Nuclear Magnetic Relaxation of Three Spin Systems Undergoing Hindered Rotations*†

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The longitudinal nuclear magnetic relaxation of an ensemble of spin systems exposed to a constant magnetic field $H_0\mathbf{k}$ is calculated. Each spin system consists of three identical spin-$\frac{1}{2}$ nuclei located at the vertices of an equilateral triangle. Each spin system undergoes hindered rotation about an axis that is perpendicular to the plane of the three spins, and is oriented at an angle β with the constant field. Two models for the rotation are studied: In one model there are only three possible equilibrium orientations of each system about its rotation axis and the group makes random jumps between these orientations; in the other model each group performs stochastic rotational diffusion about its rotation axis. Both models lead to results of the same form, which differ only in the definition of the correlation time τ_c of the motion. It is assumed that the relaxation is due to the magnetic dipole-dipole interactions between the nuclei within each group. The calculation is performed by use of the semiclassical form of the density operator theory of relaxation. The treatment includes terms arising from the cross correlation of different dipole-dipole interactions with one another, from the nonzero average of the dipole-dipole interactions, and from the second-order correction to the Zeeman energy due to the dipole-dipole interactions. The relaxation is, in general, the sum of four decaying exponentials. For $\beta=0$, the relaxation does not decay to zero. By use of an electronic computer, explicit solutions have been calculated for $\cos\beta=0, \pm0.1, \pm0.2, \cdots, \pm1.0$ for many values of the correlation time. Also, explicit solutions have been calculated for situations in which the axes of hindered rotation are isotropically oriented. All results are compared with the results of a calculation in which cross correlations are omitted, and are shown to differ significantly. The results are presented in a form which can be compared with experimental data, and used to determine the correlation time of the hindered rotations.

I. INTRODUCTION

THE nuclear magnetic relaxation of spin-$\frac{1}{2}$ nuclei in matter is due in many cases to nuclear magnetic dipole-dipole interactions, which are time-dependent as a result of the motion of the nuclei. The calculation of the nuclear magnetic relaxation involves certain correlation functions of each dipole-dipole interaction with itself (autocorrelations) and with other dipole-dipole interactions (cross correlations). If the cross correlation terms are omitted, the calculated relaxations of the longitudinal and transverse components of the nuclear magnetization are simple exponential decays.[1] If the cross correlation terms are included in the calculation, the longitudinal relaxation is found, in general, to be the sum of more than one decaying exponential.

Previous calculations of the relaxation of systems of three and four identical spin-$\frac{1}{2}$ nuclei in spherical molecules undergoing isotropic rotational Brownian motion in a liquid have shown that the relaxation is the sum of several decaying exponentials.[2–4] However, the values of the time constants and the coefficients of the exponentials are such that the predicted relaxation differs very little from the simple exponential decay calculated by neglecting the cross correlations.

Runnels[5] has investigated the longitudinal relaxation of molecules with three identical spin-$\frac{1}{2}$ nuclei in equivalent positions at the corners of an equilateral triangle, and has found that the relaxation is in general described by four decaying exponentials, although three suffice for isotropic motion.[2] He has shown that, for systems initially describable by a spin temperature, the effect of cross correlations always is to retard the relaxation. Runnels has also shown that an effective relaxation time T_e, which is defined by the condition that the integral from 0 to ∞ of $\exp(-t/T_e)$ have the same value as the integral of the actual relaxation, can be calculated much more easily than the actual nonexponential relaxation.

We have calculated the longitudinal nuclear magnetic relaxation of an ensemble of systems each consisting of three identical spin-$\frac{1}{2}$ nuclei at the corners of an equilateral triangle. These calculations are for the case in which the motion of each system is hindered rotation about an axis that is perpendicular to the plane of the three spins and is oriented at an angle β with the constant field. Two types of hindered rotation are considered: (1) random jumps between three equilibrium positions, and (2) rotational diffusion about the axis. It is assumed that the relaxation is due to the magnetic dipole-dipole interactions between the three nuclei. The treatment includes terms arising from the cross correlation of different dipole-dipole interactions with one another, and from the second-order correction to the Zeeman energy due to the dipole-dipole interactions.

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We have also calculated the longitudinal nuclear magnetic relaxation of an ensemble of three spin systems which undergo hindered rotation about axes which are isotropically oriented.

The situations considered in this paper are the first examples of cases in which the inclusion of cross correlations of different dipole-dipole interactions in the calculation of nuclear magnetic relaxation results in a predicted relaxation that differs significantly from a simple exponential decay.

II. FORMULATION OF THE CALCULATION

Consider a system of three identical spin-$\frac{1}{2}$ nuclei at the corners of an equilateral triangle. The spins of the nuclei are denoted by $\mathbf{I}_i$ and their gyromagnetic ratios by γ. There is a constant magnetic field $\mathbf{H}_0$ in the z direction. The magnetic dipole-dipole interaction Hamiltonian can be written as

$$\hbar G=\hbar\sum_{i<j}^{3}\sum_{k=-2}^{2}U_{ij}{}^{k}V_{ij}{}^{k}, \tag{2.1}$$

