

## Comprehensive approach to motion-induced nuclear-dipole spin-lattice relaxation in the rotating reference frame\*

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A comprehensive perturbation formalism is developed in order to relate the rotating-frame spin-lattice relaxation time  $T_{1\rho}$  to the relative motions of the nuclear spins in a crystal lattice. A general relaxation equation valid in the entire temperature region is derived, from which both the strong-collision (so-called Slichter-Ailion theory) and weak-collision theory (valid in the motionally narrowed temperature region) are obtained as special cases. In the low-field transition region between the two theoretical approaches mentioned above, i.e., in the temperature region where the low-field  $T_{1\rho}$  minimum occurs, the relaxation properties are not governed by internal motions alone (as it is true in the temperature region where the  $T_{1\rho}$  minimum occurs in a high rotating field), but the spin dynamics associated with processes of internal equilibration of the spin system play an important role. The results are illustrated by a random-walk mechanism of self-diffusion in cubic crystals.

### I. INTRODUCTION

Since the pioneering work of Bloembergen, Purcell, and Pound (BPP) on the effect of internal motions in liquids on NMR,<sup>1</sup> a great depth of understanding of the diffusion-induced relaxation properties of crystals has been achieved. The experimental techniques and the accuracies in the measurements of the spin-lattice relaxation time  $T_1$  in the laboratory frame and  $T_{1\rho}$  in the rotating frame, and the spin-spin relaxation time  $T_2$  have been improved considerably during the last decade. Also, the theoretical methods have been extended to include point-defect mechanisms of self-diffusion through their effects, e.g., on (i) the temperature, or field, dependences of the relaxation times, or (ii) on the variation of  $T_1$ ,  $T_2$ , and  $T_{1\rho}$  as a function of the crystallographic orientation of the strong constant external field  $H_0$ .<sup>2-4</sup>

For the investigation of slow atomic or molecular motions in crystals spin-lattice relaxation is usually studied in the rotating frame, since there the quasiconstant rotating field  $H_1 \ll H_0$  results in a much slower Larmor precession of the spins and hence in an extended inherent time scale (characterized by  $\omega_1 = \gamma H_1$ ) in terms of which internal motions may be analyzed.

The main theoretical methods for relating the microscopic features of a given mechanism of motion to the macroscopic relaxation time  $T_{1\rho}$  are the following two:

(i) If  $H_1$  may be considered as large compared to the local field  $H_{L\rho}$  in the rotating frame (typically several gauss) the time-dependent dipolar Hamiltonian  $\mathcal{H}_d(t)$  in the spin Hamiltonian

$$\mathcal{H}_\rho = \mathcal{H}_{Z\rho} + \mathcal{H}_d(t) \quad (1.1)$$

may be treated as a small perturbation inducing transitions among the discrete levels of the Zeeman Hamiltonian  $H_{Z\rho}$ . This method was first applied by Look and Lowe,<sup>5</sup> starting from the Hebel-Slichter equation.<sup>6</sup>

(ii) In a weak relaxation field  $H_1 \approx H_{L\rho}$  the conventional perturbation approach fails. Slichter and Ailion<sup>7</sup> (SA) suggested calculating directly the change of the dipolar energy due to jumping. This energy change is communicated to the Zeeman Hamiltonian and thus to the magnetization of the sample through a process called thermal mixing of dipolar and Zeeman heat reservoirs, i.e., through the establishment of a common spin temperature in a time of the order of  $T_m$  (thermal mixing time).

One of the basic assumptions underlying the SA approach is that between consecutive jumps this spin temperature is established, i.e., that  $\tau \gg T_m$ . Here,  $\tau$  denotes the mean time of stay of an atom at a given lattice site. The related temperature region is called "strong-collision" or "low-temperature" region. As the field  $H_1$  is increased  $T_m$  becomes very long because of the very different spacings of the Zeeman and dipolar energy levels. Therefore, the concept of a common spin temperature breaks down ( $\tau \ll T_m$ ) and the related region is called "weak-collision," "motionally narrowed," or "high-temperature" region.

Within the frameworks of either concept described above, the so-called encounter model has provided a deeper understanding of the effect of correlated diffusion mechanisms on  $T_{1\rho}$ .<sup>2,3</sup> An interesting feature<sup>3</sup> is the result of an extrapolation of  $T_{1\rho}$  obtained in the strong-collision region ( $H_1 \approx H_{L\rho}$ ,  $\tau_d \ll T_m \ll \tau_{\text{NMR}}$ , with  $\tau_d$  denoting the mean time between consecutive jumps of a point defect

and  $\tau_{\text{NMR}}$  accounting for the mean time between consecutive encounters) to the weak-collision region ( $H_1 \gg H_{L\rho}$ ): The two approaches yield identical results. This suggests strongly that the two different physical concepts may be treated in terms of a more general formalism which includes both weak and strong collisions.

In the present paper a general perturbation method recently developed by Jacquinot and Goldman<sup>8</sup> is applied to a modified rotating-frame spin Hamiltonian. The result will be a general equation for  $T_{1\rho}$  valid for the entire temperature and field range including the transition region from the SA theory to the weak-collision approach.

## II. MOTION-INDUCED SPIN-LATTICE RELAXATION IN THE ROTATING FRAME

### A. Basic Hamiltonian

We consider a system of  $N$  interacting spins with quantum number  $I$  and gyromagnetic ratio  $\gamma$  in a constant magnetic field  $\vec{H}_0 = H_0 \hat{z}$  and an alternating field  $\vec{H}_1 = H_1(\hat{x} \cos \omega t + \hat{y} \sin \omega t)$ . In the laboratory frame the Hamiltonian of the spin system is given by (in units of  $\hbar$ )

$$\begin{aligned} \mathcal{H}_{\text{lab}} = & \omega_0 \sum_j I_{jz} + \omega_1 \cos \omega t \sum_j I_{jx} \\ & + \omega_1 \sin \omega t \sum_j I_{jy} + \mathcal{H}_d(t), \end{aligned} \quad (2.1)$$

where  $\omega_0 = \gamma H_0$  and  $\omega_1 = \gamma H_1$ .  $\mathcal{H}_d(t)$  denotes the Hamiltonian associated with the time-dependent dipolar couplings among the spins.

The transformation of Eq. (2.1) into the coordinate system rotating with frequency  $\omega$  around the direction of  $\vec{H}_0$  (rotating frame) is provided by the unitary operator

$$U(t) = e^{i\omega I_z t}, \quad (2.2)$$

with

$$I_z = \sum_j I_{jz}. \quad (2.3)$$

From a transformation of the Schrödinger equation into the rotating frame we obtain for the Hamiltonian  $\mathcal{H}_\rho$  in the rotating frame

$$\mathcal{H}_\rho = \Delta I_z + \omega_1 I_x + \mathcal{H}_{d\rho}(t), \quad (2.4)$$

with  $\Delta = \omega_0 - \omega$  and

$$\mathcal{H}_{d\rho}(t) = e^{i\omega I_z t} \mathcal{H}_d(t) e^{-i\omega I_z t}. \quad (2.5)$$

The dipolar Hamiltonian may be written in the well-known semiclassical form<sup>9</sup>

$$\mathcal{H}_d(t) = \frac{1}{2} \sum_i \sum_j \sum_{q=-2}^{+2} F_{ij}^{(q)}(t) A_{ij}^{(q)}, \quad (2.6)$$

with the classical "lattice" functions

$$\begin{aligned} F_{ij}^{(0)} &= r_{ij}^{-3} (1 - 3 \cos^2 \theta_{ij}), \\ F_{ij}^{(1)} &= r_{ij}^{-3} \sin \theta_{ij} \cos \theta_{ij} e^{-i\phi_{ij}}, \\ F_{ij}^{(2)} &= r_{ij}^{-3} \sin^2 \theta_{ij} e^{-2i\phi_{ij}}, \end{aligned} \quad (2.7)$$

where  $r_{ij}$ ,  $\theta_{ij}$ , and  $\phi_{ij}$  denote the polar coordinates of the vector  $\vec{r}_{ij}$  from spin  $i$  to spin  $j$  with respect to the so-called magnetic coordinate system (with its axis parallel to  $\vec{H}_0$ ).<sup>9</sup>

The quantum-mechanical spin operators  $A_{ij}^{(q)}$  are given by<sup>9</sup>

$$\begin{aligned} A_{ij}^{(0)} &= \frac{2}{3} \alpha [-I_{iz} I_{jz} + \frac{1}{4} (I_i^+ I_j^- + I_i^- I_j^+)], \\ A_{ij}^{(1)} &= \alpha (I_{iz} I_j^+ + I_i^+ I_{jz}), \\ A_{ij}^{(2)} &= \frac{1}{2} \alpha I_i^+ I_j^+, \end{aligned} \quad (2.8)$$

with

$$\begin{aligned} \alpha &= -\frac{3}{2} \gamma^2 \hbar, \\ F_{ij}^{(-q)} &= F_{ij}^{(q)*}, \quad F_{ij}^{(q)} = F_{ji}^{(q)}, \\ A_{ij}^{(-q)} &= A_{ij}^{(q)\dagger}, \quad A_{ij}^{(q)} = A_{ji}^{(q)}. \end{aligned} \quad (2.9)$$

The dipolar Hamiltonian [Eq. (2.6)] may be rewritten as<sup>4</sup>

$$\mathcal{H}_d(t) = \mathcal{H}_d^{(0)}(t) + \mathcal{H}_d^{(n)}(t), \quad (2.10)$$

where  $\mathcal{H}_d^{(0)}(t)$  includes the secular parts of  $\mathcal{H}_d(t)$  [terms  $q=0$  in Eq. (2.6)] while  $\mathcal{H}_d^{(n)}(t)$  denotes the nonsecular contributions (terms  $q \neq 0$ ).

