

# Nuclear Magnetic Resonance and Relaxation of Four Spin Molecules in a Liquid\*

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The semiclassical form of the density operator theory of relaxation is employed to calculate the longitudinal and transverse relaxation and the resonance line shape of a liquid sample whose molecules contain four identical spin 1/2 nuclei at the corners of an equilateral tetrahedron. The relaxation is assumed to be due to the time dependence of the intramolecular dipole-dipole interactions that results from the classical rotational diffusion of the molecules. The calculation is not restricted to correlation times shorter than the Larmor period, but it is restricted to correlation times much shorter than the reciprocal coupling frequency. The second-order correction to the Zeeman energy due to the dipole-dipole interactions is included. The longitudinal relaxation is found to be, in general, the sum of three exponentials decaying with different time constants, but in the limit of either short or long correlation time there are only two exponentials. The expression for short correlation time agrees with the author's previous calculation. The transverse magnetization  $M_x + iM_y$ , in the absence of a radio-frequency field, is, in general, found to be

the sum of three terms each precessing with slightly different frequencies and decaying exponentially with different time constants. In the case of short correlation time the precession frequencies are the same, and the amplitude decays in the same manner as the longitudinal magnetization for short correlation time. The resonance line shape, correct to first order in the magnitude of the radio frequency field, can be expressed in terms of a complex susceptibility  $\chi = \chi' + i\chi''$ , which is shown to be proportional to  $\int_0^\infty [M_x(t) + iM_y(t)] \exp(i\omega t) dt$ , where  $M_x(t) + iM_y(t)$  is the transverse magnetization after a 90° pulse. The saturation behavior of the resonance line shape is calculated for the case of short correlation time. The numerical values occurring in the expressions for the longitudinal and transverse relaxation and the resonance line shape are such that there is little difference between the results calculated here and the results obtained by neglecting in the calculation the effects of the correlations of different dipole-dipole interactions with one another.

## 1. INTRODUCTION

THE longitudinal nuclear magnetic relaxation of liquid molecules containing either three or four identical spin 1/2 nuclei has previously been calculated for the cases in which the nuclei are arranged equidistantly from one another at the corners, respectively, of a triangle or a tetrahedron.<sup>1,2</sup> The following assumptions were made: (a) The relaxation is due to intramolecular dipole-dipole interactions between the spins; (b) the molecules diffuse rotationally as spheres in a viscous fluid; (c) the initial state of the spin system is a Boltzmann distribution with spin temperature  $T_s$ ; and (d) the correlation time is short. The result obtained for both the three and four spin molecules was that, although the spins are all in equivalent positions, the longitudinal relaxation after a 180° pulse is the sum of two exponentials. However, the coefficient multiplying one of the exponentials is much smaller than the coefficient multiplying the other, and the relaxation differs little from the simple exponential decay predicted by a calculation in which correlations of the different dipole-dipole interactions with one another are neglected.<sup>3</sup>

It is of interest to determine whether effects of larger magnitude due to cross correlations of the dipole-dipole interactions are present in (a) the longitudinal relaxation when the correlation time is not short compared to the Larmor period, (b) the transverse relaxation, or (c) the resonance line shape. In this paper, we calculate

the longitudinal and transverse free relaxation of the four-spin system without assuming from the beginning that the correlation time is short compared to the Larmor period, although it is assumed that the correlation time is much less than the reciprocal coupling frequency. We also calculate the resonance line shape to first order in the radio-frequency field without assuming a short correlation time, and the saturation behavior of the resonance line shape in the case of short correlation time.

A feature of the calculation is the inclusion of the second-order correction to the Zeeman interaction resulting from the dipolar interactions, which average to zero in first order. These terms are usually omitted; however, they are of the same order of magnitude as the transverse relaxation rates, and hence can be expected to produce shifts of the resonance lines by amounts comparable to the linewidths themselves.

## 2. FORMULATION OF THE CALCULATION<sup>4</sup>

The Hamiltonian of a system of spins and their molecular surroundings can be written in the form

$$\mathcal{H} = \hbar[E(s, t) + F(q) + G(s, q)], \quad (1)$$

where  $\hbar E(s, t)$  is the part of the Hamiltonian that depends only on the spin variables  $s$  and the time  $t$ ,  $\hbar F(q)$  is the energy of the molecular degrees of freedom  $q$ , and  $\hbar G(s, q)$  is the energy of the interaction of the spins and the molecular surroundings.

Consider a system of  $N$  identical nuclei in equivalent positions in the molecules of a liquid, each nucleus

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<sup>1</sup> P. S. Hubbard, Phys. Rev. **109**, 1153 (1958); **111**, 1746 (E) (1958).

<sup>2</sup> P. S. Hubbard, Ph.D. thesis, Harvard University, 1958 (unpublished).

<sup>3</sup> The relaxation of three- and four-spin systems has also been treated by I. V. Aleksandrov, Soviet Phys.—Doklady **3**, 110 (1958). His results do not agree with the results in references 1 and 2 or the present paper.

<sup>4</sup> Sections 2, 3, 4, and 5 of this paper contain a condensation of material in the author's original manuscript. A reader interested in a more detailed description of the calculation can obtain a multilithed copy of the original manuscript by writing to the author.

having a spin of 1/2 and a gyromagnetic ratio  $\gamma$ . The system is exposed to a strong constant magnetic field and a rotating transverse magnetic field:

$$\mathbf{H}(t) = H_0 \mathbf{k} + H_1 (\cos \omega t \mathbf{i} - \sin \omega t \mathbf{j}). \quad (2)$$

The part  $\hbar E$  of the Hamiltonian consists of the interaction energy of the nuclear magnetic moments with the field  $\mathbf{H}(t)$ :

$$\hbar E = -\mathbf{u} \cdot \mathbf{H}(t) = -\gamma \hbar \mathbf{I} \cdot \mathbf{H}(t), \quad (3)$$

where  $\mathbf{I} = \sum_i \mathbf{I}_i$ . Hence,

$$E = -\omega_0 I^0 - (\omega_1/2)(I^1 e^{i\omega t} + I^{-1} e^{-i\omega t}), \quad (4)$$

where  $\omega_0 \equiv \gamma H_0$ ,  $\omega_1 \equiv \gamma H_1$ ,  $I^{\pm 1} \equiv I_x \pm iI_y$ , and  $I^0 \equiv I_z$ .

The relaxation mechanism  $\hbar G$  consists of the magnetic dipole-dipole interactions between the spins.  $G$  can be written in the form

$$G = \sum_{i < j}^N \sum_{k=-2}^2 U_{ij}^k V_{ij}^k, \quad (5)$$

where the  $V_{ij}^k$  are spin operators defined by

$$V_{ij}^0 \equiv -(8/3)^{1/2} [I_i^0 I_j^0 - \frac{1}{4}(I_i^1 I_j^{-1} + I_i^{-1} I_j^1)], \quad (6a)$$

$$V_{ij}^{\pm 1} \equiv \pm (I_i^0 I_j^{\pm 1} + I_i^{\pm 1} I_j^0), \quad (6b)$$

$$V_{ij}^{\pm 2} \equiv -I_i^{\pm 1} I_j^{\pm 1}. \quad (6c)$$

The  $U_{ij}^k$  in Eq. (5) are given by

$$U_{ij}^k \equiv (6\pi/5)^{1/2} \gamma^2 \hbar r_{ij}^{-3} (-1)^k Y_2^{-k}(\theta_{ij}, \phi_{ij}), \quad (7)$$

where the  $Y_2^k$  are normalized second rank spherical

harmonics. The length of the vector  $\mathbf{r}_{ij}$  from the  $j$ th to the  $i$ th nucleus is denoted by  $r_{ij}$ , and the polar angles specifying the direction of  $\mathbf{r}_{ij}$  in the laboratory coordinate system are denoted by  $\theta_{ij}$  and  $\phi_{ij}$ .