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

$$V_{ij}{}^{0}\equiv-(8/3)^{1/2}[I_i{}^0I_j{}^0-\tfrac{1}{4}(I_i{}^1I_j{}^{-1}+I_i{}^{-1}I_j{}^1)], \tag{2.2a}$$

$$V_{ij}{}^{\pm1}\equiv\pm(I_i{}^{\pm1}I_j{}^0+I_i{}^0I_j{}^{\pm1}), \tag{2.2b}$$

and

$$V_{ij}{}^{\pm2}\equiv-I_i{}^{\pm1}I_j{}^{\pm1} \tag{2.2c}$$

in terms of the spin operators

$$I_j{}^{\pm1}\equiv I_{jx}\pm iI_{jy},\quad I_j{}^0\equiv I_{jz}. \tag{2.3}$$

The $U_{ij}{}^k$ are given by

$$U_{ij}{}^{k}=(6\pi/5)^{1/2}d(-1)^kY_2{}^{-k}(\theta_{ij},\phi_{ij}) \tag{2.4}$$

in terms of

$$d\equiv(\gamma^2\hbar/r_0{}^3), \tag{2.5}$$

where (θ_{ij},ϕ_{ij}) and r_0 are, respectively, the polar angles and the magnitude of the vector $\mathbf{r}_{ij}$ from the jth nucleus to the ith nucleus. The $Y_2{}^k(\theta,\phi)$ are normalized spherical harmonics of second order.[6]

The spin system can be described by a reduced density operator σ in the sense that the average over an ensemble of such systems of the expectation value of a spin operator such as $I^0\equiv\sum_i I_i{}^0$ is given by $\langle I^0\rangle=\mathrm{Tr}[\sigma I^0]$. It is convenient to introduce an operator χ' defined by

$$\chi'\equiv e^{iEt}(\sigma-\sigma^T)e^{-iEt}, \tag{2.6}$$

where

$$E\equiv-\omega_0I^0+\sum_{i<j}^{3}\sum_{k=-2}^{2}\langle U_{ij}{}^k\rangle_qV_{ij}{}^k \tag{2.7}$$

is the Zeeman interaction Hamiltonian of the three spins with the external magnetic field $H_0\mathbf{k}=(\omega_0/\gamma)\mathbf{k}$, plus the ensemble average over the molecular coordinates of the dipole-dipole interaction Hamiltonian, both expressed in units of $\hbar$. The reduced density operator for a spin system in thermal equilibrium, σ^T, is

$$\sigma^T\equiv e^{-\beta E}/\mathrm{Tr}[e^{-\beta E}]\approx[1-\beta E]/\mathrm{Tr}[1-\beta E], \tag{2.8}$$

where $\beta\equiv\hbar/kT$, k is the Boltzmann constant, and T is the absolute temperature of the lattice. The difference between the ensemble average of the expectation value of I^0 and the value of that quantity for an ensemble in thermal equilibrium is given in terms of χ' by

$$\langle I^0\rangle-\langle I^0\rangle^T=\mathrm{Tr}[\chi'I^{0\prime}], \tag{2.9}$$

where $I^{0\prime}=\exp(iEt)I^0\exp(-iEt)$.

It can be shown by the use of the semiclassical form of the density operator theory of relaxation,[1] that the matrix elements of χ', in a representation in which E is diagonal, are solutions of the equation

$$\frac{d}{dt}\langle\alpha|\chi'|\alpha'\rangle=i\sum_{\alpha''\alpha'''}e^{i\omega_{\alpha''\alpha'''}t}N(\alpha''\alpha''')[\delta_{\alpha'\alpha'''}\langle\alpha|\chi'|\alpha''\rangle-\delta_{\alpha\alpha''}\langle\alpha'''|\chi'|\alpha'\rangle]$$
$$+\sum_{\alpha''\alpha'''}e^{i(\omega_{\alpha\alpha'}-\omega_{\alpha''\alpha'''})t}R(\alpha\alpha'\alpha''\alpha''')\langle\alpha''|\chi'|\alpha'''\rangle, \tag{2.10}$$

where

$$N(\alpha''\alpha''')=\sum_{\alpha^{\mathrm{iv}}}\sum_{k,l=-2}^{2}\sum_{i<j}\sum_{i'<j'}I_{iji'j'}{}^{kl}[\tfrac{1}{2}(\omega_{\alpha''\alpha^{\mathrm{iv}}}-\omega_{\alpha^{\mathrm{iv}}\alpha'''})]\langle\alpha''|V_{ij}{}^k|\alpha^{\mathrm{iv}}\rangle\langle\alpha^{\mathrm{iv}}|V_{i'j'}{}^l|\alpha'''\rangle, \tag{2.11}$$

$$I_{iji'j'}{}^{kl}(\omega)=\frac{2}{\pi}\mathcal{P}\int_{-\infty}^{\infty}J_{(ij)(i'j')}{}^{kl}(\omega-z)(1+e^{\beta z})^{-1}z^{-1}dz, \tag{2.12}$$

and

$$R(\alpha\alpha'\alpha''\alpha''')=\sum_{kl}\sum_{i<j}\sum_{i'<j'}\{[J_{(i'j')(ij)}{}^{lk}(\omega_{\alpha\alpha''})+J_{(i'j')(ij)}{}^{lk}(\omega_{\alpha'\alpha'''})]\langle\alpha|V_{i'j'}{}^l|\alpha''\rangle\langle\alpha'''|V_{ij}{}^k|\alpha'\rangle$$
$$-\delta_{\alpha\alpha''}\sum_{\alpha^{\mathrm{iv}}}J_{(i'j')(ij)}{}^{lk}(\omega_{\alpha'''\alpha^{\mathrm{iv}}})\langle\alpha'''|V_{i'j'}{}^l|\alpha^{\mathrm{iv}}\rangle\langle\alpha^{\mathrm{iv}}|V_{ij}{}^k|\alpha'\rangle$$
$$-\delta_{\alpha'\alpha'''}\sum_{\alpha^{\mathrm{iv}}}J_{(i'j')(ij)}{}^{lk}(\omega_{\alpha''\alpha^{\mathrm{iv}}})\langle\alpha|V_{i'j'}{}^l|\alpha^{\mathrm{iv}}\rangle\langle\alpha^{\mathrm{iv}}|V_{ij}{}^k|\alpha''\rangle\}. \tag{2.13}$$