If the frequency of the alternating field  $\vec{H}_1$  is close to resonance, i.e., if  $\Delta = \omega_0 - \omega \ll \omega$ , the effect of the nonsecular terms in Eq. (2.10) on the Zeeman Hamiltonian in the rotating frame may be neglected, and we may replace  $\mathcal{H}_{d\rho}(t)$  in Eq. (2.4) by

$$\mathcal{H}_{d\rho}^{(0)}(t) = e^{i\omega I_z t} \mathcal{H}_d^{(0)}(t) e^{-i\omega I_z t} = \mathcal{H}_d^{(0)}(t) \quad (2.11)$$

with (see above)

$$\mathcal{H}_d^{(0)}(t) = \frac{1}{2} \sum_i \sum_j F_{ij}^{(0)}(t) A_{ij}^{(0)}. \quad (2.12)$$

For similar reasons the local field  $H_{L\rho}$  in the rotating frame is governed by the secular terms only, and we have<sup>3,4</sup>

$$H_{L\rho}^2 = H_0^2 \text{Tr}(\mathcal{H}_d^{(0)2}) / \text{Tr}(\mathcal{H}_Z^2). \quad (2.13)$$

$\mathcal{H}_Z$  denotes the Zeeman Hamiltonian in the laboratory frame

$$\mathcal{H}_Z = \omega_0 I_z. \quad (2.14)$$

Thus we can write for the rotating-frame Hamiltonian [Eq. (2.4)]

$$\mathcal{H}_\rho = \Delta I_z + \omega_1 I_x + \mathcal{H}_d^{(0)}(t). \quad (2.15)$$

The Hamiltonian (2.15) may be used to calculate the relaxation behavior of the spin system in the high-field region ( $H_1 \gg H_{L\rho}$ ) by considering  $\mathcal{H}_d^{(0)}(t)$  as a small perturbation on the Zeeman term  $\Delta I_z + \omega_1 I_x$ . In the low-field region, however, this method breaks down. Therefore, Eq. (2.15) is modified in the following way:

$$\mathcal{H}_\rho = \Delta I_z + \omega_1 I_x + \mathcal{H}_d^{(0)r'l} + \mathcal{H}_d^{(0)}(t) - \mathcal{H}_d^{(0)r'l} \quad (2.16)$$

where  $\mathcal{H}_d^{(0)r'l}$  denotes the secular dipolar Hamiltonian  $\mathcal{H}_d^{(0)}$  in a rigid lattice, i.e., in the absence of diffusion or molecular rotations. The idea underlying Eq. (2.16) is to treat the deviation of  $\mathcal{H}_d^{(0)}(t)$  from its rigid-lattice value  $\mathcal{H}_d^{(0)r'l}$  as a perturbation on the time-independent part, which now includes the rigid-lattice dipolar Hamiltonian. Since the perturbation  $\mathcal{H}_d^{(0)}(t) - \mathcal{H}_d^{(0)r'l}$  will be smaller than  $\mathcal{H}_d^{(0)r'l}$  (especially when the relaxation process is caused by a few atomic or molecular jumps only) even in zero field  $H_1$  the perturbation treatment should hold.

Thus, summarizing the considerations of this section, we rewrite Eq. (2.16) as follows:

$$\mathcal{H}_\rho = \mathcal{H}_{0\rho} + \mathcal{H}_{1\rho}(t), \quad (2.17)$$

with

$$\mathcal{H}_{0\rho} = \Delta I_z + \omega_1 I_x + \mathcal{H}_d^{(0)r'l} \quad (2.18)$$

and

$$\mathcal{H}_{1\rho}(t) = \mathcal{H}_d^{(0)}(t) - \mathcal{H}_d^{(0)r'l}. \quad (2.19)$$

#### B. Application of the Jacquinot-Goldman method

Recently Jacquinot and Goldman<sup>8</sup> have suggested a method to calculate the time evolution of the density operator of a spin system which may be described by a Hamiltonian of the type of Eq. (2.17) in the rotating frame. For an operator  $Q$  which is a quasiconstant of the spin system in the rotating frame they derived the following master equation:

$$\frac{d}{dt} \langle Q \rangle = - \int_0^\infty \text{Tr} \{ \langle [Q, \tilde{\mathcal{H}}_{1\rho}(t)] [\mathcal{H}_{1\rho}(t'), \sigma^* - \sigma_L] \rangle_{t'} \} dt, \quad (2.20)$$

where  $\langle Q \rangle$  denotes the expectation value of  $Q$ , i.e.,  $\langle Q \rangle = \text{Tr}(\sigma Q)$ , and the brackets  $\langle \rangle_{t'}$  account for an average over the time  $t'$ . Here, the interaction representation of  $\mathcal{H}_{1\rho}(t)$  has been introduced by

$$\tilde{\mathcal{H}}_{1\rho}(t) = e^{i\mathcal{H}_{0\rho}t} \mathcal{H}_{1\rho}(t) e^{-i\mathcal{H}_{0\rho}t}. \quad (2.21)$$

If the field  $H_1$  is large enough to saturate the laboratory frame resonance we may assume that a spin temperature  $\Theta$  exists in the rotating frame. Then, in the high-temperature approximation, the

density matrix  $\sigma^*$  in the rotating frame is given by

$$\sigma^* = 1 - \beta \mathcal{H}_{0\rho} \quad (2.22)$$

with  $\beta = 1/k\Theta$ . Similarly, the thermal equilibrium density matrix  $\sigma_L$  may be written as

$$\sigma_L = 1 - \beta_L \mathcal{H}_{0\rho}, \quad (2.23)$$

where  $\beta_L$  is related to the "lattice" temperature  $\Theta_L$  by  $\beta_L = 1/k\Theta_L$ .

Inserting Eqs. (2.22) and (2.23) into Eq. (2.20) we obtain

$$\frac{d}{dt} \langle Q \rangle = (\beta - \beta_L) \int_0^\infty \text{Tr} \{ \langle [Q, \tilde{\mathcal{H}}_{1\rho}(t)] [\mathcal{H}_{1\rho}(t'), \mathcal{H}_{0\rho}] \rangle_{t'} \} dt. \quad (2.24)$$

For the calculation of spin-lattice relaxation we have to choose  $Q = \mathcal{H}_{0\rho}$ . With Eq. (2.22) we obtain for the rate of change of the expectation value of  $\mathcal{H}_{0\rho}$ :

$$\begin{aligned} \frac{d}{dt} \langle \mathcal{H}_{0\rho} \rangle &= \text{Tr} \left( \frac{d\sigma^*}{dt} \mathcal{H}_{0\rho} \right) \\ &= - \frac{d\beta}{dt} \text{Tr}(\mathcal{H}_{0\rho}^2) \end{aligned} \quad (2.25)$$

since  $\mathcal{H}_{0\rho}$  is traceless. Inserting Eq. (2.25) into Eq. (2.24) we obtain the relaxation equation<sup>8</sup>

$$\frac{d\beta}{dt} = - \frac{1}{T_{1\rho}} (\beta - \beta_L) \quad (2.26)$$

with

$$\begin{aligned} \frac{1}{T_{1\rho}} &= \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \\ &\times \int_0^\infty \text{Tr} \{ \langle [\mathcal{H}_{0\rho}, \tilde{\mathcal{H}}_{1\rho}(t)] [\mathcal{H}_{1\rho}(t'), \mathcal{H}_{0\rho}] \rangle_{t'} \} dt. \end{aligned} \quad (2.27)$$

As pointed out above, Eq. (2.27) was derived under the assumptions that a spin temperature exists in the rotating frame and that the high-temperature approximation may be applied to the spin system. The assumptions leading to our starting equation (2.20) may be found explicitly in the appendix of Jacquinot and Goldman's paper.<sup>8</sup>

In the following Eq. (2.27) will be applied to the Hamiltonian introduced in the preceding section [Eqs. (2.17) to (2.19)].

With our spin-lattice interaction  $\mathcal{H}_{1\rho}(t)$  [Eq. (2.19)] and the secular part of the dipolar interaction [Eqs. (2.11) and (2.6)] we obtain for the interaction representation  $\tilde{\mathcal{H}}_{1\rho}(t)$  defined by Eq. (2.21)

$$\tilde{\mathcal{H}}_{1\rho}(t) = \frac{1}{2} \sum_i \sum_j [F_{ij}^{(0)}(t) - F_{ij}^{(0)r'l}] \tilde{A}_{ij}^{(0)}(t), \quad (2.28)$$

where

$$\tilde{A}_{ij}^{(0)}(t) = e^{i\mathcal{H}_{0\rho}t} A_{ij}^{(0)} e^{-i\mathcal{H}_{0\rho}t} \quad (2.29)$$

and  $F_{ij}^{(0)r'l}$  denotes the geometrical part of  $\mathcal{H}_d^{(0)}$  in a rigid lattice. Since in our semiclassical approximation the lattice operators in (2.28) are considered as classical statistical functions, the trace over lattice operators in the Jacquinot-Goldman master equation has been replaced by a time average as indicated by the brackets  $\langle \rangle_{t'}$  in Eq. (2.20). If we insert Eq. (2.28) into Eq. (2.27) and define a correlation function  $K_{ij}(t)$  by

$$K_{ij}(t) = \langle [F_{ij}^{(0)}(t) - F_{ij}^{(0)r'l}] [F_{ij}^{(0)}(t') - F_{ij}^{(0)r'l}] \rangle_{t'} \quad (2.30)$$

we obtain for the relaxation rate

$$\frac{1}{T_{1\rho}} = \frac{1}{2\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_j \int_0^\infty K_{ij}(t) \times \text{Tr} \{ [\mathcal{H}_{0\rho}, \tilde{A}_{ij}^{(0)}(t)] [A_{ij}^{(0)}, \mathcal{H}_{0\rho}] \} dt \quad (2.31)$$

In the derivation of Eq. (2.31) it was assumed that the correlation functions  $C_{ijk}(t)$  associated with the correlated motions of three spins  $i$ ,  $j$ , and  $k$  are negligible compared to the pair correlation functions  $K_{ij}(t)$ . This assumption should hold well in monatomic crystals, but not necessarily in molecular crystals where groups of atoms can move in a highly correlated manner.

