

## Relaxation of Longitudinal and Transverse Components of Nuclear Magnetization in Liquids

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In the limit of molecular rotation sufficiently rapid to give a "white spectrum" to the dipole interaction, it is shown that the longitudinal and transverse components of nuclear magnetization relax in an identical manner for a system of an arbitrary number of identical nuclei with arbitrary spin, provided Boltzmann-like initial conditions are assumed. This gives generalization to the specific result obtained by Hubbard for four equivalently located spin  $\frac{1}{2}$  nuclei as well as to the familiar  $T_1 = T_2$  for two identical spins. The Hamiltonian studied consists of Zeeman and dipole-dipole terms. If chemical shifts or scalar spin-spin interactions are included, the results remain valid for equivalent spins but cannot be applied to nonequivalent spins. As an example, Hubbard's three-spin calculation is repeated to include the transverse component, and it is illustrated that if other than Boltzmann-like initial conditions are used, the components need not relax identically.

### I. INTRODUCTION

A WELL-KNOWN feature of the theory of nuclear magnetic relaxation in liquids consisting of identical nuclei interacting through their dipole moments may be summarized as follows: For a system of two spin- $\frac{1}{2}$  nuclei, both the longitudinal (direction of the dc magnetic field along which the spins are aligned in equilibrium) and the transverse components of magnetization return to equilibrium via simple exponential decay, the longitudinal component decaying with time constant  $T_1$  and the transverse component with time constant  $T_2$ ,<sup>1-3</sup> i.e., the Bloch equations<sup>4</sup> have precise validity. If all molecular movements are rapid as compared with the precessional motion of the spins, then one finds the fundamental result  $T_1 = T_2$ .

When the system is enlarged to contain more than two spins or the nuclear spin allowed to be greater than  $\frac{1}{2}$ , the relaxation is no longer describable in such simple terms. However, we are able to show in the present paper that in the limit of a "white spectrum," and under certain other conditions, the longitudinal and transverse components still relax in an identical manner. If the Hamiltonian consists only of Zeeman and dipole-dipole terms, the treatment is valid for an arbitrary number of identical spins (whose spin need not be restricted to  $\frac{1}{2}$ ) provided that initial conditions of a Boltzmann nature are assumed, i.e., that the magnetization is initially describable in terms of a spin temperature. The results also may be extended to a system of identical spins in equivalent locations if chemical shifts or scalar spin-spin interactions are included, but they cannot be applied to nonequivalent spins in such a case.

This is because our argument requires that all spins in the system have the same resonance frequency as well as the same spin. Since the dipolar Hamiltonian averages to zero at any position within a randomly rotating molecule, this requirement is satisfied for nonequivalent spins interacting only via their dipole moments, but it is not satisfied if scalar perturbations are included.

Considerable generalization may thus be given to the original  $T_1 = T_2$  result of BPP theory and to a more recent calculation by Hubbard<sup>5</sup> in which he shows that the longitudinal and transverse components relax in identical fashion for the case of four identical spin- $\frac{1}{2}$  nuclei equivalently placed on the corners of an equilateral tetrahedron. In the neglect of interactions other than the Zeeman and dipole-dipole ones, equal transverse and longitudinal relaxation occur for liquids whose molecules consist of identical spins, once all motions are sufficiently rapid to give a white spectrum to the dipolar interaction, regardless of the number of spins involved. The fact that large differences between  $T_1$  and  $T_2$  have been observed in complex liquids,<sup>6,7</sup> and that the concept of a distribution of correlation frequencies<sup>6,7</sup> has not been completely successful in resolving these differences, was a motivation for this work.

In Sec. II proof is given of the equality of transverse and longitudinal relaxation when Boltzmann-like initial conditions are imposed. In Sec. III Hubbard's original calculation of the relaxation of the longitudinal component of magnetization in a three-spin molecule<sup>8</sup> is repeated in order to include relaxation of the transverse component as well. This example illustrates that if initial conditions other than those describable by a spin temperature are employed, the longitudinal and transverse components do not, in general, have identical relaxation.

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<sup>3</sup> I. Solomon, Phys. Rev. **99**, 559 (1955).

<sup>4</sup> F. Bloch, Phys. Rev. **70**, 460 (1946).

<sup>5</sup> P. S. Hubbard, Phys. Rev. **128**, 650 (1962).

<sup>6</sup> J. G. Powles and K. Luszczynski, Physica **25**, 455 (1959).

<sup>7</sup> J. G. Powles, Polymer **1**, 219 (1960).

<sup>8</sup> P. S. Hubbard, Phys. Rev. **109**, 1153 (1958).