[6] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

The functions $J_{(i'j')(ij)}^{lk}(\omega)$ are defined by

$$J_{(i'j')(ij)}^{lk}(\omega)\equiv\frac{1}{2}\int_{-\infty}^{\infty}C_{(i'j')(ij)}^{lk}(\tau)e^{i\omega\tau}d\tau \quad (2.14)$$

in terms of the correlation functions

$$C_{(i'j')(ij)}^{lk}(\tau)\equiv\langle[U_{i'j'}{}^{l}-\langle U_{i'j'}{}^{l}\rangle_q]_{t+\tau}[U_{ij}{}^{k}-\langle U_{ij}{}^{k}\rangle_q]_t\rangle_q. \quad (2.15)$$

The averages in Eq. (2.14) are ensemble averages over the molecular coordinates, the motions of which are assumed to be a stationary random process. Hence the correlation functions are independent of t. Replacement of t by $t-\tau$ leads to the result

$$C_{(i'j')(ij)}^{lk}(\tau)=C_{(ij)(i'j')}^{kl}(-\tau). \quad (2.16)$$

The correlation functions approach zero as τ approaches infinity. The correlation time τ_c is defined rather loosely by the condition that

$$|C_{(i'j')(ij)}^{lk}(\tau)|\ll|C_{(i'j')(ij)}^{lk}(0)| \quad \text{if} \quad \tau\gg\tau_c. \quad (2.17)$$

The conditions of validity of Eq. (2.10) are that

$$|N(\alpha''\alpha''')|\tau_c, |R(\alpha\alpha'\alpha''\alpha''')|\tau_c\ll 1, \quad (2.18)$$

and

$$\beta\omega_0\ll 1. \quad (2.19)$$

Terms on the right-hand side of Eq. (2.10) for which the frequencies of oscillation $\omega_{\alpha''\alpha'''}$ or $(\omega_{\alpha\alpha'}-\omega_{\alpha''\alpha'''})$ are large compared to the magnitudes of the nonzero $N(\alpha''\alpha''')$ and $R(\alpha\alpha'\alpha''\alpha''')$ are said to be nonsecular. Nonsecular terms can be omitted in the solution of Eq. (2.10) because their effect on the solutions for the $\langle\alpha|\chi'|\alpha'\rangle$ are negligible compared to the effect of secular terms.

III. AVERAGES AND CORRELATION FUNCTIONS

It follows from Eqs. (2.4) and (2.15) that

$$\langle U_{ij}{}^{k}\rangle_q=(6\pi/5)^{1/2}d(-1)^k\langle Y_2{}^{-k}(\theta_{ij},\phi_{ij})\rangle_q, \quad (3.1)$$

and

$$C_{(i'j')(ij)}^{lk}(\tau)=(6\pi/5)d^2(-1)^{l+k}\times\{\langle[Y_2{}^{-l}(\theta_{i'j'},\phi_{i'j'})]_{t+\tau}[Y_2{}^{-k}(\theta_{ij},\phi_{ij})]_t\rangle_q-\langle Y_2{}^{-l}(\theta_{i'j'},\phi_{i'j'})\rangle_q\langle Y_2{}^{-k}(\theta_{ij},\phi_{ij})\rangle_q\}. \quad (3.2)$$

Suppose that the only motion of each of the three spin systems in the ensemble consists of hindered rotation about an axis perpendicular to the plane of the three nuclei. The axes of rotation of the systems are parallel and make an angle β with the z axis of the laboratory coordinate system S. Consider a coordinate system S' whose axes are rotated with respect to S through Euler angles $(\alpha\beta\gamma)$, so that the z' axis is parallel to the axes of hindered rotation.[7] Spherical harmonics with polar angles (θ,ϕ) in S are related to spherical harmonics with polar angles (θ',ϕ') in S' by[8]

$$Y_l{}^k(\theta,\phi)=\sum_{k'=-l}^{l}D_{kk'}{}^{l*}(\alpha\beta\gamma)Y_l{}^{k'}(\theta',\phi'), \quad (3.3)$$

where the $D_{kk'}{}^l(\alpha\beta\gamma)$ are elements of a rotation matrix. Since $\theta_{ij}'=\pi/2$, and $Y_2{}^{k'}(\pi/2,\phi_{ij}')=Y_2{}^{k'}(\pi/2,0)\times\exp(ik'\phi_{ij}')$, it follows from Eq. (3.3) that

$$\langle Y_2{}^{-k}(\theta_{ij},\phi_{ij})\rangle_q=\sum_{k'=-2}^{2}D_{-kk'}{}^{2*}Y_2{}^{k'}(\pi/2,0)\langle\exp(ik'\phi_{ij}')\rangle, \quad (3.4)$$

where $D_{-kk'}{}^{2*}\equiv D_{-kk'}{}^{2*}(\alpha\beta\gamma)$, and

$$\langle[Y_2{}^{-l}(\theta_{i'j'},\phi_{i'j'})]_{t+\tau}[Y_2{}^{-k}(\theta_{ij},\phi_{ij})]_t\rangle_q=\sum_{l',k'=-2}^{2}D_{-ll'}{}^{2*}D_{-kk'}{}^{2*}Y_2{}^{l'}(\pi/2,0)Y_2{}^{k'}(\pi/2,0)\times e^{il'\Omega(i'j',ij)}\langle\exp[il'\phi_{ij}'(\tau)]\exp[ik'\phi_{ij}'(0)]\rangle, \quad (3.5)$$

where $\Omega(i'j',ij)$ is the fixed angle between $\mathbf{r}_{i'j'}$ and $\mathbf{r}_{ij}$, given by

$$\phi_{i'j'}'\equiv\phi_{ij}'+\Omega(i'j',ij). \quad (3.6)$$

The averages in Eqs. (3.4) and (3.5) depend only on the values of ϕ_{ij}'. We consider two models of hindered rotation.

