Nuclear Magnetic Relaxation in the Presence of Paramagnetic Ions*†

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The influence of independent processes of relaxation of paramagnetic ions on nuclear magnetic relaxation in the presence of these ions is discussed theoretically, using the Kubo and Tomita method. The nuclei are assumed to relax as a result of their contact with the ions through the usual dipole-dipole mechanism and this interaction is, in turn, considered to be of negligible influence on the ionic relaxation. Following a suggestion by Abragam, the ionic interactions are described as a coupling of the ionic spins to an effective local field varying randomly in time; this coupling is finally expressed in terms of experimentally more accessible parameters such as the ionic correlation and relaxation times. All dissipative interactions are approximated by autocorrelation functions with simple exponentially decaying time dependence, thereby limiting the applicability of this calculation to liquids and to liquid-like solids. The second-order terms in the perturbation expansion of the relaxation tensor yield contributions to the Bloch relaxation times of the system of nuclear spins that agree with previous calculations by Solomon. The fourth-order terms describing ionic relaxation yield a contribution to the nuclear relaxation times with a narrowing influence, except in the limit of very strong fields when a broadening is produced.

I. INTRODUCTION

THE relaxation of nuclear spins caused by their interaction with paramagnetic ions has been treated by several authors.[1-5] Two distinct mechanisms are obtained, one for which the interaction is randomly modulated due to additive motion of the ions and the nucleus, the other where it is due to an independent means of relaxation of the electron spin. In discussing the relaxation of protons in magnetic ion solutions, Bloembergen and Morgan[6] considered the combined influence of these two types of random modulation; this was done by inserting in the conventional formulas for the nuclear relaxation time, a correlation time obtained from the sum of the reciprocals of the correlation times of relative motion and of electron spin motion. A similar description was used by Torrey, Seevers, and Korringa[7] in a discussion of paramagnetic wall effects on the nuclear spins in liquids. The present study was undertaken to check the validity of this procedure, and to find its generalization when, e.g., the electronic or nuclear motion cannot be characterized by a single correlation time.

To this end, we have used the method of Kubo and Tomita[8] (from now on referred to as K.T.), which is based on a perturbation expansion for the induced nuclear magnetization in terms of the interaction Hamiltonian of the spin system. Our discussion will

be limited to liquids and to solids where molecular groups are free to undergo a considerable amount of internal motion,[9] thus producing a relaxation mechanism similar to the one encountered in viscous liquids. This means that the autocorrelation functions of the nuclear or ionic local field components can be approximated by exponential functions $\exp(-|t|/\tau)$, with τ a correlation time.[10] The method is applicable to the description of nuclear relaxation when the system of nuclear spins is in the liquid state with the ions in the solid state or vice versa, as long as the geometry is such that the nuclear interactions with the ions still provide the dominating mechanism of nuclear relaxation.

The spin of the nuclei as well as the effective spin of the ions will be assumed to equal $\frac{1}{2}$; our discussion, however, can easily be extended to the case of spins with arbitrary magnitude.

Section II summarizes the results of K.T. that will be applicable to this paper together with the analytical formulation of the present problem.

The discussion will be limited to cases where the contribution of the random motion of the electron spin to the nuclear relaxation is only a small correction to the contribution of the random relative motion. This permits an expansion, of which the first correction term will be calculated.

In Secs. III and IV the procedure for computing the various terms in the perturbation expansion is outlined and explicit expressions for the relaxation times are derived. The second-order expressions will reproduce Solomon's results[3] and illustrate, in simple terms, the principles involved in carrying out the considerably more involved calculations of the fourth-order terms. This is followed in Sec. V by a discussion of the various limiting cases of interest, and criteria are established for the applicability of the present method.

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II. ANALYTICAL FORMULATION OF THE PROBLEM

A. Relaxation Tensor

Consider a system of spins in the presence of a strong magnetic field H_z in the z direction and under the action of an arbitrarily small disturbance,

$$H_1(t) = H_1, \quad -\infty \le t \le 0; \\ = 0, \quad 0 < t. \tag{1}$$

The induced magnetic moment $M^{ind}(t)$ of the system due to $H_1(t)$ will then be given by

$$M^{ind}(t) = \Phi(t) \cdot H_1, \tag{2}$$

where the tensor $\Phi(t)$ will be called the relaxation tensor. Following K.T. we shall assume $\Phi(t)$ to be independent of the magnitude of H_1, provided that H_1 is small.

Once the components of $\Phi(t)$ are known, one can easily calculate the Bloch[11] relaxation times. If H_1 is assumed to be along the x direction, the x component of induced magnetization becomes

$$M_x^{ind}(t) = \Phi_{xx}(t) H_1, \tag{3}$$

and if the initial time dependence of $M_x^{ind}(t)$ can be approximated by a single exponential decay, one has

$$M_x^{ind}(t) = \chi_0 e^{-t/T_2} \cos(\omega t) H_1 \\ = \chi_0 (1 - t/T_2 + \cdots) \cos(\omega t) H_1, \tag{4}$$

where χ_0 is the static susceptibility and T_2 is the transverse relaxation time. The cosine factor is included in order to account for the precessional motion with frequency ω of the transverse magnetization in the longitudinal field H_z. $\Phi_{xx}(t)$ can now be expanded in powers of the time:

$$\Phi_{xx}(t) = \cos(\omega t)(b_x't + \cdots), \tag{5}$$

and consequently

$$1/T_2 = -b_x'/\chi_0. \tag{6}$$

The longitudinal relaxation time T_1 can similarly be obtained by writing down the expressions analogous to (4) and (5) for $M_z^{ind}(t)$ and $\Phi_{zz}(t)$, respectively, and equating coefficients of like powers of time. This time, however, the $\cos \omega t$ factor is missing since $M_z^{ind}(t)$ does not precess around a transverse axis. The result is

$$1/T_1 = -b_z'/\chi_0, \tag{7}$$

where b_z' is the coefficient of the first power of time in the expansion for $\Phi_{zz}(t)$.

No limits have so far been imposed on the magnitude of the time interval t if the definitions Eqs. (6) and (7) for the relaxation times are to remain meaningful. Such limitations will be established, as the need for them arises, in the subsequent development of this paper.

