

Spin Relaxation Processes in a Two-Proton System*

N. BLOEMBERGEN

Cruft Laboratory, Harvard University, Cambridge, Massachusetts

(Received September 11, 1956)

The general theory of nuclear spin relaxation, based on the Boltzmann transport equation for the density matrix, is applied to the very simple, nontrivial system of two identical spins $I = \frac{1}{2}$. A proton pair undergoing hindered rotation around one axis shows a resolvable doublet. The relaxation processes in this doublet are investigated. Explicit formulas for the longitudinal and transverse relaxation times are derived, which display a dependence on the angles of the axis of rotation with the external magnetic field and the radius vector. Experimental evidence for this dependence is discussed. General expressions for the Overhauser and saturation effects with two applied radio-frequency fields are given, which may also be applied to a magnetic ion or nucleus with $I = 1$ and crystalline field splitting.

I. INTRODUCTION

PAKE¹ has shown that a static pair of protons gives rise to a resonance doublet. Gutowski and Pake² extended the theory to the case of a proton pair rotating rapidly about an arbitrary axis. Again a doublet results, but with a different splitting. The theory for a static or rotating proton triangle was developed by Andrew and Bersohn.³ Numerous experimental investigations of the magnetic resonance of proton pairs, triangles, and tetrahedra have subsequently been made.⁴

The spin-lattice relaxation in these structures has, however, received little attention. Solomon^{5,6} has discussed the relaxation for a pair of nonidentical spins which undergo completely random motions and have no resolved fine structure. In this paper the relaxation effects in a doublet are discussed, when motion around only one axis is present. Two identical spins $I = \frac{1}{2}$, with dipolar interaction and a restricted motion, constitute perhaps the simplest nontrivial system, to which the general theories of nuclear spin dynamics may be applied. These have recently been formulated by various authors,⁷⁻⁹ and are based on the Boltzmann transport equation for the density matrix, introduced by Bloch.¹⁰ We shall follow a particularly concise formulation due to Redfield.⁹ This exercise in the application of the general theory will show that the experimental study of relaxation of proton pairs, and other groups of nuclear spins, may give additional information on the structure and internal motion in solids.

II. THEORY OF SPIN RELAXATION IN A PROTON PAIR

A pair of protons with dipolar and exchange interaction is embedded in a constant magnetic field H_0 taken in the z direction. The Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_m + \mathcal{H}_{\text{dip}} + \mathcal{H}_{\text{ex}}, \quad (1)$$

$$\mathcal{H}_m = \gamma \hbar (I_1^z + I_2^z) H_0, \quad (2)$$

$$\mathcal{H}_{\text{ex}} = A \mathbf{I}_1 \cdot \mathbf{I}_2, \quad (3)$$

$$\mathcal{H}_{\text{dip}} = \gamma^2 \hbar^2 r_{12}^{-3} \{ \mathbf{I}_1 \cdot \mathbf{I}_2 - 3(\mathbf{I}_1 \cdot \mathbf{r}_{12})(\mathbf{I}_2 \cdot \mathbf{r}_{12}) r_{12}^{-2} \}. \quad (4)$$

Since the Hamiltonian is symmetric in the two spins, the antisymmetric singlet state is a constant of the motion. No transitions to the triplet state can occur. The singlet state has zero magnetic moment and is unobservable in the context of this paper. The dynamical behavior of the three triplet states, denoted by $+$, 0 , $-$, corresponding to a magnetic quantum number $I_1^z + I_2^z = 1, 0$ or -1 , is described by the quantum-mechanical equation of motion for the three-by-three spin density matrix σ :

$$\partial \sigma / \partial t = -i \hbar^{-1} [\mathcal{H}, \sigma]. \quad (5)$$

Since the exchange interaction is a multiple of the unit matrix and commutes with the Hamiltonian (1), it does not affect the motion of the triplet spin system and is henceforth omitted. The dipolar interaction consists of a part which depends explicitly on the time and a time-independent part. The completely random motion in a liquid leads to an averaging-out of the dipolar interaction with a single resonance line, and has been discussed extensively. The case of interest here is a restricted motion of the proton pair around a single axis, which we shall designate the z' axis.