(1) Each group can assume only three angular orientations about its axis of rotation, which are equally spaced, and it jumps from one orientation to another with probability ν per unit time. The orientation of the axes S' can be chosen so that the three equilibrium positions correspond to $\phi_{ij}'=0$, $\pm 2\pi/3$. Since at any time the three values of ϕ_{ij}' are equally probable *a priori*, it follows that $\langle\exp(ik'\phi_{ij}')\rangle=\delta_{k'0}$. Thus, since $Y_2{}^0(\pi/2,0)=-(5/16\pi)^{1/2}$, it follows from Eqs. (3.1) and (3.4) that

$$\langle U_{ij}{}^k\rangle=-(3/8)^{1/2}d(-1)^kD_{-k0}{}^{2*}. \quad (3.7)$$

The probability that $\phi_{ij}'=r2\pi/3$ at $\tau=0$ and $\phi_{ij}'=s2\pi/3$ at a later time τ, where $r,s=0,\pm 1$, is denoted by $W_{sr}(\tau)$. It is easy to show by solution of the differential equations describing the rates of change of the probabilities of each orientation that

$$W_{sr}(\tau)=(1/9)[3\delta_{sr}\exp(-\tau/\tau_c)+1-\exp(-\tau/\tau_c)], \quad (3.8)$$

where the correlation time is defined by $\tau_c\equiv(2/3\nu)$. The average on the right hand side of Eq. (3.5) can be calculated by use of Eq. (3.8). Use of Eqs. (3.5) and (3.7) in Eq. (3.2) then leads to the following result, valid for $\tau\geq 0$:

$$C_{(i'j')(ij)}^{lk}(\tau)=(9/16)d^2(-1)^{l+k}[D_{-l2}{}^{2*}D_{-k-2}{}^{2*}e^{i2\Omega(i'j',ij)}+D_{-l-2}{}^{2*}D_{-k2}{}^{2*}e^{-i2\Omega(i'j',ij)}]e^{-\tau/\tau_c}. \quad (3.9)$$

[7] The Euler angles $(\alpha\beta\gamma)$ used here are those defined in Ref. 6.

[8] Equation (3.3) follows from Eqs. (4.28a) and p. 73 of Ref. 6.

(2) Each system undergoes stochastic rotational diffusion about its axis of hindered rotation. If the angle ϕ_{ij}' is considered to vary between 0 and 2π, the *a priori* probability density for ϕ_{ij}' is simply $(1/2\pi)$. The conditional probability density that ϕ_{ij}' has the value ϕ at time τ if it has the value ϕ_0 at time zero is

$$P(\phi,\tau;\phi_0) = (2\pi)^{-1}\sum_{n=-\infty}^{\infty}\exp[in(\phi-\phi_0)-(n^2/4\tau_c)t], \quad (3.10)$$

where τ_c is a constant related to the diffusion coefficient. Expression (3.10) is the solution of the diffusion equation which is a function only of the azimuthal angle, is periodic with period 2π, and satisfies the initial condition $P(\phi,0;\phi_0)=\delta(\phi-\phi_0)$.[9] The results obtained for $\langle U_{ij}^k\rangle$ and $C_{(i'j')(ij)}{}^{lk}(\tau)$ in this case are the same as expressions (3.7) and (3.9), respectively.

It is apparent from (3.9) that

$$C_{(i'j')(ij)}{}^{lk}(\tau)=C_{(ij)(i'j')}{}^{kl}(\tau),$$

if it is remembered that $\Omega(i'j',ij)=-\Omega(ij,i'j')$. Hence it follows from Eq. (2.16) that

$$C_{(i'j')(ij)}{}^{lk}(-\tau)=C_{(i'j')(ij)}{}^{lk}(\tau). \quad (3.11)$$

Use of Eqs. (3.9) and (3.11) in Eq. (2.14) gives

$$J_{(i'j')(ij)}{}^{lk}(\omega)=(9/16)d^2(-1)^{k+l}\tau_c[1+(\omega\tau_c)^2]^{-1} \times[D_{-l2}{}^{2*}D_{-k-2}{}^{2*}e^{i2\Omega(i'j',ij)} +D_{-l-2}{}^{2*}D_{-k2}{}^{2*}e^{-i2\Omega(i'j',ij)}]. \quad (3.12)$$

IV. LONGITUDINAL RELAXATION

Substitution of Eq. (3.7) into Eq. (2.7) gives

$$E=-\omega_0I^0-(3/8)^{1/2}d\sum_k(-1)^kD_{-k0}{}^{2*}\sum_{i<j}V_{ij}{}^k. \quad (4.1)$$

Since $d\ll\omega_0$, the eigenkets $|\alpha\rangle$ and eigenvalues $E(\alpha)$ of E can be calculated to good approximation by treating the second term in Eq. (4.1) as a perturbation. A complete set of eigenkets of $-\omega_0I^0$ which are suitable for use in the perturbation calculation are the eigenkets of $\mathbf{I}_1^2$, $\mathbf{I}_2^2$, $\mathbf{I}_3^2$, $\mathbf{I}_{12}^2\equiv(\mathbf{I}_1+\mathbf{I}_2)^2$, $\mathbf{I}^2=(\mathbf{I}_{12}+\mathbf{I}_3)^2$, and I^0. They are denoted by $|I_{12}IM\rangle$, where M is the eigenvalue of I^0, and the eigenvalues of $\mathbf{I}_1^2$, $\mathbf{I}_2^2$, and $\mathbf{I}_3^2$ are omitted since they are $\frac{1}{2}$.[10] The eigenvalues of E, correct to second order in d, can be expressed as

$$E(\alpha)=-M\omega_0+\delta_{I(3/2)}(-1)^{|M|+\frac{1}{2}}\left\{\tfrac{3}{4}dD_{00}{}^{2*}+\frac{|M|}{M}\frac{9}{8}\frac{d^2}{\omega_0} \times[D_{10}{}^{2*}D_{-10}{}^{2*}+\tfrac{1}{2}(-1)^{|M|-\frac{1}{2}}D_{20}{}^{2*}D_{-20}{}^{2*}]\right\}. \quad (4.2)$$

Matrix elements in the $|\alpha\rangle$ representation can be calculated to good approximation by use of the unperturbed eigenkets $|I_{12}IM\rangle$. However, it is important to retain the perturbed values of $E(\alpha)$. Although $d\ll\omega_0$, d is large compared to $|R(\alpha\alpha'\alpha''\alpha''')|$ and $|N(\alpha''\alpha''')|$. Hence the terms in $E(\alpha)$ due to the perturbation can affect which of the terms in Eq. (2.10) are secular.