The molecules in the liquid are assumed to undergo isotropic rotational diffusion, so that all directions of the constant magnitude vectors  $\mathbf{r}_{ij}$  are equally probable. As a result, the average of  $G$  over the molecular motion is zero, since the averages of the spherical harmonics  $Y_2^k(\theta, \phi)$  over all directions specified by  $\theta$  and  $\phi$  are zero.

According to the density operator theory or relaxation,<sup>5</sup> the spin part of a system with a Hamiltonian in the form of Eq. (1) can be described by a reduced density operator  $\sigma(s, t)$ , in terms of which the ensemble average of the expectation value of any spin operator  $Q(s)$  is given by

$$\langle Q \rangle = \text{Tr}[\sigma(s, t) Q(s)]. \quad (8)$$

If it is assumed that the molecular degrees of freedom remain in thermal equilibrium at all times, independently of the state of the spin system, it can be shown that the reduced density operator is a solution of the differential equation

$$d\sigma/dt + i[E + N, \sigma] = R(\sigma), \quad (9)$$

subject to the condition  $\text{Tr}[\sigma(t)] = 1$ . If the average value of  $G(q, s)$  over the bath coordinates in thermal equilibrium is not zero, the average value must be included in  $E$ . For the present problem it can be shown that the operators  $R(\sigma)$  and  $N$  are given, respectively, by the expressions

$$R(\sigma) = \sum_{i < j} \sum_{i' < j'} \sum_{k, l=-2}^2 J_{(ij)(i'j')}^{kl} (-l\omega_0) \{ [[V_{i'j'}^l, \sigma], V_{ij}^k] - l\beta\omega_0 [V_{ij}^k, V_{i'j'}^l] / \text{Tr}[1] \}, \quad (10)$$

and

$$N = -\frac{2}{\pi} \sum_{i < j} \sum_{i' < j'} \sum_{k, l=-2}^2 V_{ij}^k V_{i'j'}^l \int_0^\infty \{ (1 + e^{\beta\omega})^{-1} J_{(ij)(i'j')}^{kl} (\nu^{kl} - \omega) - (1 + e^{-\beta\omega})^{-1} J_{(ij)(i'j')}^{kl} (\nu^{kl} + \omega) \} \frac{d\omega}{\omega}, \quad (11)$$

where

$$\nu^{kl} \equiv \frac{1}{2}(l-k)\omega_0. \quad (12)$$

$\beta$  is defined to be  $\hbar/kT$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The function  $J_{(ij)(i'j')}^{kl}(\omega)$  is given by

$$J_{(ij)(i'j')}^{kl}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} C_{(ij)(i'j')}^{kl}(\tau) e^{i\omega\tau} d\tau, \quad (13)$$

in terms of the correlation function

$$C_{(ij)(i'j')}^{kl}(\tau) = \langle \{ U_{ij}^k(t+\tau) U_{i'j'}^l(t) \} \rangle_a. \quad (14)$$

The semiclassical form of the relaxation theory, which is used in this calculation, is obtained by evaluating the correlation functions by considering the time dependence of the functions  $U_{ij}^k(\theta_{ij}, \phi_{ij})$  to be due to the variation with time of the angles  $\theta_{ij}$  and  $\phi_{ij}$  as the molecule undergoes classical rotational diffusion in the

liquid. By the same procedure used previously,<sup>1,2</sup> which makes use of Furry's theory of isotropic rotational Brownian motion,<sup>6</sup> the correlation functions can be shown to be

$$C_{(ij)(i'j')}^{kl}(\tau) = \delta_{k,-l} (-1)^k (\gamma^2 \hbar / r_0^3)^2 \left( \frac{3}{10} \right) \times (1 - \frac{3}{2} \sin^2 \beta_{(ij)(i'j')}) \exp(-|\tau|/\tau_c), \quad (15)$$

where  $\beta_{(ij)(i'j')}$  is the angle between the vectors  $\mathbf{r}_{ij}$  and  $\mathbf{r}_{i'j'}$ , which are rigidly fixed in the molecule. The correlation time  $\tau_c$  is given by  $\tau_c \equiv (6D)^{-1}$ , where  $D$  is the rotational diffusion coefficient introduced by Furry. It has been argued that the rotational diffusion coefficient is related to the radius,  $a$ , of the spherical molecules and the viscosity,  $\eta$ , of the liquid by the relation<sup>1,2</sup>

$$D = kT/8\pi\eta a^3. \quad (16)$$

<sup>5</sup> P. S. Hubbard, Revs. Modern Phys. **33**, 249 (1961).

<sup>6</sup> W. H. Furry, Phys. Rev. **107**, 7 (1957).

Since the Stokes formula for the translational diffusion coefficient  $D_0$  is  $D_0 = kT/6\pi a\eta$ , it follows that the rotational and translational diffusion coefficients are related by

$$D = D_0/a^2. \quad (17)$$

From (13) and (15), it follows that

$$J_{(ij)(i'j')}^{kl}(\omega) = \delta_{-k,l}(-1)^k 4J(\omega)(1 - \frac{3}{2} \sin^2 \beta_{(ij)(i'j')}), \quad (18)$$

where  $J(\omega)$  is an even function of  $\omega$  defined by

$$J(\omega) \equiv (3/40)(\gamma^2 \hbar / r_0^3)^2 \tau_c [1 + (\omega \tau_c)^2]^{-1}, \quad (19)$$

the common distance between the nuclei being denoted by  $r_0$ .

The conditions of validity of Eq. (9) are

$$\tau_c \ll |R|^{-1}, \quad |N|^{-1}, \quad (20)$$

where  $|R|$  and  $|N|$  are the magnitudes of the operators given, respectively, by Eq. (10) and Eq. (11). Furthermore, expressions (10) and (11) have been obtained on the assumption that

$$\beta\omega_1, \beta\omega_0, \beta\omega \ll 1, \quad (21)$$

and the expressions are correct only to first order in  $\beta\omega_1$ ,  $\beta\omega_0$ , and  $\beta\omega$ . In addition, it has been assumed that when a radio-frequency field is present, it is small in magnitude and its frequency is near resonance, so that

$$\omega_1, |\Delta_0| \ll \omega_0, \tau_c^{-1}, \quad (22)$$

where  $\Delta_0 \equiv \omega_0 - \omega$ . In order to evaluate in closed form the integral that occurs in  $N$ , Eq. (11), it will be assumed that  $\beta \ll \tau_c$ , which is usually the case in liquids.

A complete set of spin vectors for the system of four spin 1/2 nuclei consists of 16 vectors. It is convenient to choose a coupled representation in which the operators  $\mathbf{I}_1^2, \mathbf{I}_2^2, \mathbf{I}_3^2, \mathbf{I}_4^2, \mathbf{I}_{12}^2 \equiv (\mathbf{I}_1 + \mathbf{I}_2)^2, \mathbf{I}_{34}^2 \equiv (\mathbf{I}_3 + \mathbf{I}_4)^2, \mathbf{I}^2 \equiv (\sum_i \mathbf{I}_i)^2$ , and  $\mathbf{I}^0 \equiv \sum_i \mathbf{I}_i^0$  are diagonal. The eigenvectors will be denoted by  $|I_{12}I_{34}IM\rangle$ , the eigenvalues that are always 1/2 being omitted. The three quantum numbers  $I_{12}I_{34}I$  will sometimes be abbreviated by  $\alpha$ , so that  $|\alpha M\rangle \equiv |I_{12}I_{34}IM\rangle$ .