## II. EQUALITY OF TRANSVERSE AND LONGITUDINAL RELAXATION

### A. Formal Preliminaries

Abragam<sup>9</sup> has intimated the fundamental reason why  $T_1 = T_2$  in the two-identical-spin case, and the approach here will be to give a perhaps more detailed statement of the reasoning and to extend it to a number of identical spins. The point of departure is the semi-classical theory of relaxation as developed by Redfield<sup>10</sup> in which the spin variables are treated quantum mechanically and the lattice coordinates classically. This is the same technique used in previous calculations<sup>8</sup> and is described in detail by Abragam.<sup>9</sup>

Following Abragam's notation as closely as possible, we therefore write the Hamiltonian of the spin system as

$$\mathcal{H} = \hbar\mathcal{H}_0 + \hbar\mathcal{H}_1, \quad (1)$$

where  $\hbar\mathcal{H}_0$  is the Zeeman Hamiltonian and  $\hbar\mathcal{H}_1$  is the relaxation-inducing perturbation. The state of the spin system is characterized by the time-dependent density matrix,  $\sigma(t)$ , and thus the expectation value of any operator,  $Q$ , acting on the spin variables is given by

$$\langle Q \rangle = \text{tr}[\sigma Q]. \quad (2)$$

Development of the density matrix with time is conveniently described by the interaction representation — or, equivalently, the rotating frame. If  $Q$  is any operator, including the density operator, then its value in the interaction representation,  $Q^*$ , is given by

$$Q^* = \exp(i\mathcal{H}_0 t) Q \exp(-i\mathcal{H}_0 t). \quad (3)$$

Time-dependent perturbation theory then yields as the equation of motion for the interaction — representation density matrix,  $\sigma^*$ ,

$$\frac{d\sigma^*}{dt} = -\tau_c \langle [\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t), \sigma^*]] \rangle_{\text{av}}, \quad (4)$$

under the following conditions and assumptions:

(1) The random motions of the lattice coordinates are all sufficiently rapid that the correlation function of  $\mathcal{H}_1^*(t)$  reduces to

$$\langle \mathcal{H}_1^*(t) \mathcal{H}_1^*(t-\tau) \rangle_{\text{av}} = 2\tau_c \langle \mathcal{H}_1^*(t) \mathcal{H}_1^*(t) \rangle_{\text{av}} \delta(\tau), \quad (5)$$

or, in other words,  $\mathcal{H}_1^*(t)$  has a "white spectrum." Here, as in Eq. (4), the averaging is done over the classical lattice variables. The above equation also serves as a definition of  $\tau_c$  as used in Eq. (4).

(2) The perturbation,  $\mathcal{H}_1(t)$ , is a random function of time so that any terms of the form  $\langle \mathcal{H}_{1\mu\nu}(t) \mathcal{H}_{1\mu'\nu'}(t) \rangle_{\text{av}}$  are independent of time; and it is also assumed that  $\langle \mathcal{H}_1(t) \rangle_{\text{av}} = 0$ . The quantity  $\bar{\sigma}^*$  in (4) is the difference between  $\sigma^*$  and its time-independent thermal equilibrium value,  $\sigma_T^*$ ,

$$\bar{\sigma}^* \equiv \sigma^* - \sigma_T^*. \quad (6)$$

It also should be understood that  $\sigma^*$  used in (4) is an average density operator since averaging over the lattice coordinates is assumed throughout. Detailed discussion of the derivation of (4) may be found in Abragam's text.<sup>9</sup>

### B. Symmetry of Equations

By multiplying both sides of (4) by  $Q$ , taking the trace, and noting its invariance properties and that  $\sigma^*$  may be averaged independently,<sup>9</sup> we have

$$\frac{d}{dt} \langle Q \rangle^* = -\tau_c \text{tr} \langle [\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t), Q]] \rangle_{\text{av}} \bar{\sigma}^* \quad (7a)$$

$$= -\tau_c \langle [\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t), Q]] \rangle_{\text{av}}^*, \quad (7b)$$

where  $\langle Q \rangle^*$  is the expectation value of a spin operator,  $Q$ , in the interaction representation. Relaxation of the longitudinal and transverse components of magnetization is obtained by using, respectively,  $I_z$  and  $I_x$ , the total  $z$  and  $x$  components of spin, for  $Q$ . The fundamental argument for the equality of transverse and longitudinal relaxation is based upon showing that, for identical spins,  $\mathcal{H}_1^*(t)$  may be replaced by  $\mathcal{H}_1(t)$  in (4) and (7) as a result of performing the ensemble averages. Hence, assuming the perturbation  $\mathcal{H}_1(t)$  to be symmetric in the coordinates  $x$ ,  $y$ , and  $z$ , i.e., independent of the choice of axis of quantization, if performing the operation in (7) with  $Q = I_x$  yields a single exponential decay with time constant  $T_1$ , then the symmetry of the problem demands that one also obtain a single exponential decay with time constant  $T_2 = T_1$  when  $Q$  is taken to be  $I_x$ .

