonly occurring equivalent three-spin system is the set of protons of a methyl group. Rotation of the group about the symmetry axis is probably a common occurrence in the solid state, and this would appear to be a proper problem to discuss in terms of the general theory presented here. However such is not the case, for the following reasons.<sup>12</sup> For any specified orientation of the rotation axis with respect to the magnetic field, the average of the perturbing Hamiltonian  $\mathcal{H}_1$  defined by Eqs. (2.9) does not vanish, since not all of the  $Y_{ij}^{(m)}$ 's have zero average over the motion postulated. In the development of the theory it was required that the average of  $\mathcal{H}_1$  over the motion vanish.

The remedy is to redefine the time-independent Hamiltonian  $\mathcal{H}_0$  to include, in addition to the Zeeman interaction, the average of the dipolar interactions. But then the new  $\mathcal{H}_0$  is not diagonal in the representation (2.8). Moreover, in a proper representation Eq. (2.6a) will, in principle, contain more nonsecular terms than before, since some of the originally degenerate levels will be split by energies of the order of  $\langle \mathcal{H}_1 \rangle_{av}$  and even this is large compared to elements  $R_{\alpha\alpha'\beta\beta'}$ .

Hilt and Hubbard<sup>6</sup> have recently treated the problem of spin relaxation by methyl group rotation in solids using a representation more nearly diagonal than (2.8)

TABLE II. Four-spin molecules with isotropic rotational diffusion.

$(\omega_0\tau_c)^2$	$\zeta = T_1/T_e$
1	0.99709
0.01	0.99712
0.05	0.99715
0.1	0.99704
0.3	0.99618
0.5	0.99531
0.7	0.99463
1	0.99387
2	0.99260
4	0.99180
6	0.99153
10	0.99133
50	0.99112
100	0.99109
>>1	0.99107

<sup>12</sup> The author is indebted to Professor P. S. Hubbard for valuable discussions about these points.

for a variety of orientations of the rotation axis. We shall be content here to discuss one simple, but important, situation: hindered threefold rotation about an axis parallel to the constant magnetic field. The result obtained agrees with that of Hilt and Hubbard.

The simplicity of this orientation results from the fact that the average of Eq. (2.9a) over the threefold rotation is the constant term  $(\hbar\gamma^2/r^3)\sum(A_{ij}+B_{ij})$  and this commutes with  $\mathcal{H}_0$ . The terms  $C_{ij}$  and  $D_{ij}$  vanish identically and the relaxation arises from the terms  $E_{ij}$  and  $F_{ij}$ , which average to zero over the rotation.

The addition of  $\langle \mathcal{H}_1 \rangle_{av} = (\hbar\gamma^2/r^3)\sum(A_{ij}+B_{ij})$  to  $\mathcal{H}_0$  only partially lifts the original degeneracy.<sup>13</sup> One set of exact eigenstates of  $\mathcal{H}_0' = \mathcal{H}_0 + \langle \mathcal{H}_1 \rangle_{av}$ , with the corresponding energies, is

$$\begin{aligned}
 |1'\rangle &= |1\rangle, & E_1' &= -\frac{3}{2}\omega_0 + 3\epsilon, \\
 |2'\rangle &= [|2\rangle + |3\rangle + |4\rangle]/\sqrt{3}, & E_2' &= -\frac{1}{2}\omega_0 - 3\epsilon, \\
 |3'\rangle &= [-|2\rangle + 2|3\rangle - |4\rangle]/\sqrt{6}, & E_3' &= -\frac{1}{2}\omega_0, \\
 |4'\rangle &= [|2\rangle - |4\rangle]/\sqrt{2}, & E_4' &= -\frac{1}{2}\omega_0, \\
 |5'\rangle &= [-|5\rangle + |7\rangle]/\sqrt{2}, & E_5' &= \frac{1}{2}\omega_0, \\
 |6'\rangle &= [-|5\rangle + 2|6\rangle - |7\rangle]/\sqrt{6}, & E_6' &= \frac{1}{2}\omega_0, \\
 |7'\rangle &= [|5\rangle + |6\rangle + |7\rangle]/\sqrt{3}, & E_7' &= \frac{1}{2}\omega_0 - 3\epsilon, \\
 |8'\rangle &= |8\rangle, & E_8' &= \frac{3}{2}\omega_0 + 3\epsilon,
 \end{aligned} \tag{5.3}$$