The character of the correlation function  $K_{ij}(t)$  becomes more apparent if we transform the time scale according to  $t - t' = t_1$ , from which we obtain

$$K_{ij}(t) = g_{ij}(t) + H_{ij}^{r'l} \quad (2.32)$$

with

$$g_{ij}(t) \equiv g_{ij}(t_1) = \langle F_{ij}^{(0)}(t') F_{ij}^{(0)}(t' + t_1) \rangle_{t'} \quad (2.33)$$

and

$$H_{ij}^{r'l} = - \langle F_{ij}^{(0)}(t_1 + t') \rangle_{t'} F_{ij}^{(0)r'l} - \langle F_{ij}^{(0)}(t') \rangle_{t'} F_{ij}^{(0)r'l} + (F_{ij}^{(0)r'l})^2 \quad (2.34)$$

Assuming that the value of  $\langle F_{ij}^{(0)}(t_1 + t') \rangle_{t'}$  is independent of  $t_1$  (invariance under transformations of the origin of the time scale) we see that  $H_{ij}^{r'l}$  is independent of time, while Eq. (2.33) is the definition of a classical pair correlation function.

Substituting Eq. (2.32) into Eq. (2.31) and using the equation of motion of  $\tilde{A}_{ij}^{(0)}(t)$  [see Eq. (2.29)],

$$-i \frac{d}{dt} \tilde{A}_{ij}^{(0)}(t) = [\mathcal{H}_{0\rho}, \tilde{A}_{ij}^{(0)}(t)] \quad (2.35)$$

we find

$$\frac{1}{T_{1\rho}} = \frac{-i}{2\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_j \int_0^\infty [g_{ij}(t) + H_{ij}^{r'l}] \times \text{Tr} \left( \frac{d}{dt} \tilde{A}_{ij}^{(0)}(t) [A_{ij}^{(0)}, \mathcal{H}_{0\rho}] \right) \quad (2.36)$$

Integrating Eq. (2.36) by parts and applying the commutator relationship

$$\text{Tr}(A[B, C]) = \text{Tr}([A, B]C) = \text{Tr}([C, A]B) \quad (2.37)$$

which holds for arbitrary operators  $A$ ,  $B$ , and  $C$ , we obtain

$$\frac{1}{T_{1\rho}} = \frac{i}{2\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_j \int_0^\infty \frac{dg_{ij}(t)}{dt} \times \text{Tr} \{ [\mathcal{H}_{0\rho}, \tilde{A}_{ij}^{(0)}(t)] A_{ij}^{(0)} \} \quad (2.38)$$

where

$$\tilde{A}_{ij}^{(0)}(0) = A_{ij}^{(0)} \quad (2.39)$$

has been inserted [see Eq. (2.29)], and the assumption

$$g_{ij}(\infty) = 0 \quad (2.40)$$

has been made. It is seen from Eq. (2.38) that the function  $H_{ij}^{r'l}$  does not contribute to the relaxation process.

Equation (2.38) may be simplified further by another use of Eq. (2.35) and subsequent integration by parts, from which we finally have

$$\frac{1}{T_{1\rho}} = \frac{1}{2\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_j \left( - \frac{dg_{ij}}{dt} \Big|_{t=0} \text{Tr}(A_{ij}^{(0)2}) - \int_0^\infty \frac{d^2 g_{ij}}{dt^2} \text{Tr}[\tilde{A}_{ij}^{(0)}(t) A_{ij}^{(0)}] dt \right) \quad (2.41)$$

where the relationship

$$\frac{dg_{ij}}{dt} \Big|_{t=\infty} = 0 \quad (2.42)$$

was assumed to hold.

Before we proceed further, the operators  $\tilde{A}_{ij}^{(0)}(t)$  are analyzed in more detail.

#### C. Relaxation in the doubly rotating frame (arbitrary distance from resonance)

According to Eqs. (2.29) and (2.18) the time dependence of the operators

$$\tilde{A}_{ij}^{(0)}(t) = e^{i(\Delta I_z + \omega_1 I_x + \mathcal{H}_d^{(0)r'l})t} \times A_{ij}^{(0)} e^{-i(\Delta I_z + \omega_1 I_x + \mathcal{H}_d^{(0)r'l})t} \quad (2.43)$$

is due to (i) the transformation of  $A_{ij}^{(0)}$  into the so-called doubly rotating frame, i.e., the frame rotating with frequency  $\omega_{\text{eff}}$  around the effective field  $\vec{H}_{\text{eff}} = H_{\text{eff}} \hat{z}'$ , given by

$$\vec{H}_{\text{eff}} = (H_0 - \omega/\gamma) \hat{z} + H_1 \hat{x} = (\omega_{\text{eff}}/\gamma) \hat{z}' \quad (2.44a)$$

and

$$\omega_{\text{eff}}^2 = \Delta^2 + \omega_1^2 \quad (2.44b)$$

and (ii) the operator involving the rigid-lattice dipolar Hamiltonian. Since the two transformations do not commute, the exact evaluation of Eq. (2.43) is very difficult.  $\tilde{A}_{ij}^{(0)}(t)$  as given by Eq. (2.43) may be simplified, however, by realizing that for  $t=0$

$$\tilde{A}_{ij}^{(0)}(0) \equiv A_{ij}^{(0)} \quad (2.45)$$

and that the time variation of  $\tilde{A}_{ij}^{(0)}(t)$  is governed by the two processes discussed above. Therefore, we rewrite Eq. (2.43) as follows:

$$\tilde{A}_{ij}^{(0)}(t) = e^{i3c_d^{(0)}r_1 t} [e^{i\omega_{\text{eff}} I_z' t} A_{ij}^{(0)} e^{-i\omega_{\text{eff}} I_z' t} f(\mathfrak{H}_d^{(0)r_1}, \Delta I_z + \omega_1 I_x, t)] e^{-i3c_d^{(0)}r_1 t}, \quad (2.46)$$

where the function  $f(t)$  accounts for the fact that the two transformations do not commute, and  $I_z'$  denotes the  $z'$  component of  $\tilde{\mathbf{I}}$  in the doubly rotating frame. Since for  $t=0$  Eq. (2.45) must hold, we find that  $f(t=0)$  must be unity.

If we characterize the orientation of the doubly rotating frame with respect to the rotating frame by the angle  $\vartheta$  between  $\hat{z}$  (parallel to  $\tilde{\mathbf{H}}_0$ ) and  $\hat{z}'$  (for  $\vartheta = \frac{1}{2}\pi$  the  $z'$  axis is parallel to the  $x$  axis of the rotating frame), the doubly rotating frame transformation entering Eq. (2.46) is easily carried out explicitly by transforming the individual spin operators according to

$$\begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix} = \begin{pmatrix} \cos\vartheta & 0 & \sin\vartheta \\ 0 & 1 & 0 \\ -\sin\vartheta & 0 & \cos\vartheta \end{pmatrix} \begin{pmatrix} I_{x'} \\ I_{y'} \\ I_{z'} \end{pmatrix}. \quad (2.47)$$

Using Eq. (2.47) and the results of Douglass and Jones,<sup>10</sup> we can write for  $\tilde{A}_{ij}^{(0)}(t)$ , instead of Eq. (2.46),

$$\tilde{A}_{ij}^{(0)}(t) = \sum_{p=-2}^{+2} a^{(p)} A_{ij}^{(p)'}(t) e^{i\omega^{(p)} t}, \quad (2.48)$$

where the operators  $A_{ij}^{(p)'}(t)$  entering Eq. (2.48)

$$\frac{1}{T_{1\rho}} = \frac{1}{2\text{Tr}\mathfrak{H}_{0\rho}^2} \sum_i \sum_j \left( -\text{Tr}(A_{ij}^{(0)2}) \frac{dg_{ij}(t)}{dt} \Big|_{t=0} - \sum_{p=-2}^{+2} \sum_{q=-2}^{+2} a^{(p)} a^{(q)} \int_0^\infty \frac{d^2 g_{ij}(t)}{dt^2} \text{Tr}[A_{ij}^{(p)'}(t) A_{ij}^{(q)'}] e^{i\omega^{(p)} t} dt \right). \quad (2.53)$$

The remaining problem is the calculation of the time-dependent trace over the correlation function of spin operators under the integral in Eq. (2.53). Using the independence of the trace operation of representation and inserting the definition (2.49) we may rewrite this correlation function as follows:

$$\text{Tr}[A_{ij}^{(p)'}(t) A_{ij}^{(q)'}] = \text{Tr}[A_{ij}^{(p)}(t) A_{ij}^{(q)}] = \text{Tr}[e^{i3c_d^{(0)}r_1 t} A_{ij}^{(p)} f(\mathfrak{H}_d^{(0)r_1}, \Delta I_z + \omega_1 I_x, t) e^{-i3c_d^{(0)}r_1 t} A_{ij}^{(q)}]. \quad (2.54)$$