If  $\mathcal{H}_1(t)$  is symmetric in  $x$ ,  $y$ , and  $z$ , then the definition (3) shows that  $\mathcal{H}_1^*(t)$  itself will not be symmetric in the coordinates since, for the customary dc magnetic field,  $H_0$ , applied in the  $z$  direction, we have

$$\mathcal{H}_0 = -\gamma I_z H_0, \quad (8)$$

where  $\gamma$  is the gyromagnetic ratio. We thus must show that ensemble averaging does permit the replacement of  $\mathcal{H}_1^*(t)$  by  $\mathcal{H}_1(t)$  in (4) and (7). To do this it is convenient to re-express (4) in matrix representation by

$$\frac{d}{dt} \sigma_{\alpha\alpha'}^* = \sum_{\beta\beta'} R_{\alpha\alpha',\beta\beta'}^* \sigma_{\beta\beta'}^*, \quad (9)$$

in which the Greek indices represent states of the unperturbed Hamiltonian (8). We then require that

$$R_{\alpha\alpha',\beta\beta'}^* = R_{\alpha\alpha',\beta\beta'}. \quad (10)$$

From the nature of (4) it is evident that  $R_{\alpha\alpha',\beta\beta'}^*$  consists of a combination of products of matrix elements in the form

$$\langle \mathcal{H}_{1\mu\nu}^*(t) \mathcal{H}_{1\mu'\nu'}^*(t) \rangle_{\text{av}}.$$

<sup>9</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. VIII.

<sup>10</sup> A. G. Redfield, IBM J. Res. Develop. 1, No. 1 (1957).

Hence the task reduces to demonstrating that

$$\langle \mathcal{H} \mathcal{C}_{1\mu\nu}^*(t) \mathcal{H} \mathcal{C}_{1\mu'\nu'}^*(t) \rangle_{\text{av}} = \langle \mathcal{H} \mathcal{C}_{1\mu\nu}(t) \mathcal{H} \mathcal{C}_{1\mu'\nu'}(t) \rangle_{\text{av}}. \quad (11)$$

The perturbation is now written explicitly as the mutual dipole-dipole interaction,

$$\mathcal{H} \mathcal{H} \mathcal{C}_1(t) = \sum_{j < k} \left[ \frac{\hbar^2 \gamma^2}{r_{jk}^3} \mathbf{I}_j \cdot \mathbf{I}_k - 3 \frac{(\mathbf{I}_j \cdot \mathbf{r}_{jk})(\mathbf{I}_k \cdot \mathbf{r}_{jk})}{r_{jk}^5} \right], \quad (12)$$

where the orientation of  $\mathbf{r}_{jk}$ , the vector connecting spins  $\mathbf{I}_j$  and  $\mathbf{I}_k$ , with respect to any fixed set of axes is assumed to be a random function of time. Symmetry of the perturbation is apparent from the form (12); however, as is common in relaxation calculations, it is useful to re-express (12) as

$$\mathcal{H} \mathcal{H} \mathcal{C}_1(t) = \sum_{j < k} \sum_{q=-2}^2 F_{jk}^{(q)}(t) A_{jk}^{(q)}, \quad (13)$$

where the  $F_{jk}^{(q)}(t)$  are lattice functions,

$$F_{jk}^{(0)} = r_{jk}^{-3} (1 - 3 \cos^2 \theta_{jk}), \quad (14a)$$

$$F_{jk}^{(1)} = r_{jk}^{-3} \sin \theta_{jk} \cos \theta_{jk} e^{-i\varphi_{jk}}, \quad (14b)$$

$$F_{jk}^{(2)} = r_{jk}^{-3} \sin^2 \theta_{jk} e^{-2i\varphi_{jk}}, \quad (14c)$$

where  $\theta_{jk}$  and  $\varphi_{jk}$  are the, respective, polar and azimuthal angles of  $\mathbf{r}_{jk}$  with respect to the  $x$ - $y$ - $z$  laboratory axes, and  $F_{jk}^{(-q)}$  is the complex conjugate of  $F_{jk}^{(q)}$ . The quantities  $A_{jk}^{(q)}$  are spin operators:

$$A_{jk}^{(0)} = \gamma^2 \hbar [I_{jz} I_{kz} - \frac{1}{4} (I_{j+} I_{k-} + I_{j-} I_{k+})], \quad (15a)$$

$$A_{jk}^{(1)} = -\frac{3}{2} \gamma^2 \hbar (I_{jz} I_{k+} + I_{j+} I_{kz}), \quad (15b)$$

$$A_{jk}^{(2)} = -\frac{3}{4} \gamma^2 \hbar I_{j+} I_{k+}, \quad (15c)$$

where

$$I_{j\pm} = I_{jx} \pm i I_{jy} \quad (16)$$

and  $A_{jk}^{(-q)}$  is the Hermitian conjugate of  $A_{jk}^{(q)}$ .