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B. The Hamiltonian

The Hamiltonian for a system of two different species of spins can be written in the form

$$\mathcal{3C} = \mathcal{3C}_0 + \mathcal{3C}'. \tag{8}$$

$\mathcal{3C}_0$ is the total energy of the individual particles apart from magnetic interactions, but including their Zeeman energies, and $\mathcal{3C}'$ is the sum of their magnetic interactions and will be treated as a small perturbation on $\mathcal{3C}_0$.

The unperturbed Hamiltonian $\mathcal{3C}_0$ will be written as

$$\mathcal{3C}_0 = \mathcal{3C}_m{}^N + \mathcal{3C}_m{}^e + \mathcal{3C}_z{}^N + \mathcal{3C}_z{}^e + \mathcal{3C}^e. \tag{9}$$

In this expression $\mathcal{3C}_m{}^N$ and $\mathcal{3C}_m{}^e$ are the motional energies of the nuclei and ions respectively; $\mathcal{3C}_z{}^N$ and $\mathcal{3C}_z{}^e$ are their respective Zeeman energies (in the static field H_z) and are given by

$$\mathcal{3C}_z{}^N = -\hbar\omega \sum_j I_{zj}, \\ \mathcal{3C}_z{}^e = -\hbar\Omega \sum_k S_{zk}, \tag{10}$$

with Larmor frequencies

$$\omega = \gamma_N H_z \quad \text{and} \quad \Omega = \gamma_e H_z. \tag{11}$$

The quantities γ_N and γ_e are the nuclear and ionic gyromagnetic ratios, and I_z and S_z are the z components of their respective spin angular momentum operators I and S.

$\mathcal{3C}^e$ is the Hamiltonian of the environment in which the ionic spins find themselves.

Since the ionic magnetic moment is three orders of magnitude larger than the nuclear magnetic moment, mutual interactions among the nuclei may be disregarded. The interaction between nuclei and paramagnetic ions will be taken to be of the dipole-dipole type $\mathcal{3C}'_{dd}$, and will be assumed to have negligible influence on the ionic relaxation. Following Abragam,[4] we take the ionic perturbation to be an interaction between the ionic magnetic moments and an effective local field operator V. This local field may be due to mutual magnetic interactions between the ions, spin orbit coupling, crystalline field (in a solid), or other possible sources for magnetic interactions, and its components will be defined in terms of statistical parameters such as mean square values and correlation times.

The perturbation Hamiltonian $\mathcal{3C}'$ will be written as

$$\mathcal{3C}' = \mathcal{3C}'_s + \mathcal{3C}'_{dd}, \tag{12}$$

where $\mathcal{3C}'_s$ is assumed to be linear in S_k, $[V_k, S_k] = 0$, and is given by

$$\mathcal{3C}'_s = \sum_k V_k \cdot S_k. \tag{13}$$

$\mathcal{3C}'_{dd}$ is the usual dipole-dipole interaction,

$$\mathcal{3C}'_{dd} = \mu_N \mu_e \sum_{jk} r_{jk}^{-3} \\ \times [I_j \cdot S_k - 3(I_j \cdot r_{jk})(S_k \cdot r_{jk}) r_{jk}^{-2}]. \tag{14}$$

The constants μ_N and μ_e are the nuclear and ionic

magnetic moments and are given by

$$\mu_N = \gamma_N \hbar \quad \text{and} \quad \mu_e = \gamma_e \hbar. \tag{15}$$

We choose the representation where I_z and S_z are diagonal. Moreover, we take the interaction representation, for which the time-dependence of $\mathfrak{IC}'$ is given by

$$\mathfrak{IC}'(t) = \exp(it\mathfrak{IC}_0/\hbar)\mathfrak{IC}' \exp(-it\mathfrak{IC}_0/\hbar). \tag{16}$$

Then, using Eqs. (9) and (12)–(16) one can express $\mathfrak{IC}'(t)$ in the form

$$\mathfrak{IC}'(t) = \sum_\alpha \mathfrak{IC}'^\alpha(t)e^{i\omega_\alpha t}$$
$$= \sum_\alpha \sum_{jk} \mathfrak{IC}'^\alpha_{jk}(t), \tag{17}$$

where

$$\mathfrak{IC}'^{\pm 2}_{jk}(t) = I_j^\pm S_k^\pm \varphi_{jk}^{\mp 2}(t)e^{\mp i(\omega+\Omega)t},$$

$$\mathfrak{IC}'^{\pm 1}_{jk}(t) = I_j^\pm S_{zk}\varphi_{jk}^{\mp 1}(t)e^{\mp i\omega t},$$

$$\mathfrak{IC}'^{\pm 11}_{jk}(t) = (I_{zj}S_k^\pm \varphi_{jk}^{\mp 1}(t) + S_k^\pm V_k^{\mp 1})e^{\mp i\Omega t}, \tag{18}$$

$$\mathfrak{IC}'^{\pm 00}_{jk}(t) = -\tfrac{1}{4}I_j^\pm S_k^\mp \varphi_{jk}^0(t)e^{\mp i(\omega-\Omega)t},$$

$$\mathfrak{IC}'^0_{jk}(t) = I_{zj}S_{zk}\varphi_{jk}^0(t) + S_{zk}V_k^0(t).$$

In this expression the symbols $I_j^\pm$ and $S_k^\pm$ denote the usual raising and lowering operators:

$$I^\pm = I_x \pm i I_y \quad \text{and} \quad S^\pm = S_x \pm i S_y. \tag{19}$$

The quantities $\varphi^{\pm\gamma}$ denote the usual spherical harmonics that arise as factors to the different terms in the standard expression for dipole-dipole interactions; they are given by

$$\varphi_{jk}^{\pm 2} = \tfrac{3}{4}\mu_N \mu_e r_{jk}^{-3} \sin^2\theta_{jk}e^{\pm 2i\psi_{jk}},$$

$$\varphi_{jk}^{\pm 1} = -\tfrac{3}{4}\mu_N \mu_e r_{jk}^{-3} \sin\theta_{jk} \cos\theta_{jk}e^{\pm i\psi_{jk}}, \tag{20}$$

$$\varphi_{jk}^0 = \mu_N \mu_e r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}),$$

with θ_{jk} and ψ_{jk} denoting the usual spherical polar angle and azimuth, respectively. The time dependence of φ_{jk}^γ can be written as

$$\varphi_{jk}^\gamma(t) = \exp[it(\mathfrak{IC}_m^N + \mathfrak{IC}_m^e)/\hbar]$$
$$\times \varphi_{jk}^\gamma \exp[-it(\mathfrak{IC}_m^N + \mathfrak{IC}_m^e)/\hbar]. \tag{21}$$