where

$$\epsilon = \frac{1}{4}\hbar\gamma^2r^{-3}.$$

We must now begin again with Eqs. (2.6). Due to the energy splittings induced by  $\langle \mathcal{H}_1 \rangle_{av}$  we must now include only the elements  $\tilde{\sigma}_{\alpha\alpha}$  ( $1 \leq \alpha \leq 8$ ) and  $\tilde{\sigma}_{34}$ ,  $\tilde{\sigma}_{43}$ ,  $\tilde{\sigma}_{56}$ , and  $\tilde{\sigma}_{65}$  in Eq. (2.7). The perturbing Hamiltonian in Eq. (2.6d) is now

$$-3\epsilon \sum [I_+^{(i)}I_+^{(j)}e^{-2i\varphi_{ij}} + I_-^{(i)}I_-^{(j)}e^{2i\varphi_{ij}}].$$

For the calculation of the various correlation functions the model assumed is successively uncorrelated rotations of  $\pm 120^\circ$  about the axis parallel to the field.<sup>14</sup> The total average jump rate is  $\nu$  and it is supposed that an individual jump occurs so rapidly that the fluctuating fields during the jump contribute nothing to the spin relaxation. When the analysis is carried out as before the following "normal coordinate" equations result:

$$\dot{\varphi}_1 = -\frac{3}{2}T_1^{-1}\varphi_1, \quad \dot{\varphi}_2 = \dot{\varphi}_3 = \dot{\varphi}_4 = 0, \tag{5.4a}$$

where

$$\begin{aligned}
 \varphi_1 &= \frac{1}{2}[2\tilde{\sigma}_{11} + \tilde{\sigma}_{33} + \tilde{\sigma}_{44} - \tilde{\sigma}_{55} - \tilde{\sigma}_{66} - 2\tilde{\sigma}_{88} \\
 &\quad + 2\text{Im}(\tilde{\sigma}_{34} - \tilde{\sigma}_{56})], \\
 \varphi_2 &= \frac{1}{2}[2\tilde{\sigma}_{11} + \tilde{\sigma}_{33} + \tilde{\sigma}_{44} - \tilde{\sigma}_{55} - \tilde{\sigma}_{66} - 2\tilde{\sigma}_{88} \\
 &\quad - 6\text{Im}(\tilde{\sigma}_{34} - \tilde{\sigma}_{56})], \tag{5.4b} \\
 \varphi_3 &= \frac{1}{2}[\tilde{\sigma}_{11} - \tilde{\sigma}_{33} - \tilde{\sigma}_{44} + \tilde{\sigma}_{55} + \tilde{\sigma}_{66} - \tilde{\sigma}_{88}], \\
 \varphi_4 &= \frac{1}{2}[\tilde{\sigma}_{22} - \tilde{\sigma}_{77}].
 \end{aligned}$$

<sup>13</sup> E. R. Andrew and R. Bersohn, J. Chem. Phys. **18**, 159 (1950).

<sup>14</sup> A similar model has been investigated for a two-spin system; see N. Bloembergen, Phys. Rev. **104**, 1542 (1956).

Here  $T_1$  is the relaxation time if cross effects are neglected.

$$\frac{1}{T_1} = -\frac{9\hbar^2\gamma^4}{2r^6} \int_0^\infty \cos(2\omega_0\tau) \langle \exp[-2i\varphi_{ab}(t)] \times \exp[2i\varphi_{ab}(t+\tau)] \rangle_{av} d\tau = -\frac{9\hbar^2\gamma^4}{2r^6} \frac{\tau}{1+4\omega_0^2\tau^2}, \quad (5.4c)$$

where  $\tau^{-1} = \frac{3}{2}\nu$ . The first of Eqs. (5.4a) is actually an approximation resulting from a neglect of the difference between  $|E_1 - E_5|$  and  $|E_8 - E_3|$ ; the exact result is