Consider Eq. (2.10) with $\alpha=I_{12}IM$ and $\alpha'=I_{12}'I'M$. In the sums on the right-hand side of the equation, the only secular terms are those corresponding to values of α'' and α''' for which $M''=M'''$, since all other terms oscillate with a frequency of the order of magnitude of ω_0. Thus matrix elements of χ' that are diagonal in M are connected by Eq. (2.10) only to other matrix elements of χ' which are also diagonal in M.

The calculation of the elements $R(\alpha\alpha'\alpha''\alpha''')$ and $N(\alpha''\alpha''')$ from Eqs. (2.11) and (2.13) is facilitated somewhat by use of the Wigner-Eckart theorem[11] to evaluate the matrix elements of the $V_{ij}{}^k$ in the $|I_{12}IM\rangle$ representation. Nevertheless, the calculation is lengthy and tedious. It is assumed that $d\tau_c\ll1$, in which case $J_{(i'j')(ij)}{}^{lk}(\omega+d)\approx J_{(i'j')(ij)}{}^{lk}(\omega)$. In the evaluation of $N(\alpha''\alpha''')$ it is assumed that $\beta\ll\tau_c$, ω_0^{-1}. These conditions are satisfied in most physical situations of interest. As a result of the latter conditions, the factor $(1+e^{\beta z})^{-1}$ in the integrand of expression (2.12) can be replaced by $\frac{1}{2}$ with little error when ω has the values indicated in Eq. (2.11).

If one introduces the following combinations of matrix elements,

$$y_1\equiv1/2\,\mathrm{Im}[\langle0\tfrac{1}{2}\tfrac{1}{2}|\chi'|1\tfrac{1}{2}\tfrac{1}{2}\rangle+\langle0\tfrac{1}{2}-\tfrac{1}{2}|\chi'|1\tfrac{1}{2}-\tfrac{1}{2}\rangle -\langle1\tfrac{1}{2}\tfrac{1}{2}|\chi'|0\tfrac{1}{2}\tfrac{1}{2}\rangle-\langle1\tfrac{1}{2}-\tfrac{1}{2}|\chi'|0\tfrac{1}{2}-\tfrac{1}{2}\rangle], \quad (4.3a)$$

$$y_2\equiv\tfrac{3}{2}[\langle1\tfrac{3}{2}\tfrac{3}{2}|\chi'|1\tfrac{3}{2}\tfrac{3}{2}\rangle-\langle1\tfrac{3}{2}-\tfrac{3}{2}|\chi'|1\tfrac{3}{2}-\tfrac{3}{2}\rangle], \quad (4.3b)$$

$$y_3\equiv\tfrac{1}{2}[\langle1\tfrac{3}{2}\tfrac{1}{2}|\chi'|1\tfrac{3}{2}\tfrac{1}{2}\rangle-\langle1\tfrac{3}{2}-\tfrac{1}{2}|\chi'|1\tfrac{3}{2}-\tfrac{1}{2}\rangle], \quad (4.3c)$$

and

$$y_4\equiv\sum_{I_{12}IM}M\langle I_{12}IM|\chi'|I_{12}IM\rangle, \quad (4.3d)$$

it is found from Eq. (2.10) that the time derivatives of the quantities y_i depend only upon the same combinations of matrix elements. The equations can thus be written in matrix form as

$$(8/9)T_0\dot{\mathbf{y}}=\mathbf{A}\mathbf{y}, \quad (4.4)$$

where $T_0^{-1}\equiv d^2\tau_c$, and the elements of the matrix $\mathbf{A}$ are found to be

$$A_{11}=-(1,3/2)[\tfrac{1}{2}a_0+a_1+a_2], \quad (4.5a)$$

$$A_{12}=-(0,1/2)[b_1+b_2], \quad (4.5b)$$

$$A_{13}=(0,3/2)[b_1-b_2], \quad (4.5c)$$

$$A_{14}=(0,3/4)[b_1+2b_2], \quad (4.5d)$$

$$A_{21}=(0,9/8)[b_1+4b_2], \quad (4.5e)$$

[9] If the angle ϕ_{ij}' is considered to vary from $-\infty$ to ∞, the appropriate probability density is the familiar gaussian expression in $(\phi-\phi_0)$, which is characteristic of one dimensional diffusion. This density gives the same result for the correlation function as does Eq. (3.10).

[10] The $|I_{12}IM\rangle$ have been calculated by using the vector coupling coefficients given in A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1960), 2nd ed.