The terms V_k^δ denote the different components of the vector operator $\mathbf{V}_k$:

$$V_k^0 = V_k^z \quad \text{and} \quad V_k^{\pm 1} = \tfrac{1}{2}(V_k^x \pm i V_k^y). \tag{22}$$

Their time dependence is given by

$$V_k^\delta(t) = \exp[(it\mathfrak{IC}_z^e + \mathfrak{IC}_m^e + \mathfrak{IC}^e)/\hbar]$$
$$\times V_k^\delta \exp[-it(\mathfrak{IC}_z^e + \mathfrak{IC}_m^e + \mathfrak{IC}^e)/\hbar], \tag{23}$$

and the approximate relation,

$$[\varphi_{jk}^\gamma(t), V_k^\delta(t)] = 0, \tag{24}$$

will be assumed valid.

C. Perturbation Expansion of $\Phi(t)$

Using quantum statistical methods, K.T. have shown that the components of $\Phi(t)$ can be expressed as a series in powers of $\mathfrak{IC}'$

$$\Phi_{\lambda\lambda}(t) = \sum_n \Phi_{\lambda\lambda}^{(n)}(t), \tag{25}$$

where λ stands for any one of the three Cartesian coordinates and where

$$\Phi_{\lambda\lambda}^{(n)}(t) = \beta(i\hbar)^{-n} \sum_\alpha \sum_\beta \exp(i\omega_\alpha t)$$

$$\times \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \sum_\gamma \sum_\delta \cdots \sum_\nu$$

$$\times \exp[i(\omega_\gamma t_1 + \omega_\delta t_2 + \cdots + \omega_\nu t_n)]$$

$$\times \{ \langle [M_\lambda(\omega_\alpha); \mathfrak{IC}'^\gamma(t_1), \mathfrak{IC}'^\delta(t_2)\cdots\mathfrak{IC}'^\nu(t_n)]$$

$$\times M_\lambda(\omega_\beta) \rangle \}, \tag{26}$$

where β stands for $1/kT$ with k equal to Boltzmann's constant and T the absolute temperature. The factor $\exp(i\omega_\alpha t)$ describes the explicit time dependence of the magnetic moment operators, which in our representation can be expressed as

$$M_x(t) = \sum_\alpha M_x(\omega_\alpha)e^{i\omega_\alpha t} = M^+ e^{-i\omega t} + M^- e^{i\omega t},$$
$$M^\pm = \tfrac{1}{2}\mu_N \sum_j I_j^\pm. \tag{27}$$

The exponential factor under the integral sign follows from Eqs. (17) and (18). The curly brackets signify the real part of the enclosed expression and the square bracket denotes a multiple commutator,

$$[A; B, \cdots, N] = [[\cdots[A, B], \cdots], N]. \tag{28}$$

The remaining bracket $\langle \ \rangle$ indicates the process of averaging over the ensemble; explicitly, given that P is any operator,

$$\langle P \rangle = \text{Tr}(\rho P) \tag{29}$$

is the average value of P with respect to the density operator

$$\rho = \exp(-\beta\mathfrak{IC}_0)/\text{Tr}\exp(-\beta\mathfrak{IC}_0). \tag{30}$$

Expression (26) is valid provided that the energy difference for any transition $m \to n$ of statistical interest satisfies the inequality

$$|E_m - E_n|\beta \ll 1. \tag{31}$$

It can be shown that as long as the high-frequency Fourier components of the local field $\mathfrak{IC}'^\delta(t)$ are comparatively small, the individual terms under the summation sign in Eq. (26) are similarly small unless

$$\omega_\alpha + \omega_\beta + \omega_\gamma + \cdots \omega_\nu = 0. \tag{32}$$

In view of the fact that the magnitude of the static field H_z is assumed much larger than that of the local field, Eq. (32) will be a good approximation throughout the rest of this paper.

K.T. have shown that the multiple commutators under the summation sign in Eq. (26) individually satisfy the relation

$$\langle [M_\mu(\omega_\alpha); \mathfrak{IC}'^{\delta_1}(t_1)\cdots\mathfrak{IC}'^{\delta_n}(t_n)]M_\mu(\omega_\beta) \rangle$$

$$\approx (-1)^{n-k}\langle [M_\mu(\omega_\alpha); \mathfrak{IC}'^{\delta_1}(t_1)\cdots\mathfrak{IC}'^{\delta_k}(t_k)]$$

$$\times [M_\mu(\omega_\beta); \mathfrak{IC}'^{\delta_n}(t_n)\cdots\mathfrak{IC}'^{\delta_{k+1}}(t_{k+1})] \rangle, \tag{33}$$

provided that the energies $\hbar\omega_\alpha$, $\hbar\omega_\gamma\cdots$ are small[12] in comparison with $1/\beta$. This means that in a field H_z of 10 000 gauss (where the ionic magnetic energy is approximately $\hbar\Omega \simeq 10^{-16}$ cgs $\approx k$) the temperature should be $T \gg 1°$ Kelvin in order for Eq. (33) to be approximately true. In weak fields, however, Eq. (33) remains valid down to quite low temperatures. If the condition of validity for Eq. (33) is satisfied, and this will be assumed from now on, the Zeeman energy term $\mathfrak{K}_z{}^N + \mathfrak{K}_z{}^e$ may be omitted altogether from the density operator Eq. (30) when computing averages over the spin operators. Hence,

$$\rho \approx \exp[-\beta(\mathfrak{K}_m{}^N + \mathfrak{K}_m{}^e + \mathfrak{K}^e)]/$$
$$\mathrm{Tr} \exp[-\beta(\mathfrak{K}_m{}^N + \mathfrak{K}_m{}^e + \mathfrak{K}^e)]. \quad (34)$$

In this approximation, the ensemble average of any spin operator is just the trace of that operator divided by the trace of unity in spin space.