Consider a representation in which  $I_z = \sum_j I_{jz}$ , and consequently  $\mathcal{H} \mathcal{C}_0$ , Eq. (8), is diagonal. For a number of identical spins, the energy levels of the unperturbed system (8) are highly degenerate and may be labeled by the magnetic quantum number,  $m$ , of the total  $z$  component of spin,  $I_z$ . It follows from the well-known properties of the raising and lowering operators,  $I_{j+}$  and  $I_{j-}$ , respectively, that, in such a representation, the spin operator  $A_{jk}^{(q)}$  as defined in (15) has nonzero matrix elements only between states for which  $\Delta m = q$ . Then, since the eigenvalues are equally spaced with separation  $\hbar\omega$  between adjacent levels, we see from (3) that matrix elements of  $A_{jk}^{(q)}$  in the interaction representation are given by

$$A_{jk}^{(q)}{}_{\mu\nu}^* = A_{jk}^{(q)}{}_{\mu\nu} e^{-q\omega t}, \quad (17)$$

for a set of states in which  $\mathcal{H} \mathcal{C}_0$  is diagonal and where  $\omega = \gamma H_0$ .

For the ensemble average  $\langle \mathcal{H} \mathcal{C}_{1\mu\nu}^*(t) \mathcal{H} \mathcal{C}_{1\mu'\nu'}^*(t) \rangle_{\text{av}}$  we

have, from (13) and (17),

$$\langle \mathcal{H} \mathcal{C}_{1\mu\nu}^*(t) \mathcal{H} \mathcal{C}_{1\mu'\nu'}^*(t) \rangle_{\text{av}} = \sum_{i,j,k,l} \sum_{q,q'} [\langle F_{ij}^{(q)}(t) F_{kl}^{(q')}(t) \rangle_{\text{av}} \times A_{ij\mu\nu}^{(q)} A_{kl\mu'\nu'}^{(q')} e^{-i(q+q')\omega t}]. \quad (18)$$

By the definitions (14) of  $F_{ij}^{(q)}(t)$ , it is evident that

$$\langle F_{ij}^{(q)}(t) F_{ij}^{(q')}(t) \rangle_{\text{av}} = \langle |F_{ij}^{(q)}(t)|^2 \rangle_{\text{av}} \delta_{q,-q'},$$

from the orthogonality properties of spherical harmonics. Furthermore, even if the motion of  $\mathbf{r}_{ij}$  may be correlated to that of  $\mathbf{r}_{kl} \neq \mathbf{r}_{ij}$ , as is the case for a rigid molecule containing a number of spins, so that terms of the form  $\langle F_{ij}^{(q)}(t) F_{kl}^{(q')}(t) \rangle_{\text{av}}$  are not automatically zero, one may still show from an Euler-angle description of the isotropic rotation of a solid<sup>8</sup> that

$$\langle F_{ij}^{(q)}(t) F_{kl}^{(q')}(t) \rangle_{\text{av}} = \langle F_{ij}^{(q)}(t) F_{kl}^{(-q)}(t) \rangle_{\text{av}} \delta_{q,-q'}. \quad (19)$$

Since the averaging process thus restricts one to  $q+q'=0$ , the exponential time factor disappears from (18) and the expression (18) is the same in the interaction representation (rotating frame) as in the  $x$ - $y$ - $z$  laboratory system. Hence, the validity of (10) and equivalently the replacement of  $\mathcal{H} \mathcal{C}_1^*(t)$  by  $\mathcal{H} \mathcal{C}_1(t)$  in (4) and (7) is established for a rigid molecule with an arbitrary number of spins—as well as, of course, for a system in which some of the motions are uncorrelated.

It may be remarked that replacement of  $\mathcal{H} \mathcal{C}_1^*(t)$  by  $\mathcal{H} \mathcal{C}_1(t)$  in the pertinent equations means that these equations are automatically secularized as a result of ensemble averaging, i.e., all exponential time factors are already eliminated [(18) and (19)], and it is superfluous to state—for identical spins—that only secular terms should be retained in the equation of motion for  $\sigma^*$ . For nonidentical spins the longitudinal and transverse relaxation are not identical,<sup>8,9</sup> and the reason for this is readily seen from the above. Although (19) is still valid, the relation (17) no longer holds since, for example, in a system containing two spins, 1 and 2, with respective resonance frequencies  $\omega_1$ , and  $\omega_2$ , a transition in which spin 1 increases its magnetic quantum number by one unit and spin 2 decreases its magnetic quantum number by one unit has  $\Delta m = 0$  but a difference in energy between initial and final states of  $\hbar(\omega_2 - \omega_1)$ . Thus,  $A_{ij\mu\nu}^{(0)*} \neq A_{ij\mu\nu}^{(0)}$  for such a transition, and the spatial averaging is not sufficient to preserve the symmetry in  $x$ ,  $y$ , and  $z$  since the asymmetric  $\mathcal{H} \mathcal{C}_1^*(t)$  is not replaceable by the symmetric  $\mathcal{H} \mathcal{C}_1(t)$ . Or, in other words, for nonidentical spins spatial averaging does not completely secularize the equation of motion.