The calculation of this trace involves the solution of the equation of motion of  $A_{ij}^{(p)}(t)$ , namely [see Eq. (2.49)],

$$-i \frac{d}{dt} A_{ij}^{(p)}(t) = [\mathfrak{H}_d^{(0)r_1}, A_{ij}^{(p)}(t)] - i e^{i3c_d^{(0)}r_1 t} A_{ij}^{(p)} \frac{df}{dt} e^{-i3c_d^{(0)}r_1 t}, \quad (2.55)$$

which is a difficult task since it requires the knowledge of the dynamical properties of the spin system. The problem has some resemblance with the "classical" line-shape problem in a rigid lat-

have been defined by [see Eq. (2.46)]

$$A_{ij}^{(p)'}(t) = e^{i3c_d^{(0)}r_1 t} A_{ij}^{(p)} \times f(\mathfrak{H}_d^{(0)r_1}, \Delta I_z + \omega_1 I_x, t) e^{-i3c_d^{(0)}r_1 t}. \quad (2.49)$$

The prime indicates the representation of  $A_{ij}^{(p)}$  in the doubly rotating frame, i.e.,  $I_\alpha$  ( $\alpha = x, y, z$ ) has to be replaced by  $I_\alpha'$  in  $A_{ij}^{(p)}$ .

According to Douglass and Jones<sup>10</sup> the coefficients  $a^{(p)}$  are given by

$$\begin{aligned} a^{(0)} &= \frac{1}{2}(1 - 3 \cos^2 \vartheta), \\ a^{(\pm 1)} &= -\frac{1}{2} \sin \vartheta \cos \vartheta, \\ a^{(\pm 2)} &= -\frac{1}{2} \sin^2 \vartheta, \end{aligned} \quad (2.50)$$

and

$$\omega^{(0)} = 0; \quad \omega^{(\pm 1)} = \pm \omega_{\text{eff}}; \quad \omega^{(\pm 2)} = \pm 2\omega_{\text{eff}}. \quad (2.51)$$

Inserting Eq. (2.49) into Eq. (2.41) and taking into account that

$$\tilde{A}_{ij}^{(0)}(0) \equiv A_{ij}^{(0)} = \sum_{q=-2}^{+2} a^{(q)} A_{ij}^{(q)} \quad (2.52)$$

[see Eqs. (2.45) and (2.49)], we find for the relaxation rate

tice, and one might try a moment type of expansion of Eq. (2.54).<sup>9</sup> Another possible, perhaps more promising, way might be the application of orthogonal-operator methods which lead to the so-called

memory-function approach.<sup>11,12</sup>

In this paper, however, we do not attempt to solve Eqs. (2.54) and (2.55). Instead, we will show below that the short-time and long-time behavior of Eq. (2.54) will give us the special cases of weak and strong collisions, respectively, and that the intermediate region which covers the range where the low-field  $T_{1\rho}$  minimum occurs ( $\tau \approx T_m$ ) is sensitive to the specific decay properties of the correlation function (2.54).

As we see from Eq. (2.54), the time variation of our spin correlation function is governed by rigid-lattice dipolar spin operators and their transformation properties with respect to the doubly rotating frame and it should therefore describe processes of internal equilibration of the spin system in this frame. Since both secular ( $p, q = 0$ ) and nonsecular dipolar operators ( $p, q \neq 0$ ) are time dependent, Eq. (2.54) should describe the establishment of a dipolar spin temperature as well as thermal mixing, and the correlation function should decay to zero as the nuclear-spin system achieves a state of internal equilibrium. Therefore, we make the following *simplifying assumption*:

$$\text{Tr}[A_{ij}^{(p)}(t)A_{ij}^{(q)}] = \text{Tr}[A_{ij}^{(p)}A_{ij}^{(q)}]e^{-t/T_2^{r1}}, \quad (2.56)$$

where  $T_2^{r1}$  denotes the rigid-lattice spin-spin relaxation time which is a rough measure of the time required for the spin system to achieve internal equilibrium in the rotating frame. (For  $H_1 \approx H_{L\rho}$  we have  $T_2^{r1} \approx T_m$ , the time required for thermal mixing of dipolar and Zeeman heat reservoirs.<sup>4,8</sup>)

For short times ( $t \approx 0$ ) Eq. (2.56) predicts

$$\text{Tr}[A_{ij}^{(p)}(0)A_{ij}^{(q)}] = \text{Tr}[A_{ij}^{(p)}A_{ij}^{(q)}] \quad (2.57)$$

which is in agreement with results derived above [see, e.g., Eqs. (2.45) and (2.54)]. For long times ( $t \gg T_2^{r1}$ ) Eq. (2.56) assures the decay of the correlation function to zero for the intuitive reasons given above. This decay to zero establishes the main assumption imposed on the theory developed in this paper. We believe, however, Eq. (2.56) to be qualitatively correct for all times  $t$  even though the details of the decay of the trace to zero might be more complicated than simply exponential, and also, the terms  $q = 0$  might have to be characterized by a decay time  $T_2^{r1}$  different from the decay time  $T_m$  of the nonsecular terms (see also Sec. IV).

Substituting now Eq. (2.56) into Eq. (2.41) we obtain for the relaxation rate

$$\begin{aligned} \frac{1}{T_{1\rho}} &= \frac{1}{2 \text{Tr}(\mathfrak{H}_{0\rho}^2)} \sum_i \sum_j \left( -\text{Tr}(A_{ij}^{(0)})^2 \frac{dg_{ij}(t)}{dt} \Big|_{t=0} \right. \\ &\quad \left. - \sum_{p=-2}^{+2} \sum_{q=-2}^{+2} a^{(p)} a^{(q)} \text{Tr}(A_{ij}^{(p)}A_{ij}^{(q)}) \int_0^\infty \frac{d^2 g_{ij}(t)}{dt^2} e^{-(1/T_2^{r1} - i\omega^{(p)})t} dt \right). \end{aligned} \quad (2.58)$$

Equation (2.58) is valid for arbitrary distance  $\Delta = \omega_0 - \omega$  from resonance. In the following section we will limit ourselves to the case of exact resonance.

#### D. Relaxation at exact resonance

At exact resonance we have  $\Delta = 0$  and  $\vartheta = \frac{1}{2}\pi$ , and from Eqs. (2.50) and (2.51) we obtain

$$a^{(0)} = \frac{1}{2}, \quad a^{(\pm 1)} = 0, \quad a^{(\pm 2)} = -\frac{1}{2}, \quad (2.59)$$

$$\omega^{(0)} = 0, \quad \omega^{(\pm 1)} = \pm \omega_1, \quad \omega^{(\pm 2)} = \pm 2\omega_1.$$

The remaining traces in Eq. (2.58) are easily evaluated to be

$$\text{Tr}(A_{ij}^{(0)2}) = \frac{1}{6} \gamma^4 \hbar^2 [I(I+1)]^2 (2I+1)^N, \quad (2.60a)$$

$$\text{Tr}(A_{ij}^{(\pm 2)2}) = \text{Tr}(A_{ij}^{(-2)2}) = \text{Tr}(A_{ij}^{(0)}A_{ij}^{(\pm 2)}) = 0, \quad (2.60b)$$

$$\begin{aligned} \text{Tr}(A_{ij}^{(2)}A_{ij}^{(-2)}) &= \text{Tr}(A_{ij}^{(-2)}A_{ij}^{(2)}) \\ &= \frac{1}{4} \gamma^4 \hbar^2 [I(I+1)]^2 (2I+1)^N, \end{aligned} \quad (2.60c)$$

$$\begin{aligned} \text{Tr}(\mathfrak{H}_{0\rho}^2) &= \frac{1}{3} N \gamma^2 I(I+1) \\ &\quad \times (H_1^2 + H_{L\rho}^2) (2I+1)^N. \end{aligned} \quad (2.60d)$$

Since these traces are independent of the individual spin pair  $i-j$  considered we may incorporate the summations over  $i$  and  $j$  in Eq. (2.58) into the correlation function  $G(t)$  defined by

$$G(t) = \frac{1}{N} \sum_i \sum_j g_{ij}(t). \quad (2.61)$$

Inserting Eqs. (2.59)–(2.61) into Eq. (2.58) we obtain the following relationship for the spin-lattice relaxation rate at exact resonance:

$$\frac{1}{T_{1\rho}} = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left[ -\frac{1}{4} \left( \frac{dG}{dt} \right)_{t=0} - \frac{1}{16} \int_0^\infty \frac{d^2 G(t)}{dt^2} e^{-t/T_2^{r1}} dt - \frac{3}{16} \text{Re} \int_0^\infty \frac{d^2 G(t)}{dt^2} e^{-(1/T_2^{r1} - 2i\omega_1)t} dt \right], \quad (2.62)$$

where  $\text{Re}$  denotes the real part. Integrating Eq. (2.62) by parts yields

$$\frac{1}{T_{1\rho}} = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left[ -\frac{1}{16T_2^{\tau I}} \int_0^\infty \frac{dG(t)}{dt} e^{-t/\tau_2^{\tau I}} - \frac{3}{16} \text{Re} \left( \frac{1}{T_2^{\tau I}} - 2i\omega_1 \right) \int_0^\infty \frac{dG(t)}{dt} e^{-(1/\tau_2^{\tau I} - 2i\omega_1)t} dt \right]. \quad (2.63)$$

So far, no specific assumptions concerning the form of the correlation function  $G(t)$  have been made except Eqs. (2.40) and (2.42). Therefore Eqs. (2.62) and (2.63) are valid for any mechanism that causes relative motions of the nuclei like, e.g., self-diffusion or molecular reorientation.