III. SECOND-ORDER CALCULATION

A. Computation of $\Phi(t)$ to Second Order

With the help of Eqs. (26), (27), and (32)–(34) we may presently begin the computation of $\Phi_{\lambda\lambda}(t)$. The calculation of $\Phi_{xx}{}^{(0)}(t)$ is straightforward.

$$\Phi_{xx}{}^{(0)}(t) = \beta \sum_\alpha \langle M_x(\omega_\alpha) M_x(-\omega_\alpha)\rangle e^{i\omega_\alpha t} = \chi_0 \cos\omega t, \quad (35)$$

where

$$\chi_0 = \tfrac{1}{3}\beta N\mu_N{}^2 I(I+1), \quad (36)$$

with $N =$ number of nuclei, is the expression for the static susceptibility of the system of nuclear spins. $\Phi_{xx}{}^{(0)}(t)$ contains no terms that would describe a relaxation.

The first-order term $\Phi_{xx}{}^{(1)}(t)$ is identically zero since the trace of an odd power of any spin operator is zero; the same holds for the other odd orders of the xx and yy components of $\Phi_{\lambda\lambda}(t)$.

The second-order expressions $\Phi_{xx}{}^{(2)}(t)$ can easily be obtained; using Eqs. (26), (27), (32), and (33), one can write

$$\Phi_{xx}{}^{(2)}(t)$$

$$= \beta\hbar^{-2} \sum_\alpha \sum_\beta \sum_\gamma \sum_\delta \left\{ \exp(i\omega_\alpha t) \int_0^t dt_1 \int_0^{t_1} dt_2 \right.$$

$$\times \exp[i(\omega_\gamma t_1 + \omega_\delta t_2)]$$

$$\left. \times \langle [M_x(\omega_\alpha), \mathfrak{K}'^\gamma(t_1)][M_x(\omega_\beta), \mathfrak{K}'^\delta(t_2)]\rangle \right\}. \quad (37)$$

With the use of Eq. (21) and the fact that $\mathfrak{K}_m{}^N$, $\mathfrak{K}_m{}^e$, $\mathfrak{K}_z{}^N$, $\mathfrak{K}_z{}^e$, and $\mathfrak{K}^e$ all commute with each other and after rearranging the dummy indices in accordance

[12] The difference between this condition and the one stated in Eq. (31) is that while in the latter only statistically significant transitions are considered, the former is sensitive to virtual processes as well.

with Eq. (32), one can rewrite Eq. (37) in the form

$$\Phi_{xx}{}^{(2)}(t)$$

$$= \beta\hbar^{-2} \sum_\alpha \sum_\gamma \left\{ \exp(i\omega_\alpha t) \int_0^t dt_1 \int_0^{t_1} dt_2 \right.$$

$$\times \exp[i(\omega_\gamma t_1 + \omega_{-\gamma} t_2)] \langle [M_x(\omega_\alpha), \mathfrak{K}'^\gamma(t_1 - t_2)]$$

$$\left. \times [M_x(-\omega_\alpha), \mathfrak{K}'^{-\gamma}(0)]\rangle \right\}. \quad (38)$$

This integral contains factors of the form

$$\langle \sum_{jk} \varphi_{jk}{}^\gamma(t_1 - t_2) \varphi_{jk}{}^\gamma(0)\rangle.$$

Assuming exponential time dependence, one may write (as is usually done)

$$\langle \sum_{jk} \varphi_{jk}{}^\gamma(t_1 - t_2) \varphi_{jk}{}^{-\nu}(0)\rangle$$
$$= \delta_{\gamma\nu} \langle \sum_{jk} \varphi_{jk}{}^\gamma(0)\varphi_{jk}{}^{-\gamma}(0)\rangle \exp(|t_1 - t_2|/\tau_\gamma), \quad (39)$$

where $\delta_{\gamma\nu}$ is the usual Kronecker δ symbol and where τ_γ is the correlation time of the mode φ^γ. Actually τ_γ is the effective correlation time for the nuclear and ionic motion, defined by

$$1/\tau_\gamma = 1/\tau_\gamma(\text{nuclear}) + 1/\tau_\gamma(\text{ionic}). \quad (40)$$

Since the nuclear motion is usually faster than is the ionic motion, we shall refer to τ_γ as the nuclear correlation time; it is clear, however, that Eq. (40) should be consulted in any specific application.

With the explicit time dependence of the integrand in Eq. (38) thus determined, it can be integrated to give

$$\Phi_{xx}{}^{(2)}(t) = 2\beta\hbar^{-2} \cos(\omega t)$$

$$\times \sum_\gamma \{ \langle [M^+, \mathfrak{K}'^\gamma(0)][M^-, \mathfrak{K}'^{-\gamma}(0)]\rangle$$

$$\times [a_\gamma t + \exp(-a_\gamma t) - 1]a_\gamma{}^{-2} \}, \quad (41)$$

where

$$a_\gamma = 1/\tau_\gamma - i\omega_\gamma. \quad (42)$$

B. Relaxation Times

We may now evaluate $\Phi_{xx}{}^{(2)}(t)$ for a length of time which is long compared with the correlation time τ_γ. We also have to impose an upper limit on the time interval t, otherwise Eq. (6) may no longer be meaningful for the initial behavior of the relaxation process; accordingly

$$\tau_\gamma \ll t \ll T_2 \quad \text{and} \quad \tau_\gamma \ll t \ll T_1. \quad (43)$$

Using Eqs. (5), (6), (41), and the fact that because of Eq. (43) the exponentials $\exp(-a_\gamma t)$ approach zero one obtains, in agreement with Solomon,

$$\left(\frac{1}{T_2}\right)^{(2)} = \frac{1}{4\hbar^2}\left[f_0\tau_0 + \frac{\tfrac{1}{4}f_0\tau_0}{1 + \tau_0{}^2(\omega - \Omega)^2} + \frac{2f_1\tau_1}{1 + \tau_1{}^2\omega^2} \right.$$

$$\left. + \frac{4f_1\tau_1}{1 + \tau_1{}^2\Omega^2} + \frac{4f_2\tau_2}{1 + \tau_2{}^2(\omega + \Omega)^2} \right], \quad (44)$$

where

$$f_\gamma = \sum_k \langle \varphi_{jk}{}^\gamma(0) \varphi_{jk}{}^\gamma(0) \rangle \qquad (45)$$

and where the constant terms in Eq. (41), which are the second-order contribution to the static susceptibility, have been omitted.