Two resonance lines are distinguishable with this restricted motion. Let the axis of hindered rotation make an angle ψ_0 with the external magnetic field \mathbf{H}_0 . Let the radius vector \mathbf{r}_{12} make a constant angle θ' with the axis of rotation. The variable azimuth is denoted by $\phi'(\iota)$. The dipolar interaction can be expanded into spherical harmonics with respect to the z axis, and these in turn can be transformed to spherical harmonics

* Supported by the Joint Services.

¹ G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948).² H. S. Gutowski and G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950).³ E. R. Andrew and R. Bersohn, *J. Chem. Phys.* **18**, 159 (1950).⁴ See references quoted in H. S. Gutowski, *Ann. Rev. Phys. Chem.* **5**, 333 (1954).⁵ I. Solomon, *Phys. Rev.* **99**, 559 (1955).⁶ I. Solomon and N. Bloembergen, *J. Chem. Phys.* **25**, 261 (1956).⁷ R. Kubo and K. Tomita, *J. Chem. Soc. Japan* **9**, 888 (1954).⁸ F. Bloch, *Phys. Rev.* **102**, 104 (1956).⁹ A. G. Redfield, *I.B.M. Journal* (to be published). The author is indebted to Dr. Redfield for communication of his results before publication.¹⁰ R. K. Wangness and F. Bloch, *Phys. Rev.* **89**, 728 (1953).

in the primed coordinate system. The coefficients in this transformation are the irreducible representations $\mathfrak{D}^{(2)}(0, \psi_0, 0)_{mm'}$ of the group of three-dimensional rotations, described by Wigner.¹¹ With the introduction of the raising and lowering operators $I_{\pm} = I_x \pm I_y$, one can write

$$\mathfrak{H}_{\text{dip}} = +\gamma^2 \hbar^2 r_{12}^{-3} (\mathbf{I}_1 \cdot \mathbf{I}_2 - 3I_1^z I_2^z) P_0^{(2)}(\theta) \quad (6a)$$

$$-\gamma^2 \hbar^2 r_{12}^{-3} (I_1^z I_2^{\pm} + I_1^{\pm} I_2^z) P_{\mp 1}^{(2)}(\theta, \phi) \quad (6b)$$

$$-\frac{1}{4} \gamma^2 \hbar^2 r_{12}^{-3} I_1^{\pm} I_2^{\pm} P_{\mp 2}^{(2)}(\theta, \phi), \quad (6c)$$

with

$$P_m^{(2)}(\theta, \phi) = \sum_{m'=-2}^2 \mathfrak{D}_{mm'}^{(2)}(0, \psi_0, 0) P_{m'}^{(2)}(\theta', \phi'). \quad (7)$$

The $P^{(2)}$ are the unnormalized spherical harmonics

$$\begin{aligned} P_0^{(2)} &= \frac{1}{2} (3 \cos^2 \theta - 1), \\ P_{\pm 1}^{(2)} &= \frac{3}{2} \sin \theta \cos \theta e^{\pm i \phi}, \\ P_{\pm 2}^{(2)} &= 3 \sin^2 \theta e^{\pm 2i \phi}. \end{aligned} \quad (8)$$

In this form all matrix elements in the $(+0-)$ representation can be written down at once, and the time-independent part is clearly separated. It consists of the terms $m'=0$ which do not depend on ϕ' . The time-dependent matrix elements occur in the form

$$\mathfrak{H}_{\alpha\alpha'}(t) = \sum_q K_{\alpha\alpha'}^q H^q(t), \quad (9)$$

which is used in the theories of Bloch and Redfield. The K^q are Hermitian spin operators which do not contain the time explicitly and the $H^q(t)$ depend only on the time-dependent lattice coordinate. The $H^q(t)$ can be chosen as the four real functions $\cos \phi'$, $\sin \phi'$, $2 \cos \phi'$ and $\sin 2\phi'$. With random time variations of ϕ' , introduce the generalized correlation functions and spectral densities of the functions $H^q(t)$ by

$$k_{qq'}(\omega) = \frac{1}{2} \int_{-\infty}^{+\infty} e^{i\omega\tau} \langle H^q(t) H^{*q'}(t-\tau) \rangle d\tau. \quad (10)$$