### III. STRONG VERSUS WEAK COLLISIONS

Without limiting ourselves to either weak or strong collisions, in the preceding section we have reformulated the problem of the calculation of spin-lattice relaxation in the rotating frame due to an arbitrary mechanism of internal motions in crystals.

The main result found there is that the relaxation rate  $T_{1\rho}^{-1}$  may be expressed in terms of *two* time constants related to the nuclear-spin system:

(i) The correlation time  $\tau_c$  entering through the "lattice correlation function"  $G(t)$  describes the time modulation of the dipolar interactions by in-

ternal motions.  $\tau_c$  is related to the time  $\tau$  between consecutive jumps or reorientations of a molecule (see Sec. V).

(ii) The spin-spin relaxation time in the absence of internal motions  $T_2^{\tau I}$  and the thermal mixing time  $T_m$  determine the decay properties of the "spin correlation functions" of dipolar operators between nuclear jumps [Eq. (2.56)], by which the regions of weak and strong collisions are connected.

In the following we will investigate how the relative magnitude of  $\tau_c$  with respect to  $T_2^{\tau I} \approx T_m$  determines the relaxation behavior in the two extreme regions.

#### A. Strong collisions

For  $\tau_c \gg T_2^{\tau I}$  an internal equilibrium is established before the correlation function  $G(t)$  can change due to relative motions of the nuclei. Therefore, Eq. (2.63) yields

$$\frac{1}{T_{1\rho}} = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left[ -\frac{1}{16T_2^{\tau I}} \left( \frac{dG}{dt} \right)_{t=0} \int_0^\infty e^{-t/\tau_2^{\tau I}} dt - \frac{3}{16} \text{Re} \left( \frac{1}{T_2^{\tau I}} - 2i\omega_1 \right) \left( \frac{dG}{dt} \right)_{t=0} \int_0^\infty e^{-(1/\tau_2^{\tau I} - 2i\omega_1)t} dt \right]. \quad (3.1)$$

The integrals in Eq. (3.1) are easily evaluated, and we have

$$\frac{1}{T_{1\rho}} = \frac{1}{4} \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left( -\frac{dG}{dt} \right)_{t=0}, \quad (3.2)$$

which is our result in the strong-collisions region for exact resonance. The equivalence of Eq. (3.2) with the basic relationships of the Slichter-Ailion theory is seen by replacing  $(dG/dt)_{t=0}$  by

$$\left( -\frac{dG}{dt} \right)_{t=0} = -\frac{G(0) - G(\tau_c)}{\tau_c}, \quad (3.3)$$

where we have used the fact that on the average  $G(t)$  changes during any time interval  $\tau_c$  just once (this is actually the definition of the correlation time  $\tau_c$ ). From Eqs. (2.13) and (2.60a) the local field is found to be<sup>3,4</sup>

$$H_{L\rho}^2 = \frac{1}{4} \gamma^2 \hbar^2 I(I+1) \sum_j |F_{ij}^{(0)}|^2, \quad (3.4)$$

which, inserted together with Eq. (3.3) into Eq. (3.2), yields

$$\frac{1}{T_{1\rho}} = \frac{H_{L\rho}^2}{H_1^2 + H_{L\rho}^2} \frac{G(0) - G(\tau_c)}{G(0)\tau_c}. \quad (3.5)$$

Here

$$\begin{aligned} G(0) &= \frac{1}{N} \sum_i \sum_j |F_{ij}^{(0)}|^2 \\ &= \sum_j |F_{ij}(0)|^2 \end{aligned} \quad (3.6)$$

is proportional to the average energy of a spin,  $E_d^b$  before a "collision," while

$$G(\tau_c) = \sum_j F_{ij}(0) F_{ij}(\tau_c) \quad (3.7)$$

is proportional to the average energy  $E_d^a$  after a "collision."<sup>3,4</sup> Thus, we can rewrite Eq. (3.5) as follows:

$$\frac{1}{T_{1\rho}} = \frac{H_{L\rho}^2}{H_1^2 + H_{L\rho}^2} \frac{1}{\tau_c} \frac{E_d^b - E_d^a}{E_d^b} \quad (3.8)$$

or

$$\frac{1}{T_{1\rho}} = \frac{H_{L\rho}^2}{H_1^2 + H_{L\rho}^2} \frac{1-p}{\tau_c} \quad (3.9)$$

with

$$p = E_d^a/E_d^b, \quad (3.10)$$

which is the well-known result of Slichter and Ailion.<sup>7</sup>

Actually, as pointed out recently,<sup>3</sup> Eqs. (3.8)–(3.10) are not valid when correlation effects in the relative motions of the nuclei have to be taken into account (like, e.g., when a spin temperature is established between consecutive *encounters* with a point defect, but not between consecutive *jumps* of the point defect). The correlation time  $\tau_c$  then depends on the relative vector from spin  $i$  to  $j$ , and hence,  $\tau_c = \tau_c(i, j)$  differs for different spin pairs. Equation (3.2) derived above nevertheless holds for an arbitrary type of motion in the strong-collision region. We only have to modify Eq. (3.3) similar to the following, using the definition of  $G(t)$  [Eq. (2.61)]:

$$\begin{aligned} \left(\frac{dG}{dt}\right)_{t=0} &= \frac{1}{N} \sum_i \sum_j \left(\frac{dg_{ij}(t)}{dt}\right)_{t=0} \\ &= \frac{1}{N} \sum_i \sum_j \frac{g_{ij}(0) - g_{ij}(\tau_c)}{\tau_c(i, j)}. \end{aligned} \quad (3.11)$$

From Eq. (3.11) it is easily verified that in the general case we obtain, instead of Eq. (3.8),

$$\begin{aligned} \frac{1}{T_{1\rho}} &= \frac{H_{L\rho}^2}{H_1^2 + H_{L\rho}^2} \frac{1}{N E_d^b} \\ &\times \sum_i \sum_j \{ [E_d^b(i, j) - E_d^a(i, j)] / \tau_c(i, j) \}, \end{aligned} \quad (3.12)$$

where  $E_d^b(i, j)$  denotes the dipolar-energy contribution from the spin-pair  $i$ - $j$  *before* a collision (i.e., an encounter, in the general case), and  $E_d^a(i, j)$  is defined similarly. Equation (3.12) reduces to the Slichter-Ailion result [Eq. (3.8)] if  $\tau_c$  does not depend on the particular spin pair, i.e., when correlations of successive jumps of atoms or point defects do not effect the relaxation behavior (like, e.g., in the case where a spin temperature is established between consecutive jumps of the point defect).

#### B. Weak collisions

For  $\tau_c \ll T_2^{\tau_1}$  the internal equilibration of the spin system is very slow, and the function  $e^{-t/T_2^{\tau_1}}$  in Eq. (2.63) remains practically unchanged while the correlation function  $G(t)$  and also its first derivative undergo their major variation with time (during a time interval of the order of several  $\tau_c$ ). Therefore, we may take

$$e^{-t/T_2^{\tau_1}} \Big|_{t=0} = 1 \quad (3.13)$$

out of the integrals in Eq. (2.63), and we obtain

$$\begin{aligned} \frac{1}{T_{1\rho}} &= \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left( -\frac{1}{16T_2^{\tau_1}} \int_0^\infty \frac{dG(t)}{dt} dt \right. \\ &\left. + \operatorname{Re} \frac{3i\omega_1}{8} \int_0^\infty \frac{dG(t)}{dt} e^{2i\omega_1 t} dt \right). \end{aligned} \quad (3.14)$$

Neglecting the first term in Eq. (3.14) [proportional to  $G(0)/T_2^{\tau_1}$ ] and integrating the second term by parts, we obtain

$$\begin{aligned} \frac{1}{T_{1\rho}} &= \frac{3\gamma^2 \hbar^2 I(I+1)}{4(H_1^2 + H_{L\rho}^2)} \omega_1^2 \\ &\times \operatorname{Re} \int_0^\infty G(t) e^{2i\omega_1 t} dt. \end{aligned} \quad (3.15)$$

Introducing the spectral density functions  $\mathcal{J}^{(a)}(\omega)$  of the correlation function  $G^{(a)}(t)$  in the standard way by

$$\mathcal{J}^{(a)}(\omega) = \int_{-\infty}^{\infty} G^{(a)}(t) e^{i\omega t} dt \quad (3.16)$$

and remembering that  $G(t) \equiv G^{(a=0)}(t)$  [see Eqs. (2.33) and (2.61)], we may rewrite Eq. (3.15) as follows:

$$\begin{aligned} \frac{1}{T_{1\rho}} &= \frac{3}{8} \gamma^4 \hbar^2 I(I+1) \\ &\times \frac{H_1^2}{H_1^2 + H_{L\rho}^2} \mathcal{J}^{(0)}(2\omega_1). \end{aligned} \quad (3.17)$$

Equation (3.17) may be rewritten in an alternative way by introducing the local field in the rotating frame from Eqs. (2.13) and (3.4), thus exhibiting more clearly the field dependence of  $T_{1\rho}^{-1}$ :

$$\frac{1}{T_{1\rho}} = \frac{3}{2} \frac{\gamma^2}{\sum_j |F_{ij}^{(0)}|^2} \frac{H_{L\rho}^2 H_1^2}{H_{L\rho}^2 + H_1^2} \mathcal{J}^{(0)}(2\omega_1). \quad (3.18)$$

Equations (3.17) and (3.18), respectively, represent our result in the weak-collision region. Extrapolating Eq. (3.17) to the high-field case ( $H_1^2 \gg H_{L\rho}^2$ ) we obtain

$$\frac{1}{T_{1\rho}} = \frac{3}{8} \gamma^4 \hbar^2 I(I+1) \mathcal{J}^{(0)}(2\omega_1), \quad (3.19)$$

which is the well-known result derived by Look and Lowe<sup>5</sup> for exact resonance by applying the Habel-Slichter equation.<sup>6</sup> [The reason why we did not obtain the nonsecular terms related to frequencies  $\omega_0$  and  $2\omega_0$  is the truncation of the rotating-frame dipolar Hamiltonian (see Sec. IIA), neglecting the nonsecular terms.]