The calculation of $(T_1)^{(2)}$, which is obtained from $\Phi_{zz}(t)$, strictly follows the procedure described above. One finds, again in agreement with Solomon,

$$\left(\frac{1}{T_1}\right)^{(2)} = \frac{1}{\hbar^2}\left[\frac{\frac{1}{8}\tau_0 f_0}{1+\tau_0^2(\omega-\Omega)^2} + \frac{\tau_1 f_1}{1+\tau_1^2\omega^2}\right.$$
$$\left. + \frac{2\tau_2 f_2}{1+\tau_2^2(\omega+\Omega)^2}\right]. \qquad (46)$$

IV. FOURTH-ORDER CALCULATION

A. Outline of the Calculation

The expressions for the relaxation times, Eqs. (44) and (46), contain no details of the ionic relaxation; mathematically, this is because the ionic interaction, Eq. (13), commutes with the nuclear magnetic moment operators and hence does not contribute to $\Phi^{(2)}(t)$. The ionic interaction may, however, be larger than the ionic-nuclear interaction, Eq. (14), in the ratio of $\mu_e/\mu_N \approx 10^3$; its influence on the nuclear relaxation times may be calculated by evaluating the contributions of the ionic perturbation, Eq. (13), to $\Phi^{(4)}(t)$.

Thus, we calculate $\Phi^{(4)}(t)$ for the case where the fourth-order contributions of the nuclear ionic interaction terms are neglected in comparison with terms involving the ionic local field V_k. Using Eqs. (26) and (33) we can write

$$\Phi_{xx}{}^{(4)}(t) = \beta\hbar^{-4} \sum_\alpha \sum_\beta \cdots \sum_\nu \left\{ \exp(i\omega_\alpha t) \right.$$

$$\times \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4$$

$$\times \exp[i(\omega_\gamma t_1 + \omega_\delta t_2 + \omega_\lambda t_3 + \omega_\nu t_4)]$$

$$\times \langle [M_x(\omega_\alpha); \mathfrak{IC}'^\gamma(t_1), \mathfrak{IC}'^\delta(t_2)]$$

$$\left. \times [M_x(\omega_\beta); \mathfrak{IC}'^\nu(t_4), \mathfrak{IC}'^\lambda(t_3)] \rangle \right\}. \qquad (47)$$

In view of Eq. (24) this can be expressed as

$$\Phi_{xx}{}^{(4)}(t) = 2\beta\hbar^{-4} \cos(\omega t)$$

$$\times \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4$$

$$\times \sum_\gamma \sum_\delta \exp[i(\omega_\gamma t_1 + \omega_\delta t_2 - \omega_\gamma t_4 - \omega_\delta t_3)]$$

$$\times \{ \langle [M^+; \mathfrak{IC}'^\gamma(t_1-t_4), \mathfrak{IC}'^\delta(t_2-t_3)]$$

$$\times [M^-; \mathfrak{IC}'^{-\gamma}(0), \mathfrak{IC}'^{-\delta}(0)] \rangle \}. \qquad (48)$$

TABLE I. Expectation values $C_{\gamma,\delta}$ of spin variables.

δ\\γ	-2	-1	11	-11	-00	0
0	4	0	2	2	$\frac{1}{4}$	0
11	8	4	0	4	0	2
-11	0	4	4	0	$\frac{1}{2}$	2

In analogy to Eq. (39) it will be assumed that the time dependence of the fluctuating field components V^λ can reasonably be approximated by

$$\langle V^\gamma(t) V^{-\mu}(0) \rangle = \delta_{\lambda\mu} \langle V^\gamma(0) V^{-\gamma}(0) \rangle \exp(-|t|/\sigma_\gamma), \qquad (49)$$

where σ_γ is the correlation time of the component λ of this effective local field. σ_γ will be referred to as the (ionic) spin correlation time.

Substituting Eqs. (39) and (49) into Eq. (48), performing the integration, and using condition (43), one obtains finally

$$\Phi_{zz}{}^{(4)}(t) = \beta\hbar^{-4}A\cos(\omega t)$$

$$\times \sum_{\gamma,\delta} \{C_{\gamma,\delta} F_{\gamma,\delta} a_\gamma^{-2}(a_\gamma+b_\delta)^{-1}\}t, \qquad (50)$$

where the fourth-order contribution of the static susceptibility has been omitted, and where the $C_{\gamma,\delta}$ are averages over the spin variables and their values needed in this calculation are given in Table I. Also,

$$F_{\gamma,\delta} = \langle \sum_{jk} \varphi_{jk}{}^\gamma(0) \varphi_{jk}{}^{-\gamma}(0) V_k{}^\delta(0) V_k{}^{-\delta}(0) \rangle, \qquad (51)$$

$$a_\gamma = 1/\tau_\gamma - i\omega_\gamma \quad \text{and} \quad b_\delta = 1/\sigma_\delta - i\omega_\delta, \qquad (52)$$

$$A = (1/9)\mu_N{}^2 I(I+1)S(S+1). \qquad (53)$$

The fourth-order contribution to the transverse relaxation time $(T_2)^{(4)}$ can then be written as

$$(1/T_2)^{(4)}$$
$$= -\beta A\chi_0^{-1} \sum_{\gamma,\delta} \{C_{\gamma,\delta} F_{\gamma,\delta} a_\gamma^{-2}(a_\gamma+b_\delta)^{-1}\}. \qquad (54)$$

To obtain the fourth-order contribution to the longitudinal relaxation time, $(1/T_1)^{(4)}$, one calculates the relevant parts of $\Phi_{zz}{}^{(4)}(t)$, with the only difference that terms of the form $M_x(\omega_\alpha)\exp(i\omega_\alpha t)$ and $M_x(\omega_\beta)$ in Eq. (47) are to be replaced by M_z. The result is $(1/T_1)^{(4)}$

$$= -\beta A\chi_0^{-1} \sum_{\gamma,\delta} \{K_{\gamma,\delta} F_{\gamma,\delta} a_\gamma^{-2}(a_\gamma+b_\delta)^{-1}\}, \qquad (55)$$

where the $K_{\gamma,\delta}$ are averages over the spin variables and are given in Table II.

TABLE II. Expectation values $K_{\gamma,\delta}$ of spin variables.