Similarly, if the spins of a given molecule are identical but in nonequivalent positions, they will not have equal resonance frequencies once chemical shifts or scalar spin-spin couplings are included in the Hamiltonian. Thus, if these interactions are important, the replacement of  $\mathcal{H} \mathcal{C}_1^*(t)$  by  $\mathcal{H} \mathcal{C}_1(t)$  will be rigorously correct only if the spins are equivalent as well as identical.<sup>11</sup>

<sup>11</sup> The author is indebted to P. S. Hubbard for pointing this out.

As pointed out by Abragam and mentioned at the beginning of this section, replacement of  $\mathcal{I}_1^*(t)$  by  $\mathcal{I}_1(t)$  is sufficient to guarantee equal relaxation for  $\langle I_z \rangle$  and  $\langle I_x \rangle^*$  for the two-spin case in which the Bloch equations are valid. If several spins are involved, the decay of  $\langle I_z \rangle$  or  $\langle I_x \rangle^*$  contains a number of exponentials, however. In such a case, one can argue from the  $x, y, z$  symmetry of  $\mathcal{I}_1(t)$  that any characteristic root of the equation for  $\langle I_z \rangle$  must also serve for  $\langle I_x \rangle^*$  and vice versa. That is, if one writes as the solution to (7)

$$\langle I_z \rangle - I_0 = \sum_j a_{jz} e^{-t/T_{jz}},$$

where  $I_0$  is the thermal equilibrium value of  $\langle I_z \rangle$ , then he can equally well write

$$\langle I_x \rangle^* = \sum_j a_{jx} e^{-t/T_{jx}},$$

with  $T_{jz} = T_{jx}$ . Determination of the coefficients  $a_{jz}$  and  $a_{jx}$ , however, depends upon initial conditions; so replacement of  $\mathcal{I}_1^*(t)$  by  $\mathcal{I}_1(t)$  does not by itself make it obvious that  $\langle I_x \rangle^*$  and  $\langle I_z \rangle$  relax identically, i.e., that the exponentials combine in the same manner.

### C. Initial Conditions

Thermal equilibrium at a temperature  $T$  is described by the density matrix

$$\sigma_T = \exp(-\mathcal{H}/kT) / \text{tr}[\exp(-\mathcal{H}/kT)]. \quad (20)$$

For the present case of a spin system aligned along a dc magnetic field,  $H_0$ , in the  $z$  direction and  $kT \gg \hbar\mathcal{H}_0 \gg \hbar\mathcal{I}_1$ , we have

$$\sigma_T = \sigma_T^* = C(1 + \mathcal{M}_z), \quad (21)$$

where, from (8) and (20),

$$\lambda = \gamma \hbar H_0 / kT \quad (22)$$

and  $C^{-1} = \text{tr}[1]$ , the dimensions of the density matrix. Previous to time  $t=0$  this equilibrium distribution is rotated through a certain angle by suitable application of rf pulses; and at  $t=0$  the rf fields are removed, with the magnetization now aligned along an axis  $\zeta$ . Hence, the initial conditions are assumed to be described by the density matrix,<sup>12</sup>  $\sigma_0 = \sigma(t=0)$ ,

$$\sigma_0 = \sigma_0^* = C(1 + \lambda_s \mathcal{I}_\zeta), \quad (23)$$

where, for the sake of generality,  $\lambda_s$  may or may not be equal to  $\lambda$ . Initial conditions are thus said to be "Boltzmann-like" in the sense that a Boltzmann distribution is assumed for alignment about an arbitrary axis,  $\zeta$ .

Taking  $\alpha_x, \alpha_y$ , and  $\alpha_z$  as the respective direction cosines of the  $\zeta$  axis with  $x$ - $y$ - $z$  axes then gives for  $\tilde{\sigma}_0 = \tilde{\sigma}(t=0)$ ,

$$\tilde{\sigma}_0 = \tilde{\sigma}_0^* = C\lambda_s(\alpha_x \mathcal{I}_x + \alpha_y \mathcal{I}_y) - C(\lambda - \lambda_s \alpha_z) \mathcal{I}_z, \quad (24)$$

<sup>12</sup> For a more rigorous treatment of initial conditions see, for example, A. Sher and H. Primakoff, Phys. Rev. **119**, 178 (1960), where it is shown that for application of a 90° pulse in the  $y$  direction, the initial condition is given by (23) with  $\xi = x$ .