The ensemble average of the expectation values of the components of the total nuclear spin of a molecule are given by

$$\langle I^\mu \rangle = \text{Tr}[\sigma I^\mu] = \sum_{\alpha M} \sum_{\alpha' M'} \langle \alpha M | \sigma | \alpha' M' \rangle \langle \alpha' M' | I^\mu | \alpha M \rangle. \quad (23)$$

Since

$$\langle \alpha' M' | I^0 | \alpha M \rangle = M \delta_{\alpha', \alpha} \delta_{M', M}, \quad (24a)$$

$$\langle \alpha' M' | I^{\pm 1} | \alpha M \rangle = [(I \mp M)(I \pm M + 1)]^{1/2} \times \delta_{\alpha', \alpha} \delta_{M', M \pm 1}, \quad (24b)$$

it follows from (23) that

$$\langle I^0 \rangle = \sum_{IM} M \sum_{I_{12}I_{34}} \langle I_{12}I_{34}IM | \sigma | I_{12}I_{34}IM \rangle, \quad (25a)$$

$$\langle I^{\pm 1} \rangle = \sum_{IM} [(I \mp M)(I \pm M + 1)]^{1/2} \times \sum_{I_{12}I_{34}} \langle I_{12}I_{34}IM | \sigma | I_{12}I_{34}I, M \pm 1 \rangle. \quad (25b)$$

Thus, the required matrix elements of  $\sigma$  are diagonal in  $\alpha \equiv I_{12}I_{34}I$ .

By taking the matrix elements of Eq. (9), one obtains

$$\begin{aligned} \frac{d}{dt} \langle \alpha M | \sigma | \alpha M' \rangle + i \langle \alpha M | [E + N, \sigma] | \alpha M' \rangle \\ = \langle \alpha M | R(\sigma) | \alpha M' \rangle, \end{aligned} \quad (26)$$

where  $E$  is given by (4),  $R(\sigma)$  by (10), and  $N$  by (11).

In order to evaluate the matrix elements of  $N$  and  $R(\sigma)$  that occur in Eq. (26), it is necessary to calculate the matrix elements of the operators  $V_{ij}^k$  defined by Eqs. (6). The operators  $V_{ij}^k$  are the components of an irreducible tensor operator of rank two with respect to  $\mathbf{I}$ ; hence, the Wigner-Eckart theorem<sup>7</sup> can be used to express their matrix elements in the  $|I_{12}I_{34}IM\rangle$  representation.

### 3. LONGITUDINAL FREE RELAXATION

In order to calculate the relaxation of  $\langle I^0 \rangle$  in the absence of an applied radio-frequency magnetic field, it is convenient to introduce the following combinations of matrix elements:

$$x_1 \equiv 2(\langle 1122 | \sigma | 1122 \rangle - \langle 112, -2 | \sigma | 112, -2 \rangle), \quad (27a)$$

$$x_2 \equiv (\langle 1121 | \sigma | 1121 \rangle - \langle 112, -1 | \sigma | 112, -1 \rangle), \quad (27b)$$

$$\begin{aligned} x_3 \equiv \sum_{I_{12}I_{34}} (\langle I_{12}I_{34}11 | \sigma | I_{12}I_{34}11 \rangle \\ - \langle I_{12}I_{34}1, -1 | \sigma | I_{12}I_{34}1, -1 \rangle). \end{aligned} \quad (27c)$$

The density operator describing the four-spin system with Hamiltonian  $-\hbar\omega_0 I^0$ , in thermal equilibrium at temperature  $T$ , is

$$\sigma^T = e^{\beta\omega_0 I^0} / \text{Tr}[e^{\beta\omega_0 I^0}] \approx \frac{1}{16}(1 + \beta\omega_0 I^0), \quad \beta = \hbar/kT. \quad (28)$$

The values of the  $x_i$  with  $\sigma$  equal to  $\sigma^T$ , correct to first order in  $\beta\omega_0$ , will be denoted by  $x_i^T$ :

$$\mathbf{x}^T = \{4, 1, 3\}(\beta\omega_0/8). \quad (29)$$

Since the thermal equilibrium value of  $\langle I^0 \rangle$ , correct to first order in  $\beta\omega_0$ , is

$$\langle I^0 \rangle^T = \beta\omega_0, \quad (30)$$

it follows from Eq. (25a) that

$$\langle I^0 \rangle - \langle I^0 \rangle^T = \sum_{i=1}^3 (x_i - x_i^T). \quad (31)$$

Differential equations for the  $x_i$  can be obtained from Eq. (26). When the differential equations for the matrix elements are combined so that the time derivative of one of the  $x_i$  occurs on the left-hand side, it is found that the other matrix elements in the equation occur only in the combinations  $x_i$ . The three resulting equations can be written in matrix form as follows:

$$d\mathbf{x}/dt = \mathbf{A}(\mathbf{x} - \mathbf{x}^T), \quad (32)$$

<sup>7</sup> A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, 1957), 2nd ed., Chap. 5.

where, with the abbreviation  $J_l \equiv J(l\omega_0)$ ,

$$\begin{aligned} A_{11} &= -18J_1 - 48J_2, & A_{12} &= 0, & A_{13} &= 12J_1, \\ A_{21} &= 0, & A_{22} &= -27J_0 - 21J_1 - 18J_2, & A_{23} &= 9J_0 - 6J_2, \\ A_{31} &= 9J_1, & A_{32} &= 27J_0 - 18J_2, & A_{33} &= -9J_0 - 25J_1 - 46J_2. \end{aligned} \quad (33)$$

The solutions of Eqs. (32) for the  $x_i(t)$  in terms of  $x_i(0)$  can be obtained by the use of Laplace transforms. The result is

$$\mathbf{x}(t) - \mathbf{x}^T$$

$$= - \sum_{k=1}^3 \{ \text{Adj}(\mathbf{A} - p_k \mathbf{I}) [\mathbf{x}(0) - \mathbf{x}^T] e^{p_k t} / D'(p_k) \}, \quad (34)$$

where  $\text{Adj}(\mathbf{A} - p\mathbf{I})$  is the adjoint matrix of the matrix  $\mathbf{A} - p\mathbf{I}$ ,  $D(p)$  is the determinant of the matrix  $\mathbf{A} - p\mathbf{I}$ ,  $D'(p)$  is the derivative with respect to  $p$  of  $D(p)$ , and  $p_1, p_2$ , and  $p_3$  are the eigenvalues of  $\mathbf{A}$ , and hence are solutions of  $D(p) = 0$ . Equation (34) is valid if the eigenvalues are distinct.

The initial condition of the spin system will be considered to be the result of the application of a rotating field  $\mathbf{H}_1 = H_1(\mathbf{i} \cos \omega_0 t - \mathbf{j} \sin \omega_0 t)$  to the system in thermal equilibrium with density operator  $\sigma^T$ , Eq. (28), for a time  $t_0$  sufficiently short that the effects of the dipole-dipole interactions can be neglected during the pulse. The density operator at the end of the pulse is<sup>2</sup>

$$\sigma_\theta = e^{i\omega_0 I^0 t_0} \exp[\beta \omega_0 (I_y \sin \theta + I^0 \cos \theta)] \times e^{-i\omega_0 I^0 t_0} / \text{Tr}[e^{\beta \omega_0 I^0}], \quad (35)$$

where  $\theta = \gamma H_1 t_0$ . Hence, to first order in  $\beta \omega_0$ ,

$$\langle \alpha M | \sigma_\theta | \alpha M \rangle = M(\beta \omega_0 / 16) \cos \theta. \quad (36)$$

For  $\sigma(0) = \sigma_\theta$ , it follows from Eqs. (27) and (28) that

$$\mathbf{x}(0) = \{4, 1, 3\} (\beta \omega_0 / 8) \cos \theta = \mathbf{x}^T \cos \theta. \quad (37)$$

By use of (28), (37), and (34), Eq. (31) can be written

$$\langle I^0 \rangle - \langle I^0 \rangle^T = \langle I^0 \rangle^T (\cos \theta - 1) \sum_{k=1}^3 a_k e^{p_k t}, \quad (38)$$

where

$$\begin{aligned} a_k = - \sum_{i=1}^3 \{ 4 \text{Adj}(\mathbf{A} - p_k \mathbf{I})_{i1} + \text{Adj}(\mathbf{A} - p_k \mathbf{I})_{i2} \\ + 3 \text{Adj}(\mathbf{A} - p_k \mathbf{I})_{i3} \} / 8 D'(p_k). \end{aligned} \quad (39)$$

The elements of  $\mathbf{A}$  are related to the quantities  $J_l$  by Eqs. (33). From Eq. (19),

$$J_l \equiv J(l\omega_0) = J_0 [1 + (l\omega_0 \tau_c)^2]^{-1}. \quad (40)$$

Because of the complexity of the expression for  $D(p)$ , it is impracticable to calculate general expressions for the roots  $p_k$  of the cubic equation  $D(p) = 0$ . Hence, the  $p_k$  and  $a_k$  will be calculated for several values of the quantity  $(\omega_0 \tau_c)$  upon which the  $J_l \equiv J(l\omega_0)$  depend.