δ\\γ	2	-2	1	-1	$+00$	-00
0	4	4	0	0	$\frac{1}{4}$	$\frac{1}{4}$
11	0	8	4	4	$\frac{1}{2}$	0
-11	8	0	4	4	0	$\frac{1}{2}$

B. Evaluation of the Relaxation Times

To evaluate the sums in Eqs. (54) and (55), one may start with the evaluation of the real part of the expression $a_\delta{}^{-2}(a_\gamma+b_\delta)^{-1}$. Using Eq. (52), one can easily show that

$$\left\{\frac{1}{a_\gamma{}^2(a_\gamma+b_\delta)}\right\}$$
$$=\tau_\gamma{}^2\bar\tau_{\gamma,\delta}\frac{1-\tau_\gamma{}^2\omega_\gamma{}^2-2\tau_\gamma\bar\tau_{\gamma,\delta}\omega_\gamma(\omega_\gamma+\omega_\delta)}{(1+\tau_\gamma{}^2\omega_\gamma{}^2)^2[1+\bar\tau_{\gamma,\delta}{}^2(\omega_\gamma+\omega_\delta)^2]},\quad (56)$$

where

$$1/\bar\tau_{\gamma,\delta}=1/\tau_\gamma+1/\sigma_\delta,\quad (57)$$

and $\bar\tau_{\gamma,\delta}$ will be called the effective correlation time for the nuclear and the ionic interactions. Furthermore, whenever terms of the form $\omega+\Omega$ appear, use can be made of the approximation

$$\Omega+\omega\approx\Omega.\quad (58)$$

The quantities $F_{\gamma,\delta}$ from Eq. (51) can be rewritten in the form

$$F_{\gamma,\delta}=N\left\langle\sum_k\varphi_{jk}{}^\gamma(0)\varphi_{jk}{}^{-\gamma}(0)V_k{}^\delta(0)V_k{}^{-\delta}(0)\right\rangle$$
$$=Nf_\gamma\langle V_k{}^\delta(0)V_k{}^{-\delta}(0)\rangle.\quad (59)$$

In order to facilitate interpretation, averages over $V_k{}^\delta(0)$ may be expressed in terms of the longitudinal and transverse ionic relaxation times $T_1{}^e$ and $T_2{}^e$, or in terms of the Larmor frequency associated with $V^\delta(0)$. The former can be accomplished by calculating $T_1{}^e$ and $T_2{}^e$ under the perturbation $\sum_k V_k(t)\cdot S_k$ according to the method outlined in Secs. II and III. One obtains

$$\langle V_k{}^{\pm1}(0)V_k{}^{\mp1}(0)\rangle$$
$$=\tfrac14\hbar^2\nu_1{}^2=\tfrac14\hbar^2(1+\sigma_1{}^2\Omega^2)(\sigma_1 T_1{}^e)^{-1},$$
$$\langle V_k{}^0(0)V_k{}^0(0)\rangle\qquad\qquad (60)$$
$$=\hbar^2\nu_0{}^2=\hbar^2[(\sigma_0 T_2{}^e)^{-1}-(2\sigma_0 T_1{}^e)^{-1}],$$

subject to the condition analogous to Eq. (43), namely, $T_1{}^e\gg\sigma_\delta$, $T_2{}^e\gg\sigma_\delta$.

Next, the quantities f_γ will be expressed in terms of the nuclear and ionic spin flip transition probabilities calculated by Solomon[3] and defined in Fig. 1.

Using Eq. (58) one may write

$$W_0=\tfrac18\tau_0 f_0\hbar^{-2}(1+\tau_0{}^2\Omega^2)^{-1},$$
$$W_1=\tfrac12\tau_1 f_1\hbar^{-2}(1+\tau_1{}^2\omega^2)^{-1},$$
$$W_1'=\tfrac12\tau_1 f_1\hbar^{-2}(1+\tau_1{}^2\Omega^2)^{-1},\qquad (61)$$
$$W_2=2\tau_2 f_2\hbar^{-2}(1+\tau_2{}^2\Omega^2)^{-1}.$$

In terms of this notation, the second-order expressions for the relaxation times $(1/T_2)^{(2)}$ and $(1/T_1)^{(2)}$ become

$$(1/T_2)^{(2)}=2W_0(1+\tau_0{}^2\Omega^2)$$
$$+\tfrac12 W_0+W_1+2W_1'+\tfrac12 W_2,\quad (62)$$
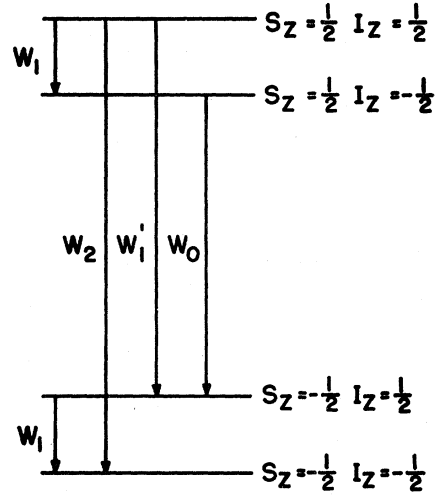$$(1/T_1)^{(2)}=W_0+2W_1+W_2.$$

FIG. 1. Schematic diagram showing the four energy levels and transition probabilities of the z components of two spins S and I.

The corresponding expressions for the fourth-order contributions to the relaxation times can be obtained by successively substituting Eqs. (56)–(61) into (54) and (55) and eliminating the quantities f_γ and $\langle\sum_k V_k{}^\delta(0)V_k{}^{-\delta}(0)\rangle$. After some algebra, one obtains the result which, combined with (62), can be written as

$$1/T_2=(1/T_2)^{(2)}+(1/T_2)^{(4)}=2W_0(1+\tau_0{}^2\Omega^2)$$
$$\times(1-w_0')+\tfrac12 W_0(1-w_0)+W_1(1-w_1)$$
$$+2W_1'(1-w_1')+\tfrac12 W_2(1-w_2),\quad (63)$$

and

$$1/T_1=(1/T_1)^{(2)}+(1/T_1)^{(4)}=W_0(1-w_0)$$
$$+2W_1(1-w_1)+W_2(1-w_2).\quad (64)$$