[11] Reference 10, Eq. (5.4.1).

$$A_{22}=-(3/8)[(6,5)a_1-(0,4)a_2], \quad (4.5f)$$

$$A_{23}=-(9/8)[(-2,1)a_1-(0,4)a_2], \quad (4.5g)$$

$$A_{24}=(3/4)(1,3/2)[a_1-4a_2], \quad (4.5h)$$

$$A_{31}=(0,9/8)b_1, \quad (4.5i)$$

$$A_{32}=[-\tfrac{1}{2}(1,3/2)a_0+(1/12)(13,27/2)a_1 - (1/3)(1,0)a_2], \quad (4.5j)$$

$$A_{33}=-[(3/2)(1,3/2)a_0+\tfrac{1}{4}(7,9/2)a_1+(1,0)a_2], \quad (4.5k)$$

$$A_{34}=\tfrac{1}{2}(1,3/2)[a_0-(3/2)a_1], \quad (4.5l)$$

$$A_{41}=(0,3)[b_1+2b_2], \quad (4.5m)$$

$$A_{42}=(0,1)[a_1+2a_2], \quad (4.5n)$$

$$A_{43}=-(0,3)[a_1-2a_2], \quad (4.5o)$$

$$A_{44}=-(1,3/2)[a_1+4a_2]. \quad (4.5p)$$

The first number in the ordered pair in each A_{ij} is the result obtained if the cross correlations are neglected; the second number is the result obtained when the cross correlations are included. The A_{ij} are expressed in terms of the quantities

$$\left.\begin{matrix} a_l \\ b_l \end{matrix}\right\} \equiv \frac{(-1)^l}{1+(l\omega_0\tau_c)^2}[D_{l2}{}^{2*}D_{-l-2}{}^{2*} \pm D_{l-2}{}^{2*}D_{-l2}{}^{2*}], \quad (4.6)$$

which, in terms of the Euler angles $\alpha\beta\gamma$ upon which the D's depend, are

$$a_0=\tfrac{3}{4}\sin^4\beta, \quad (4.7a)$$

$$\left.\begin{matrix} a_1 \\ b_1 \end{matrix}\right\} = \frac{\sin^2\beta}{1+(\omega_0\tau_c)^2}\left[\left(\frac{1+\cos\beta}{2}\right)^2 \pm \left(\frac{1-\cos\beta}{2}\right)^2\right], \quad (4.7b)$$

$$\left.\begin{matrix} a_2 \\ b_2 \end{matrix}\right\} = \frac{1}{1+(2\omega_0\tau_c)^2}\left[\left(\frac{1+\cos\beta}{2}\right)^4 \pm \left(\frac{1-\cos\beta}{2}\right)^4\right]. \quad (4.7c)$$

Since a_l and b_l depend only on the Euler angle β, it is clear that in the case of hindered rotation by jumps between three equilibrium positions, the relaxation does not depend on the orientation of the equilibrium positions in the plane perpendicular to the axis of hindered rotation.

In the derivation of the quantities A_{ij} from Eq. (2.10), it is found that the results depend only on the $R(\alpha\alpha'\alpha''\alpha''')$ and not on the $N(\alpha''\alpha''')$. Also, it is found that the secularity of the terms in the equations for the y_i is not affected by the part of the $E(\alpha)$ which involves d. This results from the fact that terms oscillating with a frequency of order of magnitude d either have zero magnitude or cancel in the linear combinations in Eq. (4.4).

If terms of order d/ω_0 due to the perturbation corrections to the unperturbed eigenkets $|I_{12}IM\rangle$ are omitted, it follows from Eqs. (2.9) and (4.3d) that

$$\langle I^0\rangle-\langle I^0\rangle^T=y_4. \quad (4.8)$$

The initial condition of the spin system will be considered to be the result of the application of a rotating field $\mathbf{H}_1=(\omega_1/\gamma)(\mathbf{i}\cos\omega_0t-\mathbf{j}\sin\omega_0t)$ to the system in thermal equilibrium with density operator σ^T [Eq. (2.8)] for a time $t_\theta\equiv\theta/\omega_1$—sufficiently short that the effects of the dipole-dipole interactions can be neglected during the pulse ($dt_\theta\ll 1$). If one uses $E\approx-\omega_0I^0$ in Eq. (2.8), it can be shown that, to first order in $\beta\omega_0$,

$$\langle I_{12}IM|\chi'(0)|I_{12}'I'M\rangle = (1/8)\beta\omega_0(\cos\theta-1)M\delta_{I_{12}I_{12}'}\delta_{II'}. \quad (4.9)$$

Hence, use of Eq. (4.9) in Eqs. (4.3) gives

$$\mathbf{y}(0)=\langle I^0\rangle^T(\cos\theta-1)\{0,3/4,1/12,1\}. \quad (4.10)$$

If cross correlations are neglected, it follows from Eqs. (4.4) and (4.5) that

$$\dot{y}_4=-(9/8)T_0^{-1}[a_1+4a_2]y_4. \quad (4.11)$$

Since $y_4=\langle I^0\rangle-\langle I^0\rangle^T$, the solution of Eq. (4.11) that satisfies the initial condition (4.10) gives the result

$$\langle I^0\rangle-\langle I^0\rangle^T=(\cos\theta-1)\langle I^0\rangle^T\exp(-t/T_1), \quad (4.12)$$

where

$$T_1^{-1}=(9/16)d^2\tau_c\{(1-\cos^4\beta)[1+(\omega_0\tau_c)^2]^{-1} + (1+6\cos^2\beta+\cos^4\beta)[1+(2\omega_0\tau_c)^2]^{-1}\}. \quad (4.13)$$

The relaxation when cross correlations are included is obtained by solving Eqs. (4.4) subject to the initial conditions (4.10), using for A_{ij} the second number in the ordered pairs in Eqs. (4.5). The result is in general the sum of four decaying exponentials:

$$\langle I^0\rangle-\langle I^0\rangle^T=(\cos\theta-1)\langle I^0\rangle^T \times\sum_{j=1}^{4}C_j\exp[(9/8)T_0^{-1}p_jt], \quad (4.14)$$

where the p_j are the eigenvalues of the matrix $\mathbf{A}$, i.e., solutions of the equation $D(p)\equiv\det(\mathbf{A}-p\mathbf{I})=0$. If the eigenvalues are distinct, the C_j are given by

$$C_j=-[D'(p_j)]^{-1}\{(3/4)B_{42}+(1/12)B_{43}+B_{44}\}, \quad (4.15)$$

where $D'(p)\equiv dD/dp$, and B_{ij} is the ij element of the adjoint matrix of $(\mathbf{A}-p_j\mathbf{I})$.