Consider first the case of short correlation time,

$(\omega_0 \tau_c) \ll 1$ . In this case  $J_2 \approx J_1 \approx J_0$ , so that  $D(p) = 0$  becomes

$$-(66J_0 + p)(p^2 + 146J_0 p + 5145J_0^2) = 0, \quad (41)$$

the roots of which are

$$\begin{aligned} p_1 &= -[73 - 2(46)^{1/2}]J_0, & p_2 &= -66J_0, \\ p_3 &= -[73 + 2(46)^{1/2}]J_0. \end{aligned} \quad (42)$$

With the values (42) for the  $p_k$ , it follows from (33) and (39) that

$$\begin{aligned} a_1 &= [92 + 13(46)^{1/2}] / 184, \\ a_2 &= 0, \\ a_3 &= [92 - 13(46)^{1/2}] / 184. \end{aligned} \quad (43)$$

The expression obtained when (42) and (43) are substituted in (38) agrees with the result previously calculated for short correlation time,<sup>1,2</sup> which was expressed in terms of a quantity  $T_0$  defined by

$$T_0^{-1} \equiv (\gamma^2 \hbar / r_0^3)^2 \tau_c = (40/3)J_0. \quad (44)$$

The condition of validity of the relaxation theory, Eq. (20), can be written for the present problem in terms of  $T_0$  as

$$\tau_c \ll T_0, \quad \text{or} \quad \tau_c^2 \ll (r_0^3 / \gamma^2 \hbar)^2. \quad (45)$$

Consider next the case of long correlation time,  $(\omega_0 \tau_c)^2 \gg 1$ . A long correlation time is not incompatible with the satisfaction of the condition of validity (45) if  $\omega_0^2 \gg (\gamma^2 \hbar / r_0^3)^2$ . The roots  $p_k$  can be calculated correct to first order in the small quantity  $\epsilon \equiv 1/(\omega_0 \tau_c)^2$  by expanding  $J_1, J_2$ , and  $p$  as power series in  $\epsilon$ ,

$$\begin{aligned} J_1 &= -J_0 \sum_{n=1}^{\infty} (-\epsilon)^n, & J_2 &= -J_0 \sum_{n=1}^{\infty} (-\epsilon/4)^n, \\ p &= \sum_{n=0}^{\infty} p^{(n)} \epsilon^n, \end{aligned}$$

substituting the above expressions in the equation  $D(p) = 0$ , and determining the coefficients  $p^{(0)}$  and  $p^{(1)}$  by equating to zero the coefficients of the  $\epsilon^0, \epsilon^1$ , and  $\epsilon^2$  terms. The results are

$$\begin{aligned} p_1 &= -3[11 - (10)^{1/2}]J_0 \epsilon, \\ p_2 &= -3[11 + (10)^{1/2}]J_0 \epsilon, \\ p_3 &= -(36 + 26\epsilon)J_0. \end{aligned} \quad (46)$$

The coefficients  $a_k$  obtained by using the above values of  $p_k$  in Eq. (39), retaining terms to the first power of

TABLE I. Coefficients in expression (38) for the longitudinal relaxation.

$(\omega_0\tau_c)^2$	$a_1$	$-p_1/J_0$	$a_2$	$-p_2/J_0$	$a_3$	$-p_3/J_0$	$T_1^{-1}/J_0$
$\ll 1$	0.9792	59.435	0.0000	66.000	0.0208	86.565	60.000
0.01	0.9798	57.503	0.0009	64.863	0.0193	84.692	58.035
0.05	0.9772	50.958	0.0090	60.728	0.0138	78.600	51.429
0.1	0.9742	44.752	0.0172	56.216	0.0086	73.214	45.195
0.3	0.9708	30.660	0.0280	43.177	0.0012	62.302	31.049
0.5	0.9705	23.655	0.0293	35.203	0.0002	57.142	24.000
0.7	0.9707	19.383	0.0293	29.848	0.0000	53.889	19.690
1.0	0.9711	15.338	0.0289	24.410	0.0000	50.651	15.600
2.0	0.9722	9.1602	0.0278	15.347	0.0000	45.271	9.3333
4.0	0.9731	5.1216	0.0269	8.8752	0.0000	41.391	5.2235
6.0	0.9734	3.5623	0.0265	6.2532	0.0000	39.807	3.6343
8.0	0.9737	2.7323	0.0263	4.8290	0.0000	38.944	2.7879
10.0	0.9738	2.2164	0.0262	3.9338	0.0000	38.400	2.2616
50.0	0.9742	0.4645	0.0258	0.8362	0.0000	36.511	0.4741
$\gg 1$	0.9743	23.51 $\epsilon$	0.0257	42.49 $\epsilon$	0.0000	36+26 $\epsilon$	24.00 $\epsilon$

$\epsilon$  in the numerator and denominator, are

$$\begin{aligned} a_1 &= [10 + 3(10)^{1/2}]/20, \\ a_2 &= [10 - 3(10)^{1/2}]/20, \\ a_3 &= 0. \end{aligned} \quad (47)$$

For intermediate values of  $(\omega_0\tau_c)^2$ , the cubic equation  $D(p)=0$  does not factor in an obvious manner. By use of an electronic computer, the roots  $p_k$  and the coefficients  $a_k$  have been calculated for many intermediate values of  $(\omega_0\tau_c)^2$ . Some of the results are given in Table I. The calculation was performed for many more values than are listed in the table, but the tabulated values are representative. The results obtained above for the cases of short and long correlation time are also listed.

It has previously been shown that, if cross correlations between different dipole-dipole interactions are neglected, the longitudinal relaxation of a system of spin 1/2 nuclei is a simple exponential decay.<sup>5,8</sup> In terms of the present notation, the relaxation time  $T_1$  for the four-spin system when cross correlations are neglected can be shown to be

$$T_1^{-1} = 12J_0\{[1 + (\omega_0\tau_c)^2]^{-1} + 4[1 + (2\omega_0\tau_c)^2]^{-1}\}. \quad (48)$$

The values of  $T_1^{-1}$  for the different values of  $(\omega_0\tau_c)^2$

$$\begin{aligned} B_{11} &= (-3/2)(9J_0 + 13J_1 + 22J_2), & B_{12} &= 0, & B_{13} &= -6(J_1 - 2J_2), \\ B_{21} &= 0, & B_{22} &= -(3/2)(13J_0 + 25J_1 + 6J_2), & B_{23} &= 9J_1, \\ B_{31} &= -9(J_1 - 2J_2), & B_{32} &= 9J_1, & B_{33} &= -(1/2)(39J_0 + 71J_1 + 50J_2), \end{aligned} \quad (52)$$

and  $\mathbf{d}$  is a diagonal matrix with elements

$$\begin{aligned} d_1 &= (3/2)\omega_0\tau_c(-J_1 + 20J_2), \\ d_2 &= (3/2)\omega_0\tau_c(7J_1 + 12J_2), \\ d_3 &= (13/2)\omega_0\tau_c(J_1 + 4J_2). \end{aligned} \quad (53)$$

The solution of Eq. (51) can be obtained by the use of

<sup>8</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. VIII.

given in Table I are listed in the last column of the table for the purpose of comparison with the more rigorous results calculated in this paper.

It is apparent from Table I that for all values of  $(\omega_0\tau_c)^2$  the coefficient  $a_1$  is much larger than  $a_2$  or  $a_3$ , so that the relaxation is approximately a simple exponential decay. Furthermore, the time constant,  $-(p_1)^{-1}$ , of the dominant exponential is in all cases approximately equal to the relaxation time  $T_1$  calculated by neglecting cross correlations.