The correlation function is essentially zero for $\tau \ll \tau_c$, the correlation time. Redfield⁹ has shown that for short correlation times—that is, for

$$\tau_c \hbar^{-1} (E_{\alpha} - E_{\beta}) \ll 1, \quad (11)$$

where $E_{\alpha} - E_{\beta}$ represents the difference between any pair of energy levels of the time-independent Hamiltonian, the equation of motion can be written in the operator form

$$\begin{aligned} \frac{\partial \sigma}{\partial t} &= -i \hbar^{-1} [\mathfrak{H}_0 + \mathfrak{H}_{\text{dip}}^{\text{stat}}, \sigma] \\ &\quad - \sum_{\alpha\alpha'} [K^{\alpha}, [K^{\alpha'}, \sigma - \sigma^{(T)}]] k_{\alpha\alpha'}(0). \end{aligned} \quad (12)$$

Here $\sigma^{(T)}$ is the diagonal spin density matrix corresponding to thermal equilibrium at the lattice temperature T .

$$\sigma_{\alpha\alpha}^{(T)} = \exp(-E_{\alpha}/kT) / \sum_{\alpha} \exp(-E_{\alpha}/kT). \quad (13)$$

Equation (12) gives a complete dynamical description for any magnitude of the external field H_0 , including zero. It contains all interference and nonsecular perturbation effects between the five independent elements of the density matrix, whose trace is normalized to unity. The five independent coupled differential equations, represented by the operator relation Eq. (12), would still be difficult to solve, but the problem is considerably simpler than the complete motion of two nonidentical spins, which is described by nine coupled equations.¹²

Considerable simplification results if nonsecular perturbations are neglected and the time-independent Hamiltonian is diagonal in the representation chosen. The latter situation occurs when the external field is large, $\mathfrak{H}_0 \gg \mathfrak{H}_{\text{dip}}$, and only first-order perturbation theory to the time-independent part of $\mathfrak{H}_{\text{dip}}$ is applied. One obtains the result of Gutowski and Pake²:

$$\begin{aligned} E_+ &= \gamma \hbar H_0 - \frac{1}{4} \gamma^2 \hbar^2 r_{12}^{-3} (3 \cos^2 \psi_0 - 1), \\ E_0 &= +\frac{1}{2} \gamma^2 \hbar^2 r_{12}^{-3} (3 \cos^2 \psi_0 - 1), \\ E_- &= -\gamma \hbar H_0 - \frac{1}{4} \gamma^2 \hbar^2 r_{12}^{-3} (3 \cos^2 \psi_0 - 1). \end{aligned} \quad (14)$$

Redfield⁹ shows that application of second-order perturbation theory with the random time-dependent part leads to the following equation for the density matrix:

$$\begin{aligned} \frac{\partial \sigma_{\alpha\alpha'}}{\partial t} &= -i \hbar (E_{\alpha} - E_{\alpha'}) \sigma_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \sigma_{\beta\beta'} \\ &\quad \times (\alpha, \alpha', \beta, \beta' = +, 0, -). \end{aligned} \quad (15)$$

Only secular perturbations will be retained. The secular elements of the relaxation matrix, which satisfy the condition

$$|E_{\alpha} - E_{\beta} - E_{\alpha'} + E_{\beta'}| R_{\alpha\alpha'\beta\beta'}^{-1} \ll 1 \quad (16)$$

are time-independent constants, given by

$$\begin{aligned} R_{\alpha\alpha'\beta\beta'} &= \sum_{qq'} [\{k_{qq'}(\omega_{\alpha'} - \omega_{\beta'}) + k_{qq'}(\omega_{\alpha} - \omega_{\beta})\} K_{\alpha\beta}^q K_{\alpha'\beta'}^{q'} \\ &\quad - \delta_{\alpha'\beta'} \sum_{\gamma} k_{qq'}(\omega_{\alpha} - \omega_{\gamma}) K_{\gamma\beta}^q K_{\gamma\alpha'}^{q'} \\ &\quad - \delta_{\alpha\beta} \sum_{\gamma} k_{qq'}(\omega_{\gamma} - \omega_{\alpha'}) K_{\beta'\gamma}^q K_{\alpha'\gamma'}^{q'}] \end{aligned} \quad (17)$$

provided the correlation time satisfies the condition

$$R_{\alpha\alpha'\beta\beta'} \tau_c \ll 1. \quad (18)$$

If $R_{\alpha\alpha'\beta\beta'} \tau_c \sim 1$, a transition from time-dependent to time-independent character of the perturbation takes place. This case, which has been discussed extensively in the literature,⁷ will not be pursued here.