The quantities w are the fourth-order contribution to the relaxation times and are defined as

$$w_0'=\nu_1{}^2\tau_0\bar\tau_{0,1}(1+\bar\tau_{0,1}{}^2\Omega^2)^{-1},$$
$$w_0=X_0[Y_{0,0}+Z_0(1+\bar\tau_{0,1}{}^2\omega^2)^{-1}],$$
$$w_1=\tau_1\bar\tau_{1,1}\nu_1{}^2[1-\tau_1(\tau_1+2\bar\tau_{1,1})\omega^2]$$
$$\times(1+\tau_1{}^2\omega^2)^{-1}(1+\bar\tau_{1,1}{}^2\Omega^2)^{-1},$$
$$w_1'=X_1[Y_{1,0}+Z_1],\qquad\qquad (65)$$
$$w_2=X_2[Y_{2,0}+Z_2(1+\bar\tau_{2,1}{}^2\omega^2)^{-1}],$$
$$X_\gamma=\tau_\gamma(1+\tau_\gamma{}^2\Omega^2)^{-1},$$
$$Y_{\gamma,\delta}=\bar\tau_{\gamma,\delta}\nu_\delta{}^2[1-\tau_\gamma(\tau_\gamma+2\bar\tau_{\gamma,\delta})\Omega^2](1+\bar\tau_{\gamma,\delta}{}^2\Omega^2)^{-1},$$
$$Z_\gamma=\tfrac12\bar\tau_{\gamma,1}\nu_1{}^2(1-\tau_\gamma{}^2\Omega^2).$$

V. DISCUSSION OF RESULTS

A. Limits of Applicability

From Eq. (57), it is clear that $\bar\tau_{\gamma,\delta}\to0$ as $\sigma_\delta\to0$, and all the fourth-order terms w in Eq. (65) become negligible in comparison with unity if the correlation

times σ_δ become sufficiently small. This is to be expected since as the correlation time of an interaction becomes arbitrarily small, the influence of this interaction vanishes in the limit, as can be seen from Eq. (49). In the rigid case when $\sigma_\delta \to \infty$, $\bar{\tau}_{\gamma,\delta}$ will approach τ_γ and the corrections to the nuclear relaxation times become the ones given in Eq. (65) with $\bar{\tau}_{\gamma,\delta}$ replaced by τ_γ.

From Eqs. (63) and (64) it is clear that the calculation breaks down if any of the quantities w satisfies $w \gtrsim 1$. If the applied field H_z is weak, such that $\sigma_\delta^2\Omega^2 \ll 1$, $\tau_\gamma^2\Omega^2 \ll 1$, one can use the expression for w_0' in Eq. (65) to get

$$\nu_1^2 \tau_0 \bar{\tau}_{0,1} \ll 1 \tag{66}$$

as the necessary condition for the validity of our calculation. More generally, in weak fields one must have

$$(\tau_\gamma \bar{\tau}_{\gamma,\delta})^{\frac{1}{2}} \nu_\delta \ll 1 ; \tag{67}$$

i.e., the ionic local field must be so weak that the Larmor period associated with it is smaller than the geometric mean of the nuclear and effective correlation times; otherwise the expressions Eqs. (63) and (64) become meaningless.

If the applied field H_z is strong, such that $\bar{\tau}_{\gamma,\delta}^2\omega^2 \gg 1$, it is easily seen that all terms in Eq. (65) except w_0' will become negative and contribute no dangerous terms to the relaxation times. Considering Eq. (63), we see that w_0' carries an additional factor of $(1+\tau_0^2\Omega^2)$ so that it is the dominating factor of W_0 in strong fields. Therefore, a criterion of validity of this calculation in strong fields becomes

$$\nu_1^2/\Omega^2 \ll \bar{\tau}_{0,1}/\tau_0, \tag{68}$$

or, using the condition $\sigma_1^2\Omega^2 \gg 1$ in Eqs. (57) and (60), one has

$$(\sigma_1+\tau_0)/T_1^e \ll 1. \tag{69}$$

This last inequality is only meaningful as long as the second equalities in Eq. (60) can be defined; specifically if $T_1^e \lesssim \sigma_1$, Eq. (68) has to be used.

In the more frequent case when $\sigma_\delta^2\Omega^2 \gg 1$ and $\tau_\gamma^2\Omega^2 \gg 1$ but $\bar{\tau}_{\gamma,\delta}^2\omega^2 \ll 1$ one has, in addition to condition (69) involving τ_0, an identical condition for τ_1 as well.

For long ionic correlation times $\sigma_1 \gg \tau_0$ and one has $\bar{\tau}_{0,1} \approx \tau_0$ and Eq. (68) becomes $\nu_1^2 \ll \Omega^2$; this condition simply states that H_z must be much stronger than the local field, in agreement with one of the basic assumptions underlying our perturbation expansion.

B. Relaxation in Strong and Weak Fields

In this section we will evaluate the relaxation times, Eqs. (63) and (64), for the limiting case when $\bar{\tau}_{\gamma,\delta}^2\omega^2 \gg 1$. Using Eqs. (60) and (69) it can easily be shown that the quantities w in Eq. (65) then reduce to

$$w_0' \approx (\tau_0+\sigma_1)/T_1^e \ll 1,$$
$$w_0 \approx -\tfrac{1}{2}(\tau_0+\sigma_1)\Omega^2(T_1^e\omega^2)^{-1},$$
$$w_1 \approx -(\tau_1+3\sigma_1)/T_1^e \ll 1, \tag{70}$$
$$w_1' \approx -\tfrac{1}{2}(\tau_1+\sigma_1)\bar{\tau}_{1,1}^2\Omega^2/T_1^e,$$
$$w_2 \approx -\tfrac{1}{2}(\tau_2+\sigma_1)\Omega^2(\omega^2 T_1^e)^{-1},$$

indicating that details of the ionic relaxation may have an appreciable broadening influence on nuclear relaxation in strong fields.