#### 4. TRANSVERSE FREE RELAXATION

The calculation of the relaxation of  $\langle I^1 \rangle = \langle I_x \rangle + i\langle I_y \rangle$  in the absence of an applied radio-frequency magnetic field is similar to the calculation of the longitudinal relaxation given in the previous section. The following combinations of matrix elements are introduced:

$$y_1 \equiv 2(\langle 1121 | \sigma | 1122 \rangle + \langle 112, -2 | \sigma | 112, -1 \rangle), \quad (49a)$$

$$y_2 \equiv 6^{1/2}(\langle 1120 | \sigma | 1121 \rangle + \langle 112, -1 | \sigma | 1120 \rangle), \quad (49b)$$

$$\begin{aligned} y_3 \equiv \sqrt{2} \sum_{I_{12}I_{34}} & (\langle I_{12}I_{34}10 | \sigma | I_{12}I_{34}11 \rangle \\ & + \langle I_{12}I_{34}1, -1 | \sigma | I_{12}I_{34}10 \rangle). \end{aligned} \quad (49c)$$

It follows from Eq. (25b) that

$$\langle I^1 \rangle = \sum_{k=1}^3 y_k. \quad (50)$$

Differential equations for the  $y_i$  are obtained from Eq. (26). When the differential equations for the matrix elements of  $\sigma$  are combined so that the time derivative of one of the  $y_i$  occurs on the left-hand side, the other matrix elements in the equation occur only in the combinations  $y_i$ . The three resulting equations can be written in matrix form as follows:

$$\frac{d}{dt}(\mathbf{y}e^{i\omega_0 t}) + i\mathbf{d}(\mathbf{y}e^{i\omega_0 t}) = \mathbf{B}(\mathbf{y}e^{i\omega_0 t}), \quad (51)$$

where

Laplace transforms. The result can be written

$$\begin{aligned} \mathbf{y}(t) = - \sum_{k=1}^3 & [\text{Adj}(\mathbf{B} - i\mathbf{d} - q_k \mathbf{I}) \mathbf{y}(0)] \\ & \times e^{(q_k - i\omega_0)t} / D'(q_k), \end{aligned} \quad (54)$$

where  $\text{Adj}(\mathbf{B} - i\mathbf{d} - q_k \mathbf{I})$  is the adjoint matrix of the matrix  $(\mathbf{B} - i\mathbf{d} - q_k \mathbf{I})$ ,  $D'(q)$  is the derivative with respect to  $q$  of the determinant  $D(q)$  of  $(\mathbf{B} - i\mathbf{d} - q \mathbf{I})$ , and  $q_1$ ,  $q_2$ , and  $q_3$  are the eigenvalues of  $\mathbf{B} - i\mathbf{d}$ , and

hence solutions of the equation  $D(q)=0$ . The roots  $q_k$  must be distinct in order for (54) to be valid.

The initial conditions are again considered to be the result of the application to the system in thermal equilibrium of a transverse magnetic field rotating with the Larmor frequency  $\omega_0$ . After a short pulse of duration  $t_0=\theta/\gamma H_1$ , the density operator is given by Eq. (35). Hence, correct to first order in  $\beta\omega_0$ ,

$$\langle \alpha M | \sigma_\theta | \alpha, M+1 \rangle + \langle \alpha, -M-1 | \sigma_\theta | \alpha, -M \rangle = (\beta\omega_0/16) [(I-M)(I+M+1)]^{1/2} e^{-i\omega_0 t_\theta}, \quad (55)$$

so that, with  $\sigma(0)=\sigma_\theta$ ,

$$y(0) = (1/8) \{2, 3, 3\} \beta\omega_0 \sin\theta \exp[i(\pi/2 - \omega_0 t_\theta)]. \quad (56)$$

By use of (54) and (56) in (50), one obtains

$$\langle I^1 \rangle = \langle I^0 \rangle^T i e^{-i\omega_0 t_\theta} \sin\theta \sum_{k=1}^3 b_k e^{(q_k - i\omega_0)t}, \quad (59)$$

where  $\langle I^0 \rangle^T = \beta\omega_0$ , and

$$b_k = - \sum_{j=1}^3 \{ 2 \text{Adj}(\mathbf{B} - i\mathbf{d} - q_k \mathbf{I})_{j1} + 3 \text{Adj}(\mathbf{B} - i\mathbf{d} - q_k \mathbf{I})_{j2} + 3 \text{Adj}(\mathbf{B} - i\mathbf{d} - q_k \mathbf{I})_{j3} \} / 8D'(q_k). \quad (60)$$

Consider the case of short correlation time,  $\omega_0\tau_c \ll 1$ . Since in this case  $J_1 \approx J_2 \approx J_0$ , and  $d_1 \approx d_2 \approx d_3 \approx 0$ , the equation  $D(q)=0$  becomes

$$-(66J_0 + q)[q^2 + 146J_0q + 5145J_0^2] = 0,$$

which is the same as Eq. (41) with  $p$  replaced by  $q$ . Hence, the three roots  $q_k$  are equal, respectively, to the solutions  $p_k$  given by Eqs. (42). Furthermore, use of these values of  $q_k$  to evaluate expression (60) for the quantities  $b_k$  results in values that are, respectively, equal to the  $a_k$  of Eq. (43). Thus, as expected, in the case of short correlation time the transverse relaxation is the same as the longitudinal relaxation.

If the correlation time is not short, the matrix  $\mathbf{B} - i\mathbf{d}$  is complex and non-Hermitian. Hence its eigenvalues,  $q_k$ , are in general complex. The real part of  $q_k$  is denoted by  $q_k'$  and the imaginary part by  $q_k''$ :

$$q_k = q_k' + i q_k'', \quad k=1, 2, 3. \quad (61)$$

The secular equation,  $D(q)=0$ , is a cubic equation with complex coefficients. It can be written in the form  $D(q) = F_1(q', q'') + i F_2(q', q'') = 0$ , where  $F_1$  and  $F_2$  are real functions of the real variables  $q'$  and  $q''$ . Hence the real and imaginary parts of each of the three roots can be obtained by solving simultaneously the equations  $F_1(q', q'') = 0$  and  $F_2(q', q'') = 0$ . The solutions of the equations for several values of  $\omega_0\tau_c$ , have been obtained on an electronic computer by use of Newton's iterative method. Some of the results are given in Table II.

The coefficients  $b_k$  in Eq. (59) are in general complex,

$$b_k = b_k' + i b_k'' = |b_k| \exp(i\phi_k). \quad (62)$$

TABLE II. Coefficients in expression (63a) for the transverse relaxation.  $J_0 = (3/40)(\gamma^2 \hbar / r_0^3)^2 \tau_c$ .