Two interesting results concerning the field dependence of  $T_{1\rho}^{-1}$  at temperatures above ( $\omega_1 \tau_c \ll 1$ ) and below the  $T_{1\rho}$  minimum ( $\omega_1 \tau_c \gg 1$ ) are included in Eqs. (3.17) and (3.18). They will be discussed in Secs. III B 1 and III B 2.



### 1. Field dependence at temperatures below the $T_{1\rho}$ minimum

For  $\omega_1\tau_c \gg 1$  the correlation functions describing microscopic atomic or molecular motions predict the following form of  $\mathcal{J}^{(q)}(\omega)$ :

$$\mathcal{J}^{(q)}(\omega) = c_1/\omega_1^2\tau_c, \quad (3.20)$$

where  $c_1$  denotes a constant depending on the microscopic characteristics of the mechanism which modulates the dipolar interactions. Inserting Eq. (3.20) into Eq. (3.18) we find (for  $\omega = \omega_1 = \gamma H_1$ )

$$\frac{1}{T_{1\rho}} = \frac{3}{2} \frac{c_1}{\sum_j |F_{ij}^{(0)}|^2} \frac{H_{L\rho}^2}{H_1^2 + H_{L\rho}^2} \frac{1}{\tau_c}, \quad (3.21)$$

i.e., in the weak-collision region we expect a Slichter-Ailion type of field dependence for  $\omega_1\tau_c \gg 1$ . It is to be noted, however, that in a low relaxation field ( $H_1 \lesssim H_{L\rho}$ )  $T_{1\rho}$  accepts its minimum value at about  $\tau_c \approx T_2^{r1}$ , so that the condition  $\omega_1\tau_c \gg 1$  is equivalent with the strong-collision assumption  $\tau_c \gg T_2^{r1}$ , and hence Eq. (3.21) does not hold in weak fields, and the strong-collision result [Eq. (3.12)] applies instead. {The difference between Eqs. (3.21) and (3.12) lies only in the constant prefactors of the term  $H_{L\rho}^2 / [(H_1^2 + H_{L\rho}^2)\tau_c]$ .} As  $H_1$  is increased, however, the  $T_{1\rho}$  minimum is shifted into the weak-collision region and Eq. (3.21) applies under the condition  $H_1^2 \gg H_{L\rho}^2$ , from which we obtain the related Look and Lowe formula for  $\omega_1\tau_c \gg 1$  [see Eqs. (3.19) and (3.20)]. This is in agreement with the fact observed earlier<sup>3</sup> that the result of a proper extrapolation<sup>13</sup> of the strong-collision result to high fields yields a relationship which is identical with the high-field weak-collision predictions.

### 2. Field dependence at temperatures above the $T_{1\rho}$ minimum

The condition  $\omega_1\tau_c \ll 1$  imposed on Eqs. (3.17) and (3.18) implies that even in a low field ( $H_1 \lesssim H_{L\rho}$ ) we are at the high-temperature side of the  $T_{1\rho}$  minimum.

Similarly to Eq. (3.20) we may write for the spectral density function in this temperature region

$$\mathcal{J}^{(0)}(\omega) = c_2\tau_c, \quad (3.22)$$

where  $c_2$  is another constant depending on the microscopic features of the internal motions. Inserting Eq. (3.22) into Eq. (3.18) we obtain the interesting relationship

$$\frac{1}{T_{1\rho}} = \frac{3}{2} \frac{\gamma^2 c_2 \tau_c}{\sum_j |F_{ij}^{(0)}|^2} \frac{H_1^2 H_{L\rho}^2}{H_1^2 + H_{L\rho}^2}, \quad (3.23)$$

i.e., a field dependence of  $T_{1\rho}$  on the high-temperature side of the  $T_{1\rho}$  minimum is predicted. The character of this effect is exhibited more clearly by rewriting Eq. (3.23) as follows:

$$\frac{1}{T_{1\rho}} = \frac{3}{2} \frac{\gamma^2 c_2 \tau_c}{\sum_j |F_{ij}^{(0)}|^2} \frac{H_{L\rho}^2}{1 + H_{L\rho}^2/H_1^2}. \quad (3.24)$$

It is easily verified from Eq. (3.24) that for  $H_1^2 \gg H_{L\rho}^2$  the relaxation time  $T_{1\rho}$  becomes independent of  $H_1$  in agreement with the prediction of Look and Lowe<sup>5</sup> [see Eqs. (3.19) and (3.22)]. For small values of the  $H_1$ , however, a rather strong field dependence is expected ( $T_{1\rho}^{-1} \sim H_1^2$ ).

To our knowledge, this effect has never been observed experimentally. For the reasons given below we are somewhat doubtful about the applicability of our weak-collision result (3.18) to low relaxation fields:

(i) The perturbation [see Eq. (2.19)]

$$\mathcal{H}_{1\rho}(t) = \mathcal{H}_d^{(0)}(t) - \mathcal{H}_d^{(0)r1} \quad (3.25)$$

might not be *much* smaller than the unperturbed Hamiltonian at exact resonance [see Eq. (2.18) with  $\Delta = 0$ ]

$$\mathcal{H}_{0\rho} = \gamma H_1 I_x + \mathcal{H}_d^{(0)r1} \quad (3.26)$$

since when many jumps occur during the relaxation process  $\mathcal{H}_d^{(0)}(t)$  may become much smaller than  $\mathcal{H}_d^{(0)r1}$  so that  $\mathcal{H}_{1\rho}(t)$  may increase towards  $\mathcal{H}_d^{(0)r1}$  while  $\mathcal{H}_{0\rho}$  remains unaffected. On the other side, our calculations are based upon the assumption that  $H_1$  is strong enough to saturate the resonance line (see Sec. II B), so that in Eq. (3.26) there will always be at least a small Zeeman term.

(ii) The assumption of a spin temperature in the rotating frame [see Sec. II B, Eq. (2.22)] implies in the high-temperature approximation that

$$\begin{aligned} \frac{d}{dt}(\mathcal{H}_{0\rho}) &= -\frac{d\beta}{dt} \text{Tr}(\mathcal{H}_{0\rho}^2) \\ &= -\frac{d\beta}{dt} [\text{Tr}(\mathcal{H}_{Z\rho}^2) + \text{Tr}(\mathcal{H}_d^{(0)r1^2})]. \end{aligned} \quad (3.27)$$

As a consequence of Eq. (3.27) the total spin-lattice relaxation rate  $T_{1\rho}^{-1}$  consists of a weighted average of the related partial relaxation rates, which results in the field dependence of  $T_{1\rho}^{-1}$ . The assumption of a spin temperature for both  $\mathcal{H}_{Z\rho}$  and  $\mathcal{H}_d^{(0)r1}$  might not hold anymore in the motionally narrowed region, although no motion-dependent parameters enter into these two constants of the motion.

Despite the two arguments given above the validity range of Eqs. (3.17) and (3.18) is not quite clear. Systematic experimental investigations in the corresponding field and temperature region are desirable to clarify the arguments involved.

## IV. INTERMEDIATE REGION

It is well-known that for  $H_1 \lesssim H_{L\rho}$  the relaxation time  $T_{1\rho}$  passes through its minimum at temperatures for which  $\tau_c \approx T_2^{r1}$  (see also Sec. III). Without

using a specific correlation function  $G(t)$  the solution of Eqs. (2.62) and (2.63) is not possible in this temperature region, where neither of the conditions  $\tau_c \gg T_2^r$  and  $\tau_c \ll T_2^r$  holds. Nevertheless, some of the qualitative features of this low-field  $T_{1\rho}$  minimum may be understood along the following lines.

Let us go back to Sec. II C where the spin correlation function (2.54) was simplified by the phenomenological assumption (2.56). Reformulating this assumption in a more general fashion, we write

$$\text{Tr}[A_{ij}^{(p)}(t)A_{ij}^{(q)}] = \text{Tr}(A_{ij}^{(p)}A_{ij}^{(q)})k^{(p,q)}(t), \quad (4.1)$$

where the "reduced" spin correlation function  $k^{(p,q)}(t)$  may be qualitatively different for different values of  $q$  and  $p$  [i.e., the decay of  $k^{(0,0)}(t)$  may be characterized, e.g., by the establishment of a dipolar spin temperature, while the terms  $k^{(p,q)}(t)$  for  $p, q \neq 0$  may describe, e.g., thermal mixing

between Zeeman and dipolar thermal reservoirs]. The initial conditions imposed on  $k^{(p,q)}(t)$  are obtained by comparing Eqs. (4.1) and (2.54). They are

$$k^{(p,q)}(0) = 1. \quad (4.2)$$

We assume  $k^{(p,q)}(t)$  to be normalized, so that

$$\int_0^\infty k^{(p,q)}(t) dt \approx T_{\text{int}}^{(p,q)} \quad (4.3)$$

and that  $k^{(p,q)}(t)$  decays to zero as  $t$  goes to infinity, i.e.,

$$k^{(p,q)}(\infty) = 0, \quad (4.4)$$

where  $T_{\text{int}}^{(p,q)}$  denotes a time constant characterizing the establishment of internal spin equilibrium (e.g.,  $T_{\text{int}}^{(0,0)} \sim T_2^r$ ,  $T_{\text{int}}^{(p,q \neq 0)} \sim T_m$ ) between jumps.