$$\begin{aligned} \frac{d}{dt} \{ \ln[2\bar{\sigma}_{11} - \bar{\sigma}_{55} - \bar{\sigma}_{66} - 2 \operatorname{Im}\bar{\sigma}_{56}] \} &= -\frac{3}{2} \frac{1}{T_1'}, \\ \frac{d}{dt} \{ \ln[2\bar{\sigma}_{88} - \bar{\sigma}_{33} - \bar{\sigma}_{44} - 2 \operatorname{Im}\bar{\sigma}_{34}] \} &= -\frac{3}{2} \frac{1}{T_1''}, \end{aligned} \quad (5.4d)$$

where  $T_1'$  and  $T_1''$  are given by (5.4c) with  $4\omega_0^2$  replaced by  $(2\omega_0 + 3\epsilon)^2$  and  $(2\omega_0 - 3\epsilon)^2$ , respectively. For high fields, however, this is only an academic point.

The free relaxation of the nuclear magnetism of  $N$  similarly oriented methyl groups is given by

$$M_z(t) - M_z^{(T)} = N\hbar\gamma(\varphi_1 + \frac{1}{3}\varphi_2 + \frac{1}{3}\varphi_3 + \varphi_4). \quad (5.5a)$$

Assuming an initial high-spin temperature, we have

$$m(t) = \frac{1}{3} + \frac{2}{3} \exp(-\frac{3}{2}t/T_1). \quad (5.5b)$$

In fact, this same result is obtained by using the equations of Sec. 2 and ignoring the difficulties mentioned above. The underlying reason for the agreement can be traced to the fact that the coefficients  $R_{\alpha\alpha'\beta\beta'}$  vanish if  $\bar{\sigma}_{\alpha\alpha'}$  is one of the matrix elements in Eqs. (5.4b) and  $\beta\beta' = 23, 32, 24, 42, 57, 75, 67$ , or  $76$ . That is, even if the energy splittings and resulting nonsecularity of the terms were not invoked, they still would not contribute to the relaxation. This turns out to be true for all orientations of the rotation axis with respect to the field, but it is not evident *a priori* that such is the case and the proper way to treat the general problem is that of Hilt and Hubbard.<sup>6</sup>

The important observation about the result (5.5b) is that equilibrium is never attained if cross-correlation effects are correctly included, whereas the relaxation is quite normal if they are neglected. This example is the first to show that this neglect can lead to serious error. Of course, in a physical situation equilibrium eventually would be attained by means of some other relaxation mechanism; there would be, for example, additional dipolar interactions from outside the methyl group as well as some high-frequency out-of-plane vibrations.

**3. Hindered tetrahedron rotation.** For a final example using the general formalism of Sec. 2 we consider the following model, which is probably of limited practical importance but which does show again the greater importance of cross-correlations when the motion is anisotropic. The three spins are assumed to occupy

three of the corners of a regular tetrahedron, the remaining corner being occupied by a similar atom having little if any magnetically effective coupling to the three spins. An example might be  $\text{NDH}_3^+$ , bearing in mind the smaller magnetic moments of the nitrogen and deuterium nuclei. The motion postulated consists of jumps between twelve discrete orientations determined by the lattice by means of rotations about each of the four threefold axes of the group having effectively tetrahedral symmetry. The average total jump rate is  $\nu$  and we again suppose that the transit time is so short that fluctuating fields during the transit contribute nothing to the spin relaxation. It is further assumed that all tetrahedral groups in the ensemble have the same permissible orientations with respect to crystal axes, that all twelve orientations of a group are equally likely, and that rotations about each of the four threefold axes occur at the same average rate  $\nu/4$ . For this model the dipolar interactions have zero average over the motion.