from (6), (21), and (23). Consider now  $(d/dt)\langle I_z \rangle$  at  $t=0$ . This is obtained from (7a) by using  $I_z$  for  $Q$  and replacing  $\tilde{\sigma}^*$  by  $\tilde{\sigma}_0$ . We first note that

$$\text{tr}[\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_x]] I_z \rangle_{\text{av}}] = 0 \quad (25)$$

as a result of the spatial averaging. This is because, by the same reasoning (19) used to replace  $\mathcal{I}_1^*(t)$  by  $\mathcal{I}_1(t)$  in (4), products of energy-representation matrix elements in the form  $\langle \mathcal{I}_{1\mu\nu}(t) \mathcal{I}_{1\mu'\nu'}(t) \rangle_{\text{av}}$  are nonzero only if  $\omega_{\mu\nu} = \omega_{\nu'\mu'}$ , where  $\omega_{\mu\nu} = \omega(m_\mu - m_\nu)$  with  $m_\mu$  and  $m_\nu$  the respective magnetic quantum numbers of the states  $\mu$  and  $\nu$ . But since  $I_z$  has matrix elements only between states for which  $\Delta m = 0$  and  $I_x$  has matrix elements only for  $\Delta m = \pm 1$  transitions, it follows that  $\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_x]] I_z \rangle_{\text{av}}$  can have no diagonal elements in this particular representation and is therefore traceless in any representation. Thus, the time derivative of  $\langle I_z \rangle$  at  $t=0$  is given by

$$\left( \frac{d}{dt} \langle I_z \rangle \right)_{t=0} = -\tau_c \frac{(\langle I_z \rangle_{t=0} - I_0)}{\text{tr}[I_z^2]} \times \text{tr}[\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_x]] I_z \rangle_{\text{av}}], \quad (26)$$

where (24) has been used in (2) to obtain  $\langle I_z \rangle_{t=0} - I_0$ .

For the transverse components it is somewhat simpler to calculate  $\langle I_\pm \rangle^* = \langle I_x \pm iI_y \rangle^*$  than  $\langle I_x \rangle^*$  itself. Proceeding in an identical manner, one can show that

$$\left( \frac{d}{dt} \langle I_+ \rangle^* \right)_{t=0} = \frac{-\tau_c \langle I_+ \rangle_{t=0}^*}{\text{tr}[I_x^2]} \times \text{tr}[\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_x]] I_x \rangle_{\text{av}}]. \quad (27)$$

The argument leading to (27) is the same as that used to deduce (26): Spatial averaging eliminates all diagonal elements of  $\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_\pm]] I_\pm \rangle_{\text{av}}$  as well as of  $\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_x]] I_x \rangle_{\text{av}}$ . We are thus left with an expression of the form

$$\text{tr}[\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_+]] I_- \rangle_{\text{av}}],$$

and invariance properties of the trace are used to show that

$$\begin{aligned} \text{tr}[\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_+]] I_- \rangle_{\text{av}}] \\ = 2 \text{tr}[\langle [\mathcal{I}_1(t), [\mathcal{I}_1(t), I_x]] I_x \rangle_{\text{av}}]. \end{aligned}$$

From (26) and (27) it, thus, follows that if  $\mathcal{I}_1(t)$  is symmetric in  $x, y$ , and  $z$ , then

$$\begin{aligned} \left( \frac{d}{dt} \langle I_+ \rangle^* \right)_{t=0} / \langle I_+ \rangle_{t=0}^* \\ = \left( \frac{d}{dt} \langle I_z \rangle \right)_{t=0} / (\langle I_z \rangle_{t=0} - I_0). \quad (28) \end{aligned}$$

Higher order derivatives may also be evaluated at  $t=0$  and similar reasoning employed to show that, for any order,

$$\left(\frac{d^n}{dt^n}\langle I_+ \rangle^*\right)_{t=0} / \langle I_+ \rangle^*_{t=0} = \left(\frac{d^n}{dt^n}\langle I_z \rangle\right)_{t=0} / (\langle I_z \rangle_{t=0} - I_0). \quad (29)$$

The procedure is to take successive derivatives of (4) with respect to  $t$ , perform the required trace operations, and note that, because of ensemble averaging, when calculating the relaxation of  $\langle I_z \rangle$  only the term in  $I_z$  need be included in the expression for  $\bar{\sigma}_0$  (24), and that a similar rule applies for relaxation of the transverse component. Assuming Taylor series expansions for  $\langle I_z \rangle$  and  $\langle I_+ \rangle^*$  we therefore conclude that

$$\frac{\langle I_z \rangle - I_0}{\langle I_z \rangle_{t=0} - I_0} = \frac{\langle I_+ \rangle^*}{\langle I_+ \rangle^*_{t=0}}, \quad (30)$$

so that the longitudinal and transverse components relax in a completely identical manner.