¹¹ E. P. Wigner, *Gruppen-theorie* (E. Vieweg, Braunschweig, 1931), Chap. 15.

¹² A. Zahlen and E. P. Gross, *Bull. Am. Phys. Soc. Ser. II*, **1**, 216 (1956).

The nonsecular elements which do not satisfy (16) will be neglected. In general they give rise to very small oscillatory components in the density matrix element. Unless there are partially or completely overlapping resonance lines, the condition (16) is only satisfied for

$$E_\alpha - E_\beta - E_{\alpha'} + E_{\beta'} = 0. \quad (19)$$

This observation is important. It implies that diagonal matrix elements of σ relax independently of the values of the off-diagonal elements. Off-diagonal elements relax independently of the diagonal elements and off-diagonal elements with another frequency. This statement justifies the procedure, generally adopted, to treat longitudinal and transverse relaxation independently. Solomon's treatment⁵ for the relaxation processes in HF is therefore justified, and corresponds exactly to solving Eqs. (15) and (17) for that case.

Here the general theory will be applied to a proton pair. Assume first that the proton pair gives rise to a well-resolved doublet. This is the experimental criterion that the condition of secularity (16) is only satisfied for $E_\alpha - E_{\alpha'} = E_\beta - E_{\beta'}$. Some simplification results in our particular case, if complex functions $H^q(t) = \exp(\pm i\phi')$ and $\exp(\pm 2i\phi')$ are used. Two simple models for the random motion of the ϕ' coordinate will be investigated.

(a) Random jumps between three equilibrium positions ϕ_0' , $\phi_0' \pm 120^\circ$ occur at an average rate of $(3\tau)^{-1}$ transitions per second to either of the two adjacent positions. The correlation functions are in this case

$$\langle H^q(t)H^{*q'}(t+\tau) \rangle = e^{-t/\tau} \delta_{qq'}, \quad (20)$$

and the nonvanishing spectral densities are

$$k_{qq}(\omega) = \tau / (1 + \omega^2 \tau^2). \quad (21)$$

(b) There are a very large number of equilibrium positions and a stochastic diffusion process describes the motion in azimuthal angle. The probability to find the pair at an angle $\phi_0' + \phi'$ at time t , when it was at ϕ_0' for $t=0$, is given by the Gaussian distribution

$$p(\phi', t) = \frac{1}{2(\pi t \tau^{-1})^{1/2}} \exp(-\phi'^2 \tau / 4t) d\phi'. \quad (22)$$

The correlation functions are in this case

$$\langle e^{\pm i\phi'}(t) e^{\mp i\phi'}(0) \rangle = \int_{-\infty}^{+\infty} p(\phi', t) e^{i\phi'} d\phi' = e^{-t/\tau}, \quad (23a)$$

$$\langle e^{\pm 2i\phi'}(t) e^{\mp 2i\phi'}(0) \rangle = e^{-4t/\tau}. \quad (23b)$$

Again the spectral densities vanish for $q \neq q'$.

$$k_{q, q'=\pm 1} = \tau / (1 + \omega^2 \tau^2), \quad (24a)$$

$$k_{q, q'=\pm 2} = \frac{1}{4} \tau / (1 + \frac{1}{4} \omega^2 \tau^2). \quad (24b)$$

The nonvanishing spin matrix elements $K_{\alpha\beta}^q$ are obtained from Eqs. (6), (7), (8) and (9).

$$\begin{aligned} K_{++}^q &= K_{--}^q = -\frac{1}{2} K_{00}^q = -\gamma^2 \hbar^2 r_{12}^{-3} \\ &\quad \times \frac{1}{2} \mathfrak{D}_{0,q}^{(2)}(0, \psi_0, 0) P_q^{(2)}(\theta'), \\ K_{+0}^q &= K_{0-}^q = -\gamma^2 \hbar^2 r_{12}^{-3} 2^{-1/2} \mathfrak{D}_{1,q}^{(2)}(0, \psi_0, 0) P_q^{(2)}(\theta'), \\ K_{0+}^q &= K_{-0}^q = -\gamma^2 \hbar^2 r_{12}^{-3} 2^{-1/2} \mathfrak{D}_{-1,q}^{(2)}(0, \psi_0, 0) P_q^{(2)}(\theta'), \\ K_{+-}^q &= -\frac{1}{4} \gamma^2 \hbar^2 r_{12}^{-3} \mathfrak{D}_{2,q}^{(2)}(0, \psi_0, 0) P_q^{(2)}(\theta'), \\ K_{-+}^q &= -\frac{1}{4} \gamma^2 \hbar^2 r_{12}^{-3} \mathfrak{D}_{-2,q}^{(2)}(0, \psi_0, 0) P_q^{(2)}(\theta'). \end{aligned} \quad (25)$$

The $P_q^{(2)}(\theta')$ functions are given by Eqs. (8), if the exponential factor depending on ϕ' is omitted.