$(\omega_0\tau_c)^2$ $T_2^{-1}/J_0$	$b_1'$ $-q_1'/J_0$	$b_1''$ $-q_1''/J_0$	$b_2'$ $-q_2'/J_0$	$b_2''$ $-q_2''/J_0$	$b_3'$ $-q_3'/J_0$	$b_3''$ $-q_3''/J_0$
0.0	0.9792	0.0000	0.0000	0.0000	0.0208	0.0000
60.000	59.435	0.0000	66.000	0.0000	86.565	0.0000
0.01	0.9777	-0.002	0.0008	0.0002	0.0215	0.0018
59.241	58.671	2.8484	64.829	2.7506	85.007	3.0510
0.05	0.9534	-0.016	0.0234	0.0126	0.0232	0.0039
56.571	44.903	5.5880	60.726	5.4436	79.800	6.0584
0.1	0.8610	-0.077	0.1150	0.0720	0.0240	0.0048
53.844	52.896	6.7282	56.692	6.8878	74.860	7.5549
0.3	0.3501	-0.049	0.6279	0.0461	0.0031	0.0221
46.531	43.404	6.8714	47.871	8.9693	62.834	9.1132
0.5	0.2500	0.0000	0.7308	0.0000	0.0192	0.0000
42.000	37.500	6.3640	43.175	9.1924	55.825	9.1924
0.7	0.2182	0.0145	0.7647	-0.0120	0.0171	-0.003
38.805	33.638	5.8730	39.948	9.0511	50.958	8.9971
1.0	0.2010	0.0219	0.7845	-0.016	0.0145	-0.005
35.400	29.805	5.2660	36.546	8.6865	45.798	8.5976
2.0	0.1948	0.0237	0.7966	-0.013	0.0086	-0.011
29.333	23.606	4.0287	30.553	7.5096	36.619	7.3965
4.0	0.2051	0.0177	0.7940	-0.002	0.0008	-0.016
24.706	19.302	2.9426	26.030	6.0333	29.609	5.9300
6.0	0.2135	0.0132	0.7918	0.0056	-0.005	-0.019
22.766	17.581	2.4224	24.146	5.1716	26.668	5.0804
8.0	0.2193	0.0102	0.7916	0.0111	-0.011	-0.021
21.697	16.650	2.1050	23.112	4.5953	25.047	4.5134
10.0	0.2236	0.0082	0.7928	0.0154	-0.016	-0.024
21.020	16.065	1.8861	22.458	4.1762	24.020	4.1012
50.0	0.2431	0.0011	0.9291	0.1175	-0.172	-0.119
18.648	14.046	0.8475	20.185	1.9766	20.417	1.9282
100.0	0.2464	0.0004	0.6593	0.5991	0.0943	-0.600
18.327	13.775	0.5996	19.882	1.4359	19.926	1.3445
1000.0	0.2496	0.0000	0.3788	0.113	0.3715	-0.111
18.033	13.528	0.1897	19.540	0.4727	19.542	0.4121

As a result of the initial condition, Eq. (56), the complex numbers  $b_k$  must have a sum of unity:  $b_1 + b_2 + b_3 = 1$ .

By use of Eqs. (61) and (62), Eq. (59) for  $\langle I^1 \rangle$  after a  $\theta$  deg pulse can be written in either of the two forms

$$\langle I^1 \rangle = i \langle I^0 \rangle^T \sin\theta \sum_{k=1}^3 (b_k' + i b_k'') e^{q_k' t} e^{-i[(\omega_0 - q_k'')t + \omega_0 t_\theta]} \quad (63a)$$

$$= i \langle I^0 \rangle^T \sin\theta \sum_{k=1}^3 |b_k| e^{q_k' t} e^{-i[(\omega_0 - q_k'')t - \phi_k + \omega_0 t_\theta]}. \quad (63b)$$

The values of  $b_k'$  and  $b_k''$  corresponding to the values of  $\omega_0\tau_c$  in Table II are included in the table.

If cross correlations between different dipole-dipole interactions are neglected, the relaxation of the magnitude of  $\langle I^1 \rangle$  is a simple exponential decay. For the four-spin system, the time constant of the decay can be shown to be<sup>5,8</sup>

$$T_2^{-1} = 6J_0 \{ 3 + 5[1 + (\omega_0\tau_c)^2]^{-1} + 2[1 + (2\omega_0\tau_c)^2]^{-1} \}. \quad (64)$$

Values of  $T_2^{-1}/J_0$  are listed in Table II for the purpose of comparison with the other values in the table, which have been obtained without neglecting cross correlations or the second-order corrections to the Zeeman interaction.

The voltage induced in a coil, whose axis is in the  $x$  direction, by the precessing magnetization after a  $\theta$  pulse, is proportional to  $d\langle I_x \rangle / dt$ . With the assumption

that  $\omega_0 \gg |q_k' + iq_k''|$ , it follows from Eq. (63a) that

$$\frac{d}{dt} \langle I_x \rangle = \omega_0 \langle I^0 \rangle^T \sin \theta C(t) \cos[\omega_0 t + \omega_0 t_\theta - \phi(t)], \quad (65)$$

where

$$\tan \phi(t) = \frac{\sum_{k=1}^3 e^{q_k' t} (b_k'' \cos q_k'' t + b_k' \sin q_k'' t)}{\sum_{k=1}^3 e^{q_k' t} (b_k' \cos q_k'' t - b_k'' \sin q_k'' t)}, \quad (66)$$

$$C(t) = \left\{ \left[ \sum_{k=1}^3 e^{q_k' t} (b_k'' \cos q_k'' t + b_k' \sin q_k'' t) \right]^2 + \left[ \sum_{k=1}^3 e^{q_k' t} (b_k' \cos q_k'' t - b_k'' \sin q_k'' t) \right]^2 \right\}^{1/2}. \quad (67)$$

If the voltage is amplified by a receiver with bandwidth broad enough to include the three frequencies ( $\omega_0 - q_k''$ ), the voltage presented to a detector following the amplifier is proportional to (65). Since  $C(t)$  and  $\phi(t)$  are slowly varying functions of time, the output of the detector is proportional to  $C(t)$ .

The time dependence of expression (67) for  $C(t)$  is difficult to visualize. In view of the values in Table II, it appears at first glance that  $C(t)$  might differ considerably from  $\exp(-t/T_2)$ , at least for intermediate and large values of  $\omega_0 \tau_c$ . However, such is not the case. If  $\exp(-t/T_2)$  is factored out of (67), the expression can be written  $C(t) = \exp(-t/T_2) C_1(t)$ . For several values of  $\omega_0 \tau_c$ , numerical values from Table II have been substituted into the expression for  $C_1(t)$  obtained from Eq. (67). It was found, in all the cases investigated, that  $C_1(t)$  is very nearly unity for all values of  $t$  for which  $\exp(-t/T_2)$  has appreciable magnitude. Hence, the transverse relaxation appears to differ very little from the simple exponential decay predicted by the calculation in which cross correlations are neglected.

## 5. RESONANCE LINE SHAPE

The resonance line shape depends upon the steady-state expression for  $\langle I^1 \rangle = \langle I_x \rangle + i \langle I_y \rangle$ . The quantity  $\langle I^1 \rangle$  is given by  $\sum y_k$  in terms of the  $y_k$  defined by Eqs. (49). As in Sec. 4, differential equations for the  $y_k$  can be obtained from Eq. (26). If variables  $Y_k \equiv y_k \times \exp(i\omega t)$  are introduced, the equations governing their time dependence can be written in matrix form as

$$d\mathbf{Y}/dt = [\mathbf{B} - i(\Delta_0 \mathbf{I} + \mathbf{d})] \mathbf{Y} + i\omega_1 \mathbf{P}, \quad (68)$$

where  $\Delta_0 \equiv \omega_0 - \omega$ . The elements of  $\mathbf{B}$  are given by (52) and the elements of  $\mathbf{d}$  by (53).  $\mathbf{P}$  is the column matrix

$$\mathbf{P} \equiv \{x_1 - 2x_2 + \tilde{z}, 3x_2 - \tilde{z}, x_3\}. \quad (69)$$

The  $x_k$  are defined by (27), and  $\tilde{z}$  is defined by

$$\tilde{z} \equiv 6^{1/2} (\langle 1120 | \sigma | 1122 \rangle - \langle 112, -2 | \sigma | 1120 \rangle) e^{i2\omega t}. \quad (70)$$

Equations for the time derivatives of the quantities  $x_k$  can be obtained from Eq. (26), as was done in Sec. 3, except now the terms multiplied by  $\omega_1$  must be included. The equations can be written in matrix form as

$$d\mathbf{x}/dt = \mathbf{A}(\mathbf{x} - \mathbf{x}^T) + \omega_1 \mathbf{Q}. \quad (71)$$

The elements of  $\mathbf{A}$  are given by (33).  $\mathbf{Q}$  is the column matrix

$$\mathbf{Q} \equiv \{-2Y_1'', Y_1'' - Y_2'', -Y_3''\}, \quad (72)$$

where  $Y_k''$  is the imaginary part of  $Y_k$ . In obtaining Eq. (71), use has been made of the fact that the operator  $\sigma$  is Hermitian.