#### D. Summary

A system containing an arbitrary number of identical spins coupled by their dipole interactions has been shown to possess equal transverse and longitudinal relaxation in the limit of a "white spectrum" for the molecular motion. The basic reason is that the averaging necessitated by the random character of the lattice functions limits the number of nonzero matrix elements to the point that, for the relaxation part of the problem, the perturbation,  $\hbar\mathcal{H}_1(t)$ , has the same appearance in the rotating frame as it does in the laboratory frame—provided the spins are identical and chemical shifts or scalar spin-spin interactions may be neglected—and is, thus, symmetric in  $x$ ,  $y$ , and  $z$  in the rotating frame as well as in the laboratory frame. This enables one to say that any exponential characterizing relaxation of the  $z$  component must also characterize relaxation of the  $x$  component. If initial conditions describable by a Boltzmann distribution of spins aligned along an arbitrary axis (such as obtained by a rotation of the thermal equilibrium magnetization into the  $x$ - $y$  plane by a  $90^\circ$  pulse) are assumed, the stronger statement is then made that the exponentials combine in the same manner so that the longitudinal and transverse components relax in identical fashion. Although only the dipole-dipole interaction has been explicitly treated, it is evident that any perturbation symmetric in  $x$ ,  $y$ , and  $z$  which possesses the orthogonality relations necessary to replace  $\mathcal{H}_1^*(t)$  by  $\mathcal{H}_1(t)$  in (4) satisfies the requirements for equal transverse and longitudinal relaxation.

### III. EXAMPLE: THREE SPIN- $\frac{1}{2}$ NUCLEI ON VERTICES OF EQUILATERAL TRIANGLE

By way of example and as illustration of the fact that arbitrary initial conditions do *not* produce equal relaxation of the transverse and longitudinal components, we treat the case of a rigid molecule consisting of three spin- $\frac{1}{2}$  nuclei located on the vertices of an equilateral triangle. Hubbard<sup>8</sup> has already discussed this problem and solved for the decay of the  $z$  component, and he has also shown the equality of longitudinal and transverse relaxation for four equivalent spin- $\frac{1}{2}$  nuclei.<sup>5</sup> It is, however, instructive to extend his earlier work, which employs simpler notation than that used in Ref. 5, to include  $x$ - $y$  components as well. He introduces a representation defined by the states

$$\begin{aligned} |1\rangle &= |+++ \rangle, & |5\rangle &= |+- - \rangle, \\ |2\rangle &= |-++ \rangle, & |6\rangle &= |-- - \rangle, \\ |3\rangle &= |+- + \rangle, & |7\rangle &= |-- + \rangle, \\ |4\rangle &= |++ - \rangle, & |8\rangle &= |--- \rangle, \end{aligned} \quad (31)$$

in an obvious notation in which the  $z$  component of an individual spin is diagonal and has eigenvalue  $\pm\frac{1}{2}$ . According to (2) and (6), we have

$$\langle I_z \rangle - I_0 = \frac{1}{2}(3x + y) \quad (32)$$

and

$$\langle I_+ \rangle^* = u + v, \quad (33)$$

with

$$x \equiv \bar{\sigma}_{11} - \bar{\sigma}_{88}, \quad (34a)$$

$$y \equiv \bar{\sigma}_{22} + \bar{\sigma}_{33} + \bar{\sigma}_{44} - \bar{\sigma}_{55} - \bar{\sigma}_{66} - \bar{\sigma}_{77}, \quad (34b)$$

$$u \equiv \bar{\sigma}_{12}^* + \bar{\sigma}_{13}^* + \bar{\sigma}_{14}^* + \bar{\sigma}_{58}^* + \bar{\sigma}_{68}^* + \bar{\sigma}_{78}^*, \quad (35a)$$

$$v \equiv \bar{\sigma}_{26}^* + \bar{\sigma}_{27}^* + \bar{\sigma}_{35}^* + \bar{\sigma}_{37}^* + \bar{\sigma}_{45}^* + \bar{\sigma}_{46}^*. \quad (35b)$$

Since it is necessary to solve a set of simultaneous equations indicated by (9), additional matrix elements in the combinations

$$z \equiv \text{Re}(\bar{\sigma}_{23} + \bar{\sigma}_{24} + \bar{\sigma}_{34} - \bar{\sigma}_{56} - \bar{\sigma}_{57} - \bar{\sigma}_{67}) \quad (36a)$$

and

$$w \equiv \bar{\sigma}_{25}^* + \bar{\sigma}_{36}^* + \bar{\sigma}_{47}^* \quad (36b)$$

are also needed for the computation of  $\langle I_z \rangle$  and  $\langle I_+ \rangle^*$ , respectively.