These assumptions lead to a Markov chain on a twelve-state space, the solution of which yields the necessary spectral densities. The results are the following<sup>15</sup>:

$$\begin{aligned} j_0 &= (5+P)g_0, & k_0 &= -\frac{3}{4}(1-P)h_0, \\ j_1 &= (3-P)g_1 + (3+P)h_1, & k_1 &= -\frac{1}{2}(3+P)h_1, \\ j_2 &= \frac{1}{4}(15+P)g_2 + \frac{1}{4}(9-P)h_2, & k_2 &= -\frac{1}{8}(9-P)h_2, \\ & & l_1 &= \sqrt{3}Qh_1, \\ & & l_2 &= -\frac{1}{2}\sqrt{3}Qh_2, \end{aligned} \quad (5.6a)$$

where

$$\begin{aligned} g_n &= (5/24)\tau[1 + (n\omega_0\tau)^2]^{-1}, \\ h_n &= (5/32)\tau[(9/4) + (n\omega_0\tau)^2]^{-1}, \quad \tau = \nu^{-1}, \end{aligned} \quad (5.6b)$$

and

$$\begin{aligned} P &= 7 \cos^4\theta - 6 \cos^2\theta - 4\sqrt{2} \cos 3\varphi \sin^3\theta \cos\theta, \\ Q &= 5 \cos^3\theta - 3 \cos\theta + \sqrt{2} \cos 3\varphi \sin^3\theta. \end{aligned} \quad (5.6c)$$

Here the angles  $\theta$  and  $\varphi$  are the polar angles of  $\mathbf{H}$  in a right-handed coordinate system with the  $z$  axis directed along an altitude (threefold axis) of the tetrahedron and the  $x$  axis directed along an altitude of a face of the tetrahedron.

It may be seen that if cross-correlations are neglected the relaxation, governed by

$$T_1^{-1} = 2\kappa(j_1 + 4j_2),$$

becomes independent of orientation in the short correlation time limit, where  $g_0 = g_1 = g_2$  and  $h_0 = h_1 = h_2$ . This is a general property of systems with cubic symmetry.<sup>16</sup>

At the expense of redundancy  $P$  and  $Q$  can be written more symmetrically in terms of the cosines  $\alpha_i$  of the

<sup>15</sup> The solution of this and related problems will be described in a subsequent publication.

<sup>16</sup> M. Eisenstadt and A. G. Redfield, Phys. Rev. **132**, 635 (1963).



angles between  $\mathbf{H}$  and the four threefold axes.

$$P = -27\alpha_1\alpha_2\alpha_3\alpha_4, \quad (5.7a)$$

$$Q = (27/4)(\alpha_1\alpha_2\alpha_3 + \alpha_1\alpha_2\alpha_4 + \alpha_1\alpha_3\alpha_4 + \alpha_2\alpha_3\alpha_4),$$

the restraints on the  $\alpha_i$ 's being

$$\begin{aligned} \sum_i \alpha_i &= 0, \\ \sum_i \alpha_i^2 &= \frac{4}{3}. \end{aligned} \quad (5.7b)$$

For a general orientation of the magnetic field with respect to the crystal axes, the free longitudinal relaxation is described by a sum of four decaying exponentials. To determine whether or not it is worth the effort to calculate the complete relaxation it suffices to calculate  $\zeta$ , given by Eq. (4.2). The most economical way to span all possible values of  $\zeta$  is to regard  $P$  and  $Q$  as the independent orientation variables. It is necessary, then, to know the possible values of  $P$  and  $Q$ ; using Eqs. (5.7) and the method of Lagrange multipliers it can be shown that the image in the  $P, Q$  plane of the  $\theta, \varphi$  plane is the region bounded by the lines

$$Q^2 = (2 \mp \Pi)^2 (1 \mp \Pi), \quad (5.8a)$$

where

$$\Pi = (1 - P)^{1/2}. \quad (5.8b)$$

This is a curvilinear triangle with all sides concave and vertices at  $(-3, 0)$ ,  $(1, 2)$ , and  $(1, -2)$ , where the first of each pair is the value of  $P$ . Some special points (all on the perimeter) of this region are the following:

- $(1, \pm 2)$   $\mathbf{H}$  parallel to a threefold axis,
- $(-3, 0)$   $\mathbf{H}$  parallel to a twofold axis,
- $(0, 0)$   $\mathbf{H}$  parallel to an edge,
- $(0, \pm\sqrt{2})$   $\mathbf{H}$  parallel to an altitude of a face.