Inserting Eq. (4.1) into Eq. (2.53) we arrive at a relationship similar to Eq. (2.62):

$$\frac{1}{T_{1\rho}} = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left[ \frac{1}{4} \left( \frac{dG}{dt} \right)_{t=0} - \frac{1}{16} \int_0^\infty \frac{d^2 G(t)}{dt^2} k^{(0,0)}(t) dt - \frac{3}{16} \text{Re} \int_0^\infty \frac{d^2 G(t)}{dt^2} k^{(2,-2)}(t) e^{2i\omega_1 t} dt \right], \quad (4.5)$$

where it was assumed that  $k^{(p,-p)}(t)$  is equal to  $k^{(-p,p)}(t)$ . From Eq. (4.5) the relationships (3.2) and (3.17) deduced in Sec. III for the extreme cases of strong collisions and weak collisions, respectively, may be obtained without specifying the functions  $k^{(p,q)}(t)$  in more detail than by Eqs. (4.2)–(4.4).

Thus, we obtain under the strong-collision assumption that  $k^{(p,q)}(t)$  decays much faster than the lattice correlation function  $G(t)$

$$\frac{1}{T_{1\rho}} = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left[ -\frac{1}{4} \left( \frac{dG}{dt} \right)_{t=0} - \frac{1}{16} \left( \frac{d^2 G}{dt^2} \right)_{t=0} \int_0^\infty [k^{(0,0)}(t) + 3k^{(2,-2)}(t) e^{2i\omega_1 t}] dt \right], \quad (4.6)$$

and under the weak-collision assumption that  $G(t)$  decays much faster than any of the reduced spin correlation functions  $k^{(p,q)}(t)$

$$\frac{1}{T_{1\rho}} = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2} \left[ -\frac{1}{4} \left( \frac{dG}{dt} \right)_{t=0} - \frac{1}{16} k^{(0,0)}(0) \int_0^\infty \frac{d^2 G}{dt^2} dt - \frac{3}{16} k^{(2,-2)}(0) \text{Re} \int_0^\infty \frac{d^2 G}{dt^2} e^{2i\omega_1 t} dt \right]. \quad (4.7)$$

With Eqs. (4.2)–(4.4) it is easily confirmed that the above relationships reproduce the general results found in Sec. III, namely, that the relaxation rate in the weak-collision region is characterized by the *Fourier transform* of  $G(t)$ , and the short-time behavior of  $k^{(p,q)}(t)$  [Eq. (4.2)], while in the strong-collision region the relaxation process is governed by the *first time derivative* of  $G(t)$  and the integral decay properties of  $k^{(p,q)}(t)$  [Eq. (4.3)].

It is interesting to note that in these two extreme cases the *explicit* time variation of the spin correlation function does not enter at all. Therefore, spin-lattice relaxation (orientation dependence of  $T_{1\rho}$ , shape and width of the high-field  $T_{1\rho}$  minimum as a function of temperature, etc.) is governed by the internal motions alone.

In the low-field intermediate region, i.e., if

$G(t)$  and  $k^{(p,q)}(t)$  decay about equally fast, the observable relaxation phenomena are a product of both internal motions *and* spin dynamics. This is demonstrated by the third term on the right-hand side of Eq. (4.5), which indicates that the low-field  $T_{1\rho}$  minimum is properly described by the Fourier transform of the product of lattice *and* spin correlation function.

## V. APPLICATION TO RANDOM-WALK SELF-DIFFUSION

So far in this paper the conclusions arrived at were valid for an arbitrary mechanism of internal movements which modulate the dipolar interactions between the nuclear spins in a crystal lattice containing one sort of spin only. In the following we apply the results of Secs. II–IV to the simple case

of self-diffusion by the uncorrelated random motions of the nuclei. Although in many cases this mechanism is somewhat unrealistic in its description of the relative motions of the nuclei in crystals,<sup>2</sup> it will demonstrate all the important features pointed out in rather general terms in the preceding sections.

#### A. General relationships

The correlation function  $G(t)$  for random-walk diffusion in a crystal lattice was first calculated by Torrey.<sup>14</sup> Recently, this approach was generalized by Wolf<sup>15</sup> in a way that lends itself to the application to point-defect diffusion mechanisms.<sup>2</sup> The main result found there<sup>15</sup> is that  $G(t)$  has the following form:

$$G(t) = e^{-t/\tau_c} \sum_{s=0}^{\infty} \frac{B_s}{s!} \left(\frac{t}{\tau_c}\right)^s, \quad (5.1)$$

where  $s$  denotes the number of random jumps of an atom, and  $B_s$  corresponds to the lattice sums

$$B_s = \sum_{\vec{r}_j^0} F_{ij}^{(0)}(\vec{r}_j^0) \sum_{\vec{r}^*} W_s(\vec{r}_j^0, \vec{r}^*) F_{ij}^{(0)}(\vec{r}_j^0 + \vec{r}^*). \quad (5.2)$$

Here,  $\vec{r}_j^0$  denotes the vector from spin  $i$  (assumed to be located at the origin) to spin  $j$  before a jump, while  $W_s(\vec{r}_j^0, \vec{r}^*)$  denotes the probability that the relative displacement vector after  $s$  jumps of the two spins is equal to  $\vec{r}^*$ . The factors  $B_s$  have been computed numerically for  $s=0$  to  $s=20$  for an arbitrary orientation of the strong constant external field  $\vec{H}_0$ , and it was shown<sup>15</sup> that the sum over  $s$  in Eq. (5.1) converges fairly well so that it suffices to include the first 20 terms only.

The correlation time  $\tau_c$  is related to the mean time  $\tau$  of stay of an atom at a given lattice site by<sup>14,15</sup>

$$\tau_c = \frac{1}{2} \tau, \quad (5.3)$$

since the dipolar interaction between a randomly migrating pair of spins changes whenever either one of the two spins jumps.

Since we plan to treat the low-field  $T_{1\rho}$  minimum as well as the extreme cases (see Sec. IV) we have to select a specific spin-operator correlation function  $k^{(p,q)}(t)$ . Like in Sec. II [Eq. (2.56)] we choose the same simple exponential decay function for all values of  $p$  and  $q$ , i.e., we insert

$$k^{(p,q)}(t) = e^{-t/\tau_2^{p,q}} \quad (5.4)$$

into Eq. (4.5), from which we obtain Eq. (2.62):

$$\frac{1}{T_{1\rho}} = C \left[ -\frac{1}{4} \left( \frac{dG}{dt} \right)_{t=0} - \frac{1}{16} \int_0^{\infty} \frac{d^2G}{dt^2} e^{-t/\tau_2^{p,q}} dt - \frac{3}{16} \operatorname{Re} \int_0^{\infty} \frac{d^2G}{dt^2} e^{-(1/\tau_2^{p,q} - 2i\omega_1)t} dt \right], \quad (5.5)$$

with

$$C = \frac{\gamma^2 \hbar^2 I(I+1)}{H_1^2 + H_{L\rho}^2}. \quad (5.6)$$

From Eq. (5.1) the first two time derivatives of  $G(t)$  are readily calculated:

$$\frac{dG}{dt} = \frac{e^{-t/\tau_c}}{\tau_c} \left[ \sum_{s=0}^{\infty} \frac{B_s}{s!} \left(\frac{t}{\tau_c}\right)^s + \sum_{s=1}^{\infty} \frac{B_s}{(s-1)!} \left(\frac{t}{\tau_c}\right)^{s-1} \right] \quad (5.7)$$

and

$$\frac{d^2G}{dt^2} = \frac{e^{-t/\tau_c}}{\tau_c^2} \left[ \sum_{s=0}^{\infty} \frac{B_s}{s!} \left(\frac{t}{\tau_c}\right)^s + \sum_{s=1}^{\infty} \frac{2B_s}{(s-1)!} \left(\frac{t}{\tau_c}\right)^{s-1} + \sum_{s=2}^{\infty} \frac{B_s}{(s-2)!} \left(\frac{t}{\tau_c}\right)^{s-2} \right]. \quad (5.8)$$

Inserting Eqs. (5.7) and (5.8) into Eq. (5.5) and defining an "effective" correlation time  $\tau_{\text{eff}}$  according to

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_c} + \frac{1}{T_2^{p,q}}, \quad (5.9)$$

we see that the integral may be easily evaluated and we arrive at the relationship

$$\begin{aligned} \frac{1}{T_{1\rho}} = C & \left[ \frac{1}{4} \frac{B_0 - B_1}{\tau_c} - \frac{(y-1)^2}{16\tau_c} \sum_{s=2}^{\infty} B_s y^{s-1} + \frac{3}{16\tau_c} \sum_{s=2}^{\infty} B_s \left( \frac{4x^2 - (y-1)^2}{y^2} h_s(2x) + \frac{4x(y-1)}{y^2} l_s(2x) \right) \right. \\ & \left. - \frac{1}{16} \frac{y}{\tau_c} [B_0 - B_1(2-y)] - \frac{1}{\tau_c} \frac{3}{16} B_0 h_0(2x) + \frac{3}{16} \frac{B_1}{\tau_c} [2h_0(2x) - h_1(2x)] \right]. \quad (5.10) \end{aligned}$$

Here, the following abbreviations have been introduced:

$$y = \tau_{\text{eff}}/\tau_c, \quad x = \omega_1\tau_{\text{eff}}, \quad (5.11)$$

$$y^{s+1}/(1-ix)^{s+1} = h_s(x) + il_s(x), \quad (5.12)$$

and the following recursion formulas which are easily derived from the definition (5.12) have been used:

$$h_{s-1}(x) = (1/y)h_s(x) + (x/y)l_s(x), \quad (5.13)$$

$$l_{s-1}(x) = (1/y)l_s(x) - (x/y)h_s(x). \quad (5.14)$$

Equation (5.10) relates  $T_{1\rho}^{-1}$  in the entire temperature region to the quantities  $\tau_c$  and  $B_s$  characterizing the diffusion mechanism, and to  $T_2^{r1}$  characterizing (in our rough approximation) the spin dynamics. In the following we will discuss Eq. (5.10) in some detail.