The equal distances among the spins do, however, present a high degree of symmetry so that three independent equations are sufficient to describe the relaxation. Hubbard found that the equations for the longi-

tudinal component could be written as<sup>18</sup>

$$\left(\frac{20}{9}T_0\frac{d}{dt}+\frac{23}{4}\right)x+\frac{3}{4}y-\frac{3}{4}z=0, \quad (37a)$$

$$\frac{9}{4}x+\left(\frac{20}{9}T_0\frac{d}{dt}+\frac{59}{12}\right)y+\frac{19}{12}z=0, \quad (37b)$$

$$-\frac{9}{8}x+\frac{19}{24}y+\left(\frac{20}{9}T_0\frac{d}{dt}+\frac{55}{12}\right)z=0, \quad (37c)$$

with

$$T_0^{-1}\equiv\gamma^4\hbar^2r_0^{-6}\tau_c,$$

where  $r_0$  is the distance between any two spins. Similarly, we have arrived at the following set for the transverse components:

$$\left(\frac{20}{9}T_0\frac{d}{dt}+\frac{23}{4}\right)u+\frac{3}{4}v-\frac{3}{2}w=0, \quad (38a)$$

$$\frac{3}{4}u+\left(\frac{20}{9}T_0\frac{d}{dt}+\frac{73}{12}\right)v+\frac{5}{6}w=0, \quad (38b)$$

$$-\frac{3}{4}u+\frac{5}{12}v+\left(\frac{20}{9}T_0\frac{d}{dt}+\frac{41}{12}\right)w=0. \quad (38c)$$

Equations (37) and (38) are solvable in terms of decaying exponentials with time constants given by

$$T_a^{-1}=(207/80)T_0^{-1}, \quad (39a)$$

$$T_b^{-1}=(9/80)[19-(61)^{1/2}]T_0^{-1}, \quad (39b)$$

$$T_c^{-1}=(9/80)[19+(61)^{1/2}]T_0^{-1}, \quad (39c)$$

the same characteristic roots serving for either set of equations, as is to be expected from the general arguments of Sec. II.

Only  $T_b$  and  $T_c$  contribute to the decay of the components of magnetization; and one can show that for arbitrary initial conditions,

$$x(t=0)\equiv x_0, \quad y(t=0)\equiv y_0, \quad z(t=0)\equiv z_0,$$

with similar definitions for  $u_0$ ,  $v_0$ , and  $w_0$ , the longitudinal

and transverse components may be expressed by

$$\begin{aligned} \frac{\langle I_z \rangle - I_0}{\langle I_z \rangle_{t=0} - I_0} &= \frac{1}{2} \left[ 1 - \frac{(61)^{1/2}}{183} \left( 21 + \frac{8y_0 - (14/3)z_0}{3x_0 + y_0} \right) \right] e^{-t/T_b} \\ &+ \frac{1}{2} \left[ 1 + \frac{(61)^{1/2}}{183} \left( 21 + \frac{8y_0 - (14/3)z_0}{3x_0 + y_0} \right) \right] e^{-t/T_c}, \quad (40) \end{aligned}$$

$$\begin{aligned} \frac{\langle I_+ \rangle^*}{\langle I_+ \rangle_{t=0}^*} &= \frac{1}{2} \left[ 1 - \frac{(61)^{1/2}}{183} \left( 21 + \frac{4v_0 - 8w_0}{u_0 + v_0} \right) \right] e^{-t/T_b} \\ &+ \frac{1}{2} \left[ 1 + \frac{(61)^{1/2}}{183} \left( 21 + \frac{4v_0 - 8w_0}{u_0 + v_0} \right) \right] e^{-t/T_c}, \quad (41) \end{aligned}$$

where, by (32) and (33),

$$\frac{3x_0 + y_0}{2} = \langle I_z \rangle_{t=0} - I_0,$$

$$u_0 + v_0 = \langle I_+ \rangle_{t=0}^*.$$

We see that for arbitrary initial conditions the exponentials do not necessarily combine in the same manner for  $\langle I_+ \rangle^*$  and for  $\langle I_z \rangle$ . However, it is readily established that Boltzmann-like initial conditions (24) imply  $x_0 = y_0$ ,  $z_0 = 0$  and  $u_0 = v_0$ ,  $w_0 = 0$ ; and under these circumstances, identical relaxation results, as predicted, with

$$\begin{aligned} \frac{\langle I_z \rangle - I_0}{\langle I_z \rangle_{t=0} - I_0} &= \frac{\langle I_+ \rangle^*}{\langle I_+ \rangle_{t=0}^*} = \frac{1}{2} \left[ 1 - \frac{23}{183} (61)^{1/2} \right] e^{-t/T_b} \\ &+ \frac{1}{2} \left[ 1 + \frac{23}{183} (61)^{1/2} \right] e^{-t/T_c}, \quad (42) \end{aligned}$$

as found by Hubbard for the longitudinal component and in which the coefficient of  $e^{-t/T_b}$  is somewhat less than 1% of the coefficient of  $e^{-t/T_c}$ .

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<sup>18</sup> The coefficient of  $y$  in (37c) is erroneously typewritten as 19/12 in Ref. 8.