In general,  $(0, Q)$  corresponds to  $\mathbf{H}$  parallel to a face.

The behavior of  $\zeta$  for various values of  $(\omega_0\tau)^2$  depends on  $P$  and  $Q$ —that is, on the orientation of the field. For the field parallel to a twofold axis,  $\zeta$  first decreases slightly from  $120/121 = 0.99174$  at  $(\omega_0\tau)^2 = 0$  to a minimum of  $0.99154$  at  $(\omega_0\tau)^2 \approx 0.08$ ; it then increases to 1 as  $(\omega_0\tau)^2 \rightarrow \infty$ . Thus for such an orientation at low temperatures the relaxation is exactly the exponential decay predicted by neglecting cross-correlations. For the field parallel to a threefold axis,  $\zeta$  decreases from  $1060/1067 = 0.99344$  at  $(\omega_0\tau)^2 = 0$  to a minimum of  $0.95457$  at  $(\omega_0\tau)^2 \approx 14$  and rises slightly to  $67/70 = 0.95714$  as  $(\omega_0\tau)^2 \rightarrow \infty$ . For other orientations the inequalities  $0.95457 < \zeta < 1$  hold for all values of  $(\omega_0\tau)^2$ .

It is apparent that there is little reason to calculate the complete relaxation for all sets of conditions.

For many orientations, however,  $\zeta$  is smaller for large values of  $(\omega_0\tau)^2$ ; the limit as  $(\omega_0\tau)^2 \rightarrow \infty$  is readily obtained from (3.11) and (3.12) and can be written

$$m(t) = c_- \exp(-\epsilon_- t/T_1) + c_+ \exp(-\epsilon_+ t/T_1), \quad (5.9a)$$

where

$$\begin{aligned} c_{\pm} &= \frac{1}{2}L^{-1}(L \mp 3P \pm 27), \\ \epsilon_{\pm} &= \frac{1}{2}(57 - P)^{-1}(141 - 5P \mp L), \end{aligned} \quad (5.9b)$$

$$T_1^{-1} = 64(57 - P)^{-1}\kappa\omega_0^{-2}\tau^{-1}.$$

In these formulas,  $P$  is given by (5.6c) or (5.7a),  $\kappa$  by (2.12e), and  $L$  by

$$L = [3(387 + 42P + 19P^2)]^{1/2}. \quad (5.9c)$$

For the field directed along a threefold axis,

$$\begin{aligned} m(t) &= 0.1727 \exp(-1.542t/T_1) \\ &\quad + 0.8273 \exp(-0.887t/T_1), \end{aligned} \quad (5.10a)$$

where

$$T_1^{-1} = (12/35)\hbar^2\gamma^4r^{-6}\omega_0^{-2}\tau^{-1}. \quad (5.10b)$$

This is very nearly the largest departure of  $m(t)$  from  $m_0(t)$  predicted by this model for any set of conditions. [The parameter  $\zeta$  is slightly smaller for this orientation and  $(\omega_0\tau)^2 \approx 14$  than for very large values of  $(\omega_0\tau)^2$ .]

For this model, then, there are no cross-correlation effects as drastic as in the case of motion restricted to a plane, and what effects do exist quite possibly would be masked by other factors not considered here—intermolecular couplings, for example. Still, the anisotropy is great enough to cause a retardation which is not altogether negligible.

## 6. SUMMARY

The general relaxation equation has been obtained for the free longitudinal relaxation of a system of three identical spins  $\frac{1}{2}$  at the corners of an equilateral triangle, for the case of dipolar coupling and thermal motion preserving the equivalence of the three spins. The general problem of the nature of the eigenvalues of the relaxation matrix is as yet unsolved, but it has been demonstrated that zero eigenvalues are possible.

It has been shown that cross-correlations in such three-spin systems always retard the longitudinal relaxation from an initial spin temperature and a convenient measure of the retardation has been obtained. The cross-correlation effects for anisotropic motion can be more significant than for isotropic motion previously investigated.