Substitution of (24) and (25) into (17) and subsequently into (15), ignoring nonsecular terms with $E_\alpha - E_{\alpha'} - E_\beta + E_{\beta'} \neq 0$, leads to the following set of relaxation equations:

$$\begin{aligned} \partial \sigma_{++} / \partial t &= -(+w_1 + w_2)(\sigma_{++} - \sigma_{++}^{(T)}) \\ &\quad + w_1(\sigma_{00} - \sigma_{00}^{(T)}) + w_2(\sigma_{--} - \sigma_{--}^{(T)}), \end{aligned} \quad (26a)$$

$$\begin{aligned} \partial \sigma_{00} / \partial t &= w_1(\sigma_{++} - \sigma_{++}^{(T)}) - 2w_1(\sigma_{00} - \sigma_{00}^{(T)}) \\ &\quad + w_1(\sigma_{--} - \sigma_{--}^{(T)}), \end{aligned} \quad (26b)$$

$$\begin{aligned} \partial \sigma_{--} / \partial t &= w_2(\sigma_{++} - \sigma_{++}^{(T)}) + w_1(\sigma_{00} - \sigma_{00}^{(T)}) \\ &\quad - (w_1 + w_2)(\sigma_{--} - \sigma_{--}^{(T)}), \end{aligned} \quad (26c)$$

$$\partial \sigma_{+0} / \partial t = -(w_0 + \frac{3}{2}w_1 + \frac{1}{2}w_2 + i\omega_{+0})\sigma_{+0}, \quad (27a)$$

$$\partial \sigma_{0-} / \partial t = -(w_0 + \frac{3}{2}w_1 + \frac{1}{2}w_2 + i\omega_{0-})\sigma_{0-}, \quad (27b)$$

$$\partial \sigma_{+-} / \partial t = -(+w_1 + w_2 + i\omega_{+-})\sigma_{+-}, \quad (28)$$

with

$$w_0 = \left(\frac{3}{2}\right)^6 \gamma^4 \hbar^4 r_{12}^{-6} \tau \{ 2 \sin^2 \psi_0 \cos^2 \psi_0 \sin^2 \theta' \cos^2 \theta' + 8 \sin^4 \psi_0 \sin^4 \theta' \}, \quad (29)$$

$$\begin{aligned} w_1 &= \frac{3}{4} \gamma^4 \hbar^4 r_{12}^{-6} (1 - \cos^4 \psi_0) \sin^4 \theta' \left(\frac{\frac{1}{2} \tau}{1 + \frac{1}{16} \omega_{+0}^2 \tau^2} \right) \\ &\quad + \frac{9}{16} \gamma^4 \hbar^4 r_{12}^{-6} (4 \cos^4 \psi_0 - 3 \cos^2 \psi_0 + 1) \\ &\quad \times \sin^2 \theta' \cos^2 \theta' \left(\frac{2\tau}{1 + \omega_{+0}^2 \tau^2} \right) \\ &= \text{same expression with } \omega_{+0} \text{ replaced by } \omega_{0-}, \end{aligned} \quad (30)$$

$$\begin{aligned} w_2 &= \frac{9}{128} \gamma^4 \hbar^4 r_{12}^{-6} (1 + 6 \cos^2 \psi_0 + \cos^4 \psi_0) \\ &\quad \times \sin^4 \theta' \left(\frac{\frac{1}{2} \tau}{1 + \frac{1}{16} \omega_{+-}^2 \tau^2} \right) + \frac{9}{32} \gamma^4 \hbar^4 r_{12}^{-6} (1 - \cos^4 \psi_0) \\ &\quad \times \sin^2 \theta' \cos^2 \theta' \left(\frac{2\tau}{1 + \omega_{+-}^2 \tau^2} \right). \end{aligned} \quad (31)$$

These formulas hold for the case of stochastic diffusion of the azimuthal angle. They can immediately be changed to the case of random jumps between three equilibrium positions by using Eq. (21) rather than (24). The small difference between ω_{+0} and ω_{0-} in the

expression for w_1 has been ignored. The $\mathfrak{D}^{(2)}$ functions have been taken from Wigner. The normalized constants have been checked by direct trigonometric transformation of the functions (8), which led to the results about as quickly as the use of Wigner's general formula in this case.