In order to compare the results of our calculations with experimental data, it is convenient to measure time in units of the quantity

$$T'\equiv\omega_0/d^2=\omega_0(r_0^3/\gamma^2\hbar)^2, \quad (4.16)$$

which does not depend on the correlation time. Since $T'=\omega_0\tau_cT_0$, it follows from Eq. (4.14) that

$$\langle I^0\rangle-\langle I^0\rangle^T=(\cos\theta-1)\langle I^0\rangle^T \times\sum_{j=1}^{4}C_j\exp[-q_jt/T'], \quad (4.17)$$

where

$$q_j = -(9/8)\omega_0\tau_c p_j. \quad (4.18)$$

A Univac 1105 digital computer has been employed to calculate the quantities p_j, C_j, and q_j for $\cos\beta = 0.0$, ± 0.1, ± 0.2, $\cdots$, ± 1.0, for various values of $\omega_0\tau_c$. Newton's method was used to determine the roots p_j of $D(p)$. Each of Tables[12] I–XI contains the p_j and C_j for a particular value of $\cos\beta$ and for all the values of $\omega_0\tau_c$ for which these quantities were calculated. The tables also contain values of the reciprocal of the relaxation time T_1 that is obtained when cross correlations are omitted, calculated from Eq. (4.13) by use of the computer.

A case of particular interest is $\cos\beta = \pm 1.0$, for which $a_0 = a_1 = b_1 = 0$ and $a_2 = b_2 = [1 + (2\omega_0\tau_c)^2]^{-1}$. It follows immediately from Eqs. (4.4), (4.5), and (4.10) that

$$\langle I^0\rangle - \langle I^0\rangle^T = (\cos\theta - 1)\langle I^0\rangle^T \times \tfrac{1}{3}\{1 + 2\exp(-(27/4)T_0^{-1}[1 + (2\omega_0\tau_c)^2]^{-1}t)\}. \quad (4.19)$$

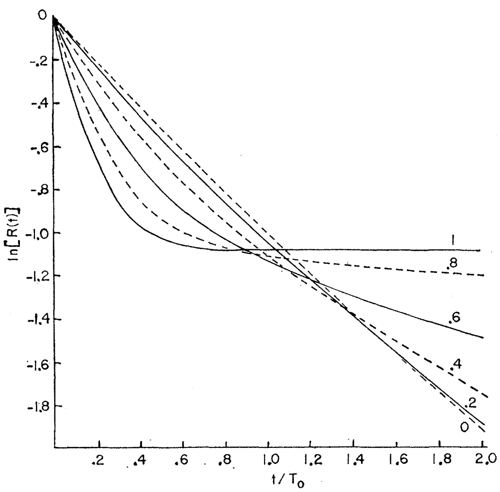

FIG. 1. Time dependence of the logarithm of the relaxation plotted as a function of t/T_0 for $(\omega_0\tau_c)^2 \ll 1$ and six values of $\cos\beta$. $R(t) \equiv [\langle I^0\rangle^T - \langle I^0\rangle]/2\langle I^0\rangle^T$ and $1/T_0 \equiv \gamma^4\hbar^2\tau_c/r_0^6$.

Hence, for $\beta = 0$, the ensemble does not relax to its thermal equilibrium distribution via the mechanism we have considered. Note that this effect occurs only if the cross correlations are included in the calculation. In a real crystal there are other relaxation mechanisms which, although usually less efficient than the mechanism considered here, would provide a means for the spins to return to thermal equilibrium. Such a mechanism might be intermolecular dipole-dipole interactions.

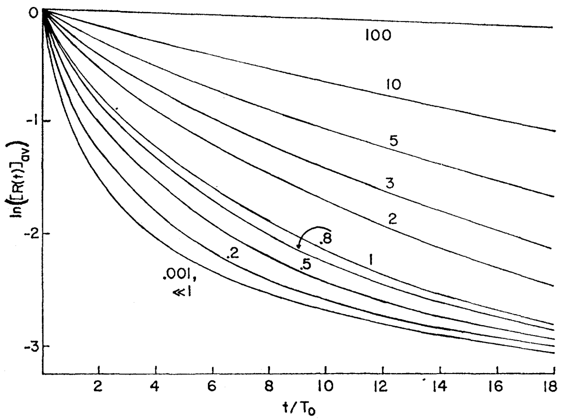

FIG. 2. Time dependence of the logarithm of the average over orientation of the relaxation plotted as a function of t/T_0 for different values of $(\omega_0\tau_c)^2$. $R(t) \equiv [\langle I^0\rangle^T - \langle I^0\rangle]/2\langle I^0\rangle^T$, and $1/T_0 \equiv \gamma^4\hbar^2\tau_c/r_0^6$.

The logarithm of the relaxation is plotted versus t/T_0 in Fig. 1 for $\omega_0\tau_c \ll 1$ and six values of $\cos\beta$. The most striking feature of this set of curves is that the vertical order is completely reversed in the interval from $t=0$ to $t = 2T_0$. Although not shown on the graph, the curves for $t/T_0 > 2$ are approximately straight lines.