A differential equation for the quantity  $\tilde{z}$  defined by (70) can be obtained from Eq. (26):

$$d\tilde{z}/dt = [C_{11} - i(2\Delta_0 + e_1)]\tilde{z} + i\omega_1(\frac{1}{2}\tilde{w} + \frac{3}{2}Y_1 - Y_2), \quad (73)$$

where

$$C_{11} \equiv -6(J_0 + 6J_1 + 4J_2), \quad (74)$$

$$e_1 \equiv (9J_1 + 48J_2)\omega_0 \tau_c, \quad (75)$$

and

$$\tilde{w} \equiv 6(\langle 112, -1 | \sigma | 1122 \rangle + \langle 112, -2 | \sigma | 1121 \rangle) e^{i3\omega t}. \quad (76)$$

A differential equation for  $\tilde{w}$  can also be obtained from (26):

$$d\tilde{w}/dt = [C_{22} - i(3\Delta_0 + e_2)]\tilde{w} + 3i\omega_1 \tilde{z}, \quad (77)$$

where

$$C_{22} \equiv -\frac{3}{2}(9J_0 + 13J_1 + 22J_2), \quad (78)$$

and

$$e_2 \equiv \frac{3}{2}(13J_1 + 44J_2)\omega_0 \tau_c. \quad (79)$$

Equations (68), (71), (73), and (77) constitute a set of simultaneous linear first-order differential equations with constant coefficients which determine the time dependence of the real variables  $x_1, x_2, x_3$  and the complex variables  $Y_1, Y_2, Y_3, \tilde{z}$ , and  $\tilde{w}$ . If it is assumed that a steady-state solution exists, as is physically justifiable, it can be obtained by setting equal to zero the time derivatives in the equations, and then solving the resulting algebraic equations. Thus, in the steady state,

$$\mathbf{Y} = -i\omega_1 [\mathbf{B} - i(\Delta_0 \mathbf{I} + \mathbf{d})]^{-1} \mathbf{P}, \quad (80)$$

$$\mathbf{x} = -\omega_1 \mathbf{A}^{-1} \mathbf{Q} + \mathbf{x}^T, \quad (81)$$

$$[C_{11} - i(2\Delta_0 + e_1)]\tilde{z} + i\omega_1(\frac{1}{2}\tilde{w} + \frac{3}{2}Y_1 - Y_2) = 0, \quad (82)$$

$$[C_{22} - i(3\Delta_0 + e_2)]\tilde{w} + 3i\omega_1 \tilde{z} = 0. \quad (83)$$

Elimination of  $\tilde{w}$  from (82) and (83) gives

$$\tilde{z} = \frac{-i\omega_1 [C_{22} - i(3\Delta_0 + e_2)](3Y_1 - 2Y_2)}{\{2[C_{11} - i(2\Delta_0 + e_1)][C_{22} - i(3\Delta_0 + e_2)] + 3\omega_1^2\}}. \quad (84)$$

If the above expression for  $\tilde{z}$  and expressions for the  $x_k$  from (81) are substituted into  $\mathbf{P}$  in Eq. (80), that equation then involves only the real and imaginary parts of the  $Y_k$ , the other variables having been eliminated. Since all terms in  $\mathbf{P}$  are at least first order in  $\omega_1$  except those arising from the  $\mathbf{x}^T$  term in (81), the

solution of (80) to first order in  $\omega_1$  is

$$\mathbf{Y} = -i\omega_1[\mathbf{B} - i(\Delta_0\mathbf{I} + \mathbf{d})]^{-1}\{2,3,3\}\beta\omega_0/8, \quad (85)$$

where the values of the elements of  $\mathbf{x}^T$  given by (29) have been used. In the calculation of the transverse relaxation in the previous section a function  $D(q)$ , defined to be the determinant of  $[\mathbf{B} - i\mathbf{d} - q\mathbf{I}]$ , was introduced, and the roots of  $D(q) = 0$  were denoted  $q_k$ . Hence, it follows from (85) that

$$\mathbf{Y} = -i\omega_1 \text{Adj}[\mathbf{B} - i(\Delta_0\mathbf{I} + \mathbf{d})]\{2,3,3\}\beta\omega_0/8D(i\Delta_0) \quad (86a)$$

$$= +i\omega_1(\beta\omega_0) \sum_{k=1}^3 \frac{\text{Adj}[\mathbf{B} - i\mathbf{d} - q_k\mathbf{I}]\{2,3,3\}}{8D'(q_k)(q_k - i\Delta_0)}, \quad (86b)$$

where the second form has been obtained by separating into partial fractions. Since from (50),  $\langle I^1 \rangle = \sum y_k = \exp(-i\omega t) \sum Y_k$ , it follows from (86b) that the steady-state expression for  $\langle I^1 \rangle$  can be written

$$\langle I^1 \rangle_s = -i\omega_1 \langle I^0 \rangle^T e^{-i\omega t} \sum_{k=1}^3 b_k(q_k - i\Delta_0)^{-1}, \quad (87)$$

where  $\langle I^0 \rangle^T = \beta\omega_0$ , the thermal equilibrium value of  $\langle I^0 \rangle$  in the absence of a radio-frequency field, and the  $b_k$  are given by (60).

Let  $n$  be the number of molecules per unit volume in the sample. The nuclear magnetization is then  $\mathbf{M} = n\gamma\hbar\langle \mathbf{I} \rangle$ . When the magnetic field (2) is present, and the spin system is in a steady state, the complex susceptibility  $\chi = \chi' + i\chi''$  is defined by the relation

$$M_x + iM_y = H_1 \chi \exp(-i\omega t). \quad (88)$$

Hence, it follows from (87) that

$$\chi = -i\gamma M_0 \sum_{k=1}^3 b_k(q_k - i\Delta_0)^{-1}, \quad (89)$$

where  $M_0 = n\gamma\hbar\langle I^0 \rangle^T$ .

The free relaxation of the transverse magnetization after a  $90^\circ$  pulse is given by  $M_x(t) + iM_y(t) = n\gamma\hbar\langle I^1 \rangle$ , where the time-dependent expression for  $\langle I^1 \rangle$  is given by (59) with  $\theta = 90^\circ$ . From (59) and (87) it follows that

$$\chi = \gamma e^{i\omega_0 t} \int_0^\infty [M_x(t) + iM_y(t)] e^{i\omega t} dt, \quad (90)$$

since the values of  $q_k$  are negative. Equation (90) is similar to a relation given by Lowe and Norberg.<sup>3</sup>

The real part  $\chi'$  and the imaginary part  $\chi''$  of Eq. (89) for  $\chi$  are

$$\chi' = \gamma M_0 \sum_{k=1}^3 [b_k'' q_k' - b_k'(q_k'' - \Delta_0)] / \times [q_k'^2 + (q_k'' - \Delta_0)^2], \quad (91)$$

$$\chi'' = -\gamma M_0 \sum_{k=1}^3 [b_k' q_k' + b_k''(q_k'' - \Delta_0)] / \times [q_k'^2 + (q_k'' - \Delta_0)^2]. \quad (92)$$

<sup>3</sup> I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

The quantities  $b_k'$ ,  $b_k''$ ,  $q_k'$ , and  $q_k''$  are given in Table II for different values of  $(\omega_0\tau_c)^2$ . It is apparent from Table II that the  $b_k'$  are larger than the corresponding  $b_k''$  by about an order of magnitude except in the cases in which both  $b_k'$  and  $b_k''$  are negligible. Thus, the terms which have appreciable magnitude in the sum over  $k$  in (92) are approximately Lorentzian absorption curves, and the terms in the sum over  $k$  in (91) are approximately dispersion curves. Each curve is centered at  $\omega = \omega_0 - q_k''$  and has half-width  $|q_k'|$ . Since the  $q_k''$  are less in magnitude than the corresponding  $q_k'$  by at least a factor of 4, the center of the resonance curve for each  $k$  is displaced from the Larmor frequency  $\omega_0$  by an amount less than the linewidth.