The set of Eqs. (26) describe the longitudinal relaxation. There are two characteristic times, as could be expected for a problem with effective spin 1. The "magnetic moment relaxation"¹³ is characterized by

$$\frac{\partial(\sigma_{++}-\sigma_{--})}{\partial t} = \frac{1}{2w_2+w_1}(\sigma_{++}-\sigma_{--}) = \frac{\sigma_{++}-\sigma_{--}}{T_1}. \quad (32)$$

The "quadrupole moment relaxation" is described by

$$\begin{aligned} \frac{\partial(\sigma_{++}+\sigma_{--}-2\sigma_{00})}{\partial t} &= \frac{1}{3w_1}(\sigma_{++}+\sigma_{--}-2\sigma_{00}) \\ &= \frac{\sigma_{++}+\sigma_{--}-2\sigma_{00}}{D_1}. \end{aligned} \quad (33)$$

The intensity of the magnetic resonance absorption lines is proportional to $\sigma_{++}-\sigma_{00}$ or $\sigma_{00}-\sigma_{--}$, and will in general approach an equilibrium according to a linear combination of two exponentials, $a \exp(-t/T_1) + b \exp(-t/D_1) + c$, where the coefficients a and b are determined by the initial conditions, and c by the lattice temperature.

The two lines have the same transverse relaxation time according to Eq. (27),

$$T_2^{-1} = w_0 + \frac{3}{2}w_1 + \frac{1}{2}w_2. \quad (34)$$

The σ_{+-} component decays with another characteristic time, but does not correspond to an observable quantity in a magnetic resonance experiment.

The transverse and longitudinal relaxation times are in general not equal even in the case of very short correlation times [Eq. (11)]. They have a different angular dependence on ψ_0 in this nonisotropic case.

For $1-3 \cos^2 \psi_0 = 0$, the two resonance lines will coincide according to Eq. (14). In this case perturbation theory should be carried to a higher order to determine the position of the energy levels, but the splitting will certainly be very small. When the frequency of the two lines becomes nearly equal, the nonsecular nature of the term R_{+00} becomes questionable. In other words, there is a term for which the left-hand side of Eq. (16) is of the order of unity. A changeover from nonsecular to secular character takes place. The term can be carried along in a rigorous manner provided the correlation time τ_c is short compared to $\hbar(E_+-E_0-E_0+E_-)^{-1}$. A set of two coupled equations for the off-diagonal elements σ_{+0} and σ_{-0} should be solved

$$\begin{aligned} \partial\sigma_{+0}/\partial t &= i\omega_{+0}\sigma_{+0} + R_{+0+0}\sigma_{+0} + R_{+00-}\sigma_{-0}, \\ \partial\sigma_{-0}/\partial t &= i\omega_{-0}\sigma_{-0} + R_{0-0-}\sigma_{-0} + R_{0-+0}\sigma_{+0}. \end{aligned} \quad (35)$$

This corresponds to a partial application of the general operator formulation, Eq. (12), which contains all interference and nonsecular effects. Equations (35) describe the frequency pulling and damping by cross-relaxation of off-diagonal elements which have nearly the same frequency. The coupled system can readily be solved for the two normal modes. This situation, which illustrates the principles and limitations involved in the distinction between secular and nonsecular perturbations is rather academic. The overlap of resonance lines is the experimental counterpart of this theory of cross-relaxation. In the case of a proton pair in a solid lattice the effect described by Eqs. (35) will be obscured completely by the interaction from neighboring moments outside the pair.