If the axes of hindered rotation of the three spin systems are oriented isotropically, the longitudinal relaxation of the ensemble, denoted by $[\langle I^0\rangle - \langle I^0\rangle^T]_{\text{av}}$, is the average over all orientations of Eq. (4.14) or (4.17):

$$[\langle I^0\rangle - \langle I^0\rangle^T]_{\text{av}} = \frac{1}{2}\int_0^\pi [\langle I^0\rangle - \langle I^0\rangle^T]\sin\beta d\beta. \quad (4.20)$$

For many values of t, the average in Eq. (4.20) has been calculated on the Univac computer by use of Simpson's formula and the values given in Tables I–XI.[12] The re-

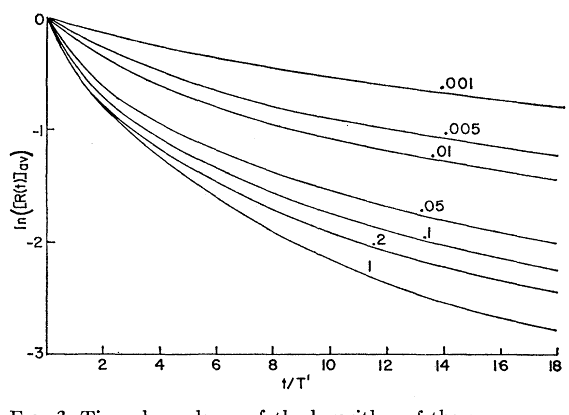

FIG. 3. Time dependence of the logarithm of the average over orientation of the relaxation plotted as a function of t/T' for different values of $(\omega_0\tau_c)^2 \leq 1$. $R(t) \equiv [\langle I^0\rangle^T - \langle I^0\rangle]/2\langle I^0\rangle^T$, and $1/T' \equiv (\gamma^4\hbar^2/r_0^6\omega_0)$.

[12] Copies of the tables are available from the authors. The tables have also have been deposited as Document No. 7799 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be obtained by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

sults obtained for the quantity $\ln\{[\langle I^0\rangle^T-\langle I^0\rangle]_{av}/2\langle I^0\rangle^T\}$ are plotted in Fig. 2 as a function of (t/T_0) and in Figs. 3 and 4 as a function of (t/T'), for representative values of $\omega_0\tau_c$. The plots using t/T' as the abscissa are the more useful for comparing with experimental data because the scaling factor T' does not depend on the correlation time τ_c. The advantages of using (t/T_0) as the abscissa are that, for a very small $\omega_0\tau_c$, one can plot more of the relaxation in a given space [compare the curves for $(\omega_0\tau_c)^2=0.001$ in the two plots], and that the relaxation for any $\omega_0\tau_c\ll1$ can be obtained by replotting the curve with that label as a function of t/T', using the assumed value of $\omega_0\tau_c$ to change the scale from T_0 to T'.

The effect of including cross correlations in the calculation of the relaxation when the axes of rotation are isotropically distributed is shown strikingly in Fig. 5. For three values of $\omega_0\tau_c$, the dashed curves give the logarithm of the relaxation when cross correlations are neglected, and the solid curves give the logarithm of the relaxation when cross correlations are included.

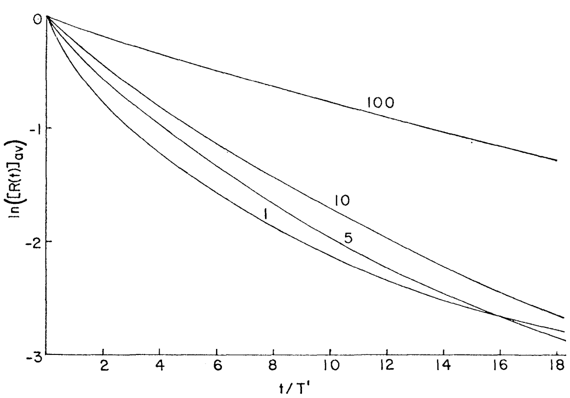

FIG. 4. Time dependence of the logarithm of the average over orientation of the relaxation plotted as a function of t/T' for different values of $(\omega_0\tau_c)^2\geq1$. $R(t)\equiv[\langle I^0\rangle^T-\langle I^0\rangle]/2\langle I^0\rangle^T$, and $1/T'\equiv(\gamma^4\hbar^2/r_0^6\omega_0)$.

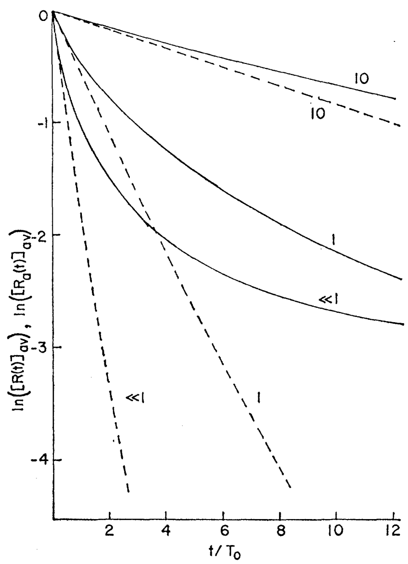

FIG. 5. Time dependence of the logarithm of the average over orientation of the relaxation plotted as a function of t/T_0 for three values of $(\omega_0\tau_c)^2$. $R(t)$ and $R_a(t)$ are given by $[\langle I^0\rangle^T-\langle I^0\rangle]/2\langle I^0\rangle^T$ for the cases in which the effects of cross correlations are included and neglected, respectively. The solid curves are $\ln([R(t)]_{av})$ and the dashed curves are $\ln([R_a(t)]_{av})$. $1/T_0\equiv\gamma^4\hbar^2\tau_c/r_0^6$.

V. CONCLUSIONS

The calculations given above predict that the longitudinal nuclear magnetic relaxation of three spin systems undergoing hindered rotations differs significantly from a simple exponential decay, as a consequence of the cross correlations of the dipole-dipole interactions. Detailed results have been calculated for situations in which the axes of rotation make an angle β with the external field, and for situations in which the axes of rotation are isotropically oriented. The results have been presented in a form which can be compared with experimental data, and used to determine the correlation time of the hindered rotations.