The more frequently encountered case where $\tau_\gamma^2\Omega^2 \gg 1$ and $\sigma_\delta^2\Omega^2 \gg 1$ but $\bar{\tau}_{\gamma,\delta}^2\omega^2 \ll 1$ gives results analogous to Eq. (70),

$$w_0' \approx (\tau_0+\sigma_1)/T_1^e,$$
$$w_0 \approx -\tfrac{1}{2}\tau_0\sigma_1\bar{\tau}_{0,1}\Omega^2/T_1^e,$$
$$w_1 \approx (\tau_1+\sigma_1)/T_1^e, \tag{71}$$
$$w_1' \approx -\tfrac{1}{2}(\tau_1+\sigma_1)\bar{\tau}_{1,1}^2\Omega^2/T_1^e,$$
$$w_2 \approx -\tfrac{1}{2}\tau_2\sigma_1\bar{\tau}_{2,1}\Omega^2/T_1^e.$$

When the applied field H_z is weak, such that $\tau_\gamma^2\Omega^2 \ll 1 \gg \sigma_\delta^2\Omega^2$, one can use Eqs. (60) and (65) to show

$$w_0' \approx \tau_0\bar{\tau}_{0,1}(\sigma_1 T_1^e)^{-1}, \quad w_0 \approx \alpha_0,$$
$$w_1 \approx \tau_0\bar{\tau}_{1,1}(\sigma_1 T_1^e)^{-1}, \quad w_1' \approx \alpha_1, \quad w_2 \approx \alpha_2, \tag{72}$$

where

$$\alpha_\gamma = \tau_\gamma[\bar{\tau}_{\gamma,0}(\sigma_0 T_2^e)^{-1} + (\bar{\tau}_{\gamma,1}\sigma_1^{-1} - \bar{\tau}_{\gamma,0}\sigma_0^{-1})(2T_1^e)^{-1}]. \tag{73}$$

If the ionic field fluctuates vary rapidly compared with the nuclear motion, one has $\sigma_\delta \ll \tau_\gamma$ and Eq. (72) reduces to

$$w_0'/\tau_0 \approx w_1/\tau_1 \approx 1/T_1^e,$$
and $\tag{74}$
$$w_0/\tau_0 \approx w_1'/\tau_1 \approx w_2/\tau_2 \approx 1/T_2^e.$$

In the limiting case of completely random nuclear motion one can evaluate the quantities f_γ in Eq. (45) by simply averaging the spherical harmonics over a sphere[8]:

$$\tfrac{3}{8}f_0 = f_1 = f_2 = \tfrac{3}{10}K^2, \tag{75}$$

where $K^2 = \hbar^2 \gamma_N \gamma_e / \langle r_{jk}^3 \rangle$.

Assuming further that $\sigma_1 = \sigma_2 = \sigma$, $\tau_0 = \tau_1 = \tau_2 = \tau$, and $\bar{\tau}_{\gamma,\delta} = \bar{\tau}$, one may use Eqs. (75), (61), and (72) to obtain

$$1/T_2 = \tfrac{1}{10}\tau K^2[10 - 13\tau\bar{\tau}(2\sigma T_1^e)^{-1} - 7\tau\bar{\tau}(2\sigma T_2^e)^{-1}],$$
$$1/T_1 = \tfrac{1}{10}\tau K^2[10 - 3\tau\bar{\tau}(\sigma T_1^e)^{-1} - 7\tau\bar{\tau}(\sigma T_2^e)^{-1}], \tag{76}$$

with the property that $T_1 = T_2$ if $T_1^e = T_2^e$. Hence, if the system of nuclei is liquid and the ions are in the solid state, $T_1 \neq T_2$ since in this case $T_2^e \ll T_1^e$.

C. Comparison with the Phenomenological Theory

The phenomenological expressions[6,7] for the relaxation times T_1 and T_2 can be obtained from Eqs. (44) and (46) if the following assumptions are introduced:
(1) Let the quantities f_γ be defined by Eq. (75),

(2) let $\tau_0=\tau_1=\tau_2=\tau$, (3) let $\tau^2\omega^2\ll1$ (this is usually the case), (4) replace $1/\tau$ by

$$1/\tau=1/\tau_c=1/\tau_r+1/\tau_s, \tag{77}$$

where, using the notation of reference 6, τ_c is the effective correlation time for nuclear ionic dipolar interaction, τ_r is the correlation time for the relative motion and τ_s is the ionic spin relaxation time.

Under these circumstances, Eqs. (44) and (46) become

$$1/T_2= (1/20)\tau_c K^2[7+13/(1+\tau_c^2\Omega^2)],$$
$$1/T_1=\tfrac{1}{10}\tau_c K^2[3+7/(1+\tau_c^2\Omega^2)]. \tag{78}$$

Using conditions 1–3, together with $T_1^e=T_2^e=T\gg\tau$ and $\sigma_0=\sigma_1=\sigma\ll\tau$, one readily finds that Eqs. (63) and (64) simplify to

$$\frac{1}{T_2}=\frac{K^2\tau}{20}\left\{7\left(1-\frac{\tau}{T}\right)+\frac{13}{1+\tau^2\Omega^2}\right.$$
$$\left.\times\left[1-\frac{\tau}{2T}\frac{1-\tau^2\Omega^2}{1+\tau^2\Omega^2}\left(\frac{1}{1+\sigma^2\Omega^2}+1+\sigma^2\Omega^2\right)\right]\right\},$$
$$\frac{1}{T_1}=\frac{K^2\tau}{10}\left\{3\left(1-\frac{\tau}{T}\right)+\frac{7}{1+\tau^2\Omega^2}\right. \tag{79}$$
$$\left.\times\left[1-\frac{\tau}{2T}\frac{1-\tau^2\Omega^2}{1+\tau^2\Omega^2}\left(\frac{1}{1+\sigma^2\Omega^2}+1+\sigma^2\Omega^2\right)\right]\right\},$$

for this isotropic case.

It can easily be shown that expressions (79) reduce to (78) for both limiting cases of weak and strong fields alike, provided that in the latter case $1\ll\tau^2\Omega^21\gg\sigma^2\Omega^2$ and that one lets $\tau=\tau_r$ and $T=\tau_s$.

VI. SUMMARY

We use the K.T. method to study nuclear magnetic relaxation in the presence of paramagnetic ions and discuss the influence on the nuclear relaxation times of independent processes of ionic relaxation. Explicit expressions have been obtained for the nuclear relaxation times when the ionic interactions can be approximated by a random local field. Criteria of validity have been established for these expressions and several limiting cases have been discussed. Phenomenological expressions that have recently been proposed for isotropic interactions are verified. In general, the ionic interactions tend to slow down nuclear relaxation in weak fields, producing a narrowing phenomenon. In the limit of very strong fields, however, nuclear relaxation is enhanced, with a corresponding broadening. In intermediate situations one will have to consider the specific cases of interest since the dependence of T_1 and T_2 on the applied field strength and correlation times is fairly involved.

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