Expressions (91) for  $\chi'(\omega)$  and (92) for  $\chi''(\omega)$  satisfy the Kramers-Kronig relations appropriate for a rotating applied radio-frequency field<sup>10</sup>:

$$\chi'(\omega_0 + y) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi''(\omega_0 + y') dy'}{y' - y}, \quad (93a)$$

$$\chi''(\omega_0 + y) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi'(\omega_0 + y') dy'}{y' - y}. \quad (93b)$$

The results obtained above for  $\chi'$  and  $\chi''$  give the resonance line shape only to first order in  $H_1$ . The resonance behavior for larger values of  $H_1$  can in principle be obtained from Eq. (80) after elimination of the  $x_k$  and  $\tilde{z}$  from  $\mathbf{P}$  by use of (81) and (84). However, the calculations are quite complicated, and will be carried out here only for the case of short correlation time.

If the correlation time is short, important simplifications occur in Eqs. (68) and (71) which permit a general solution for  $\langle I^0 \rangle$  and  $\langle I^1 \rangle$  which describes both the transient and the steady-state behavior of the spin system. When  $\omega_0\tau_c \ll 1$ ,  $J_1 \approx J_2 \approx J_0$  in the elements of  $\mathbf{B}$ , Eqs. (52), and the elements of  $\mathbf{A}$ , Eqs. (33). Also, from (53),  $d_1 \approx d_2 \approx d_3 \approx 0$ . With these values, it follows from (68) that the equation obtained by adding the expressions for  $dY_1/dt$  and  $dY_2/dt$ , and the equation for  $dY_3/dt$ , can be written in matrix form as

$$(\mathbf{I}d/dt - \mathbf{\Theta} + i\Delta_0\mathbf{I}) \begin{Bmatrix} Y_1 + Y_2 \\ Y_3 \end{Bmatrix} = i\omega_1 \begin{Bmatrix} x_1 + x_2 \\ x_3 \end{Bmatrix}, \quad (94)$$

where  $\mathbf{I}$  is the unit matrix and

$$\mathbf{\Theta} \equiv J_0 \begin{bmatrix} -66 & 15 \\ 9 & -80 \end{bmatrix}. \quad (95)$$

<sup>10</sup> See, for example, reference 8, Chap. III, Eqs. (8''').



In a similar manner, one obtains from (71)

$$(\mathbf{Id}/dt - \Theta) \left( \begin{Bmatrix} x_1 + x_2 \\ x_3 \end{Bmatrix} - \begin{Bmatrix} x_1^T + x_2^T \\ x_3^T \end{Bmatrix} \right) = -\omega_1 \begin{Bmatrix} Y_1'' + Y_2'' \\ Y_3'' \end{Bmatrix}. \quad (96)$$

Note that  $\tilde{z}$  has been eliminated, and that the same matrix  $\Theta$  occurs in both (94) and (96). Since the  $x_k$  are real, Eq. (96) contains only real numbers. However, Eq. (94) is complex; when separated into real and imaginary parts it gives two real equations. The general solution of the three equations coupling  $\{Y_1' + Y_2', Y_3'\}$ ,  $\{Y_1'' + Y_2'', Y_3''\}$ , and  $\{x_1 + x_2, x_3\}$  can be obtained relatively easily by use of matrix techniques. Without going through the details of the calculation here, we give the results for

$$\langle I^1 \rangle = \exp(-i\omega t) \sum Y_k \quad \text{and} \quad \langle I_z \rangle = \sum x_k$$

$$\begin{aligned} \langle I^1 \rangle = e^{-i\omega t} \sum_{j=1}^2 & \left\{ \frac{\omega_1(\Delta_0 - i\lambda_j)C_j(\alpha)}{(\lambda_j^2 + \omega'^2)} \right. \\ & + e^{\lambda_j t} \left[ C_j(\mathbf{D}) + \left( iC_j(\mathbf{b}) + \frac{\Delta_0}{\omega'} C_j(\mathbf{a}) \right) \sin \omega' t \right. \\ & \left. \left. + \left( iC_j(\mathbf{a}) - \frac{\Delta_0}{\omega'} C_j(\mathbf{b}) \right) \cos \omega' t \right] \right\}, \quad (97) \end{aligned}$$

$$\begin{aligned} \langle I_z \rangle - \langle I_z \rangle^T = \sum_{j=1}^2 & \left\{ -\frac{\omega_1^2 C_j(\alpha)}{(\lambda_j^2 + \omega'^2)} + e^{\lambda_j t} \left[ C_j(\mathbf{r}) \right. \right. \\ & \left. \left. - \frac{\omega_1}{\omega'} C_j(\mathbf{a}) \sin \omega' t + \frac{\omega_1}{\omega'} C_j(\mathbf{b}) \cos \omega' t \right] \right\}, \quad (98) \end{aligned}$$

where  $\omega' \equiv (\omega_1^2 + \Delta_0^2)^{1/2}$ .  $\lambda_1$  and  $\lambda_2$  are the eigenvalues of the matrix  $\Theta$ :

$$\lambda_1 = [-73 + 2(46)^{1/2}]J_0, \quad \lambda_2 = [-73 - 2(46)^{1/2}]J_0. \quad (99)$$

$\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{r}$ , and  $\mathbf{D}$  are two-dimensional vectors that are arbitrary except for the condition  $\omega_1 \mathbf{r} = \Delta_0 \mathbf{D}$ , and  $\alpha$  is the vector

$$\alpha = \{x_1^T + x_2^T, x_3^T\} = \{5, 3\} \beta \omega_0 / 8. \quad (100)$$

$C_1(\mathbf{a})$  and  $C_2(\mathbf{a})$  are scalar functions of the two elements of their arguments:

$$C_1(\mathbf{a}) \equiv \{[23 + 4(46)^{1/2}]a_1 + [23 + 2(46)^{1/2}]a_2\}/46, \quad (101a)$$

$$C_2(\mathbf{a}) \equiv \{[23 - 4(46)^{1/2}]a_1 + [23 - 2(46)^{1/2}]a_2\}/46. \quad (101b)$$

The time constants of the decaying exponentials in (97) and (98) agree with the time constants of the two

exponentials that were previously found to occur in the expressions for the free longitudinal and transverse relaxation in the case of short correlation time. The treatment in this section shows clearly why there are just two exponentials when the correlation time is short.

It follows from the steady-state part of (97) that the complex susceptibility

$$\chi = \chi' + i\chi'' = n\gamma\hbar\langle I^1 \rangle_s / [H_1 \exp(-i\omega t)]$$

for short correlation time is

$$\begin{aligned} \chi = \gamma M_0 & \left\{ \left( \frac{92 + 13(46)^{1/2}}{184} \right) \frac{(\Delta_0 - i\lambda_1)}{(\lambda_1^2 + \omega'^2)} \right. \\ & \left. + \left( \frac{92 - 13(46)^{1/2}}{184} \right) \frac{(\Delta_0 - i\lambda_2)}{(\lambda_2^2 + \omega'^2)} \right\}. \quad (102) \end{aligned}$$

The expressions for  $\chi'$  and  $\chi''$  from (102) differ from the expressions (91) and (92), when the values of the parameters for short correlation time are inserted, only in the fact that  $\omega'^2 = \omega_1^2 + \Delta_0^2$  replaces  $\Delta_0^2$ . The saturation behavior of each term in (102) is the same as the saturation behavior of the single term susceptibility obtained from the Bloch phenomenological equations.

## 9. DISCUSSION AND CONCLUSIONS

The form of the expressions obtained above for the longitudinal and transverse relaxation and the resonance line shape are quite interesting. However, the values of the parameters occurring in the expressions are such that there is little actual difference from the results obtained by neglecting in the calculation cross correlations of different dipole-dipole interactions. Nonetheless, it cannot be concluded from this calculation alone that the effect of cross correlations of dipole-dipole interactions is negligible for all types of molecules undergoing any kind of motion. While such may be the case, a general proof has yet to be given.

It must be remembered that in the calculations in this paper the relaxation was assumed to be due just to intramolecular dipole-dipole interactions. Although the effect of intermolecular interactions can be minimized by diluting the four-spin molecules in a nonmagnetic solvent, the effect of spin-rotational interactions might be significant. The author plans to investigate in detail the effect of spin-rotational interactions on the relaxation of four-spin molecules.

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