#### B. Strong-collision approach for random-walk diffusion

For  $\tau_c \gg T_2^{r1}$  it is found from Eqs. (5.9) and (5.11) that

$$\tau_{\text{eff}} = T_2^{r1}, \quad y = T_2^{r1}/\tau_c \ll 1, \quad x = \omega_1 T_2^{r1}. \quad (5.15)$$

Inserting these relationships into Eq. (5.10) it is readily verified that all terms proportional to  $y^s$  ( $s \geq 0$ ) including the terms multiplied by  $h_s(x)$  and  $l_s(x)$  are negligible in comparison to the leading term on the right of Eq. (5.10), so that we end up with

$$\frac{1}{T_{1\rho}} = \frac{C}{4} \frac{B_0 - B_1}{\tau_c}, \quad (5.16)$$

which may be rewritten, using Eqs. (5.2), (5.3), (5.6), and (3.4) as

$$\frac{1}{T_{1\rho}} = \frac{H_{L\rho}^2}{H_1^2 + H_{L\rho}^2} \frac{2(1-p)}{\tau}, \quad (5.17)$$

with

$$p = \frac{1}{G} \sum_{\tilde{\mathbf{r}}_j^0} \sum_{\tilde{\mathbf{r}}_j^0} F_{ij}^{(0)}(\tilde{\mathbf{r}}_j^0) F_{ij}^{(0)}(\tilde{\mathbf{r}}_j^0 - \tilde{\mathbf{r}}_g^0) / \sum_{\tilde{\mathbf{r}}_j^0} |F_{ij}^{(0)}(\tilde{\mathbf{r}}_j^0)|^2. \quad (5.18)$$

Here, in applying Eq. (5.2) we used the properties  $W_1(\tilde{\mathbf{r}}_j^0, \tilde{\mathbf{r}}_j^*) = 1/G$  for the  $G$  nearest-neighbor positions  $\tilde{\mathbf{r}}_j^* = \tilde{\mathbf{r}}_g^0$  around spin  $i$ , and  $W_0(\tilde{\mathbf{r}}_j^0, \tilde{\mathbf{r}}_j^*) = 0$  except  $W_0(\tilde{\mathbf{r}}_j^0, \tilde{\mathbf{0}}) = 1$  (where  $\tilde{\mathbf{0}}$  denotes the zero vector).

Equations (5.17) and (5.18) are identical with the results derived recently<sup>3</sup> from a generalized Slichter-Ailion type of theory applied to random-walk self-diffusion. This supports strongly the general form of the correlation function  $G(t)$  [Eq. (5.1)], since it is obvious that, e.g., a simple exponential correlation function [term  $s=0$  in Eq. (5.1)] would not have given us an answer compatible with the Slichter-Ailion approach (5.17). As pointed out

recently<sup>2</sup> the correlation function describing point-defect mechanisms of self-diffusion in crystals has a mathematical structure similar to Eq. (5.1). It is interesting to note that in this case we obtain complete agreement with the related Slichter-Ailion approach,<sup>3</sup> too, which is another strong argument in support of correlation functions of the type of Eq. (5.1) for describing the effect of (correlated or uncorrelated) relative motions of nuclear spins on the magnetic relaxation properties in crystals.

#### C. Weak-collision approach for random-walk diffusion

For  $\tau_c \ll T_2^{r1}$  the following relationships are derived from Eqs. (5.9) and (5.11):

$$\tau_{\text{eff}} = \tau_c, \quad y = 1, \quad x = \omega_1\tau_c, \quad (5.19)$$

which, inserted into Eq. (5.10), yield

$$\frac{1}{T_{1\rho}} = C \left( \frac{3}{16} \frac{B_0 - B_1}{\tau_c} + \frac{3}{4} \omega_1^2 \tau_c \sum_{s=2}^{\infty} B_s h_s(2x) - \frac{3}{16} B_0 h_0(2x) + \frac{3}{16} \frac{B_1}{\tau_c} [2h_0(2x) - h_1(2x)] \right). \quad (5.20)$$

With

$$h_0(x) = \frac{1}{1+x^2}, \quad h_1(x) = \frac{1-x^2}{(1+x^2)^2}, \quad (5.21)$$

[see Eq. (5.12)] we obtain finally

$$T_{1\rho} = \frac{3}{4} \frac{\gamma^4 \hbar^2 I(I+1) H_1^2 \tau_c}{H_1^2 + H_{L\rho}^2} \times \sum_{s=0}^{\infty} B_s h_s(2\omega_1\tau_c). \quad (5.22)$$

In the high-field case ( $H_1 \gg H_{L\rho}$ ) this yields (with  $\tau_c = \frac{1}{2}\tau$ )

$$\frac{1}{T_{1\rho}} = \frac{3}{8} \gamma^4 \hbar^2 I(I+1) \tau \sum_s B_s h_s(\omega_1\tau), \quad (5.23)$$

where, from Eq. (5.12) with  $y=1$ ,  $h_s(x)$  is given by

$$h_s(x) = \text{Re}[(1-ix)^{-s-1}]. \quad (5.24)$$

Comparing Eq. (5.23) with the predictions of the high-field random-walk perturbation approach<sup>15</sup> we find that the two results are identical. As found there<sup>15</sup> for  $\omega_1\tau \gg 1$  Eq. (5.23) is identical with Torrey's calculation of random walks on a lattice.<sup>14</sup>

The problems that may arise in the low-field region included in Eq. (5.22) have been discussed in Sec. III B 2.

#### D. Intermediate region in terms of random-walk diffusion

Equation (5.10) also includes the temperature and field region in which neither a strong- nor a

weak-collision approach applies. Owing to the rather crude assumption (5.4) and our reservations concerning the field dependence in the low-field weak-collision region we will not discuss this region in any detail. In principle, however, Eq. (5.10) describes the shape of the low-field  $T_{1\rho}$  minimum as a function of temperature and the field  $H_1$ .

More thought about the spin correlation functions involved is necessary before the basic properties of the spin dynamics underlying the internal equilibration processes may be deduced from the characteristics of the low-field  $T_{1\rho}$  minimum.

### VI. SUMMARY AND CONCLUSIONS

A comprehensive perturbation formalism has been proposed which applies to strong collisions as well as to weak collisions and the temperature region between the two extreme cases. Where our results can be compared with predictions from other theoretical approaches (mainly, in the low-field strong-collision region<sup>3</sup> and the high-field weak-collision region<sup>5</sup>) complete agreement is found. The transition from the Slichter-Ailion type of theory<sup>3,4</sup> to the approaches applying in the motionally narrowed region<sup>2,5</sup> is represented in terms of a correlation function of dipolar spin operators describing processes related to the establishment of internal equilibrium inside the spin system. The decay properties of this spin correlation function are not fully understood.

The main conclusions of our method may be briefly summarized as follows:

(i) While the high-field  $T_{1\rho}$  minimum is governed by the microscopic features of the related self-diffusion mechanism, in a low rotating field both self-diffusion *and* equilibration processes inside the nuclear-spin system govern shape and width of the  $T_{1\rho}$  minimum. Therefore, we think that there is

more to be learned about the spin system itself than about the diffusion mechanism(s) involved by carefully investigating the temperature region where the low-field  $T_{1\rho}$  minimum occurs (see Sec. IV).

(ii) The field dependence of  $T_{1\rho}^{-1}$  in the transition region from the Slichter-Ailion type of field dependence in the low-field strong-collision region to the high-field frequency dependence in the weak-collision region is described uniquely in terms of a dipolar spin-operator correlation function. This field range has been studied experimentally<sup>16</sup> and a quantitative comparison with these results is desirable (see Secs. III and IV).

(iii) In the low-field weak-collision region  $T_{1\rho}$  is predicted to depend on the rotating field amplitude  $H_1$ . This has to our knowledge never been observed experimentally, and some arguments are discussed indicating that our treatment in this region should be applied with great caution. Systematic experimental investigations in this field and temperature range appear highly desirable (see Sec. II B).

(iv) From the applications of the general ideas to random-walk diffusion (Sec. V) it is concluded that the mathematical form of the "lattice" correlation functions presented recently for random-walk<sup>15</sup> and for point-defect mechanisms of self-diffusion<sup>2</sup> (consisting of an exponential part multiplied by a power series in  $t/\tau_c$ ) is crucial for their applicability to the correlation function approach in the strong-collision region (see Sec. V B).

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