III. SATURATION AND OVERHAUSER EFFECT

Consider the case that two radio-frequency magnetic fields are applied. $H_1(\nu_{+0})$ has a frequency close to the resonant frequency ν_{+0} , $H_1(\nu_{0-})$ is close to the resonance frequency ν_{0-} of the other line. Assume that the amplitudes of both fields satisfy the relation

$$\gamma\hbar H_1 \ll \hbar(\nu_{+0} - \nu_{0-}) \ll \hbar\nu_{+0}. \quad (36)$$

The situation can be treated in the same manner as the "weak external field" case, considered by Bloch.¹⁴ The terminology "weak" refers to the condition (36). It will be shown here that Bloch's considerations can readily be generalized to include the case of more than one applied frequency. The radio-frequency amplitudes can each have saturating strength. Because of the assumptions made at the beginning of this section, the effect of each frequency on all transitions but one that is near resonance, can be disregarded as nonsecular perturbations.

The circularly polarized fields add the following term to the Hamiltonian:

$$\begin{aligned} \mathcal{H}_{rf} &= \frac{1}{2}\gamma\hbar H_1(\nu_{+0})\{(I_1^+ + I_2^+)e^{-i\omega_{+0}t} \\ &\quad + (I_1^- + I_2^-)e^{+i\omega_{+0}t}\} + \frac{1}{2}\gamma\hbar H_1(\nu_{0-}) \\ &\quad \times \{(I_1^+ + I_2^+)e^{-i\omega_{0-}t} + (I_1^- + I_2^-)e^{+i\omega_{0-}t}\}. \end{aligned} \quad (37)$$

The equation of motion for the off-diagonal components of the density matrix in the stationary state with driving fields become

$$\begin{aligned} -i\omega_{+0}'\sigma_{+0} &= -i\omega_{+0}\sigma_{+0} - \sigma_{+0}/T_2 \\ &\quad + \frac{1}{2}i\gamma H_1(\nu_{+0})\sqrt{2}(\sigma_{00} - \sigma_{++}), \end{aligned} \quad (38a)$$

$$\begin{aligned} -i\omega_{-0}'\sigma_{-0} &= -i\omega_{-0}\sigma_{-0} - \sigma_{-0}/T_2 \\ &\quad + \frac{1}{2}i\gamma H_1(\nu_{0-})\sqrt{2}(\sigma_{--} - \sigma_{00}). \end{aligned} \quad (38b)$$

These equations replace Eqs. (27). There are corresponding complex conjugate equations for σ_{0+} and σ_{-0} .

The steady-state solution for the diagonal components is obtained by putting the left-hand side of

¹³ F. Lurcat, *Compt. rend.* **240**, 2402, 2517 (1955).

¹⁴ F. Bloch, reference 8, Sec. III.

Eqs. (26) equal to zero and adding a term

$$-\frac{1}{2}i\gamma H_1(\nu_{+0}')\sqrt{2}(\sigma_{0+}-\sigma_{+0})$$

to the right-hand side of (26a),

$$-\frac{1}{2}i\gamma H_1(\nu_{+0}')\sqrt{2}(\sigma_{0-}-\sigma_{-0})$$

to (26c) and subtract the sum of these terms from the right-hand side of (26b). Solution of the set of steady-state equations leads, by elimination of the off-diagonal elements, to

$$(1+S_{+0})(\sigma_{++}-\sigma_{00})=\sigma_{++}^{(T)}-\sigma_{00}^{(T)} \\ -\frac{w_2}{w_1}\{\sigma_{++}-\sigma_{--}-\sigma_{++}^{(T)}-\sigma_{--}^{(T)}\}, \quad (39a)$$

$$(1+S_{0-})(\sigma_{00}-\sigma_{--})=\sigma_{00}^{(T)}-\sigma_{--}^{(T)} \\ -\frac{w_2}{w_1}\{\sigma_{++}-\sigma_{--}-\sigma_{++}^{(T)}-\sigma_{--}^{(T)}\}, \quad (39b)$$

$$\sigma_{++}+\sigma_{00}+\sigma_{--}=1. \quad (39c)$$

The two saturation parameters are defined by

$$S_{+0}=\gamma^2 H_1^2(\nu_{+0}')T_2 w_1^{-1}\{(\nu_{+0}'-\nu_{+0})^2 T_2^2+1\}^{-1}, \quad (40a)$$

$$S_{0-}=\gamma^2 H_1^2(\nu_{0-}')T_2 w_1^{-1}\{(\nu_{0-}'-\nu_{0-})^2 T_2^2+1\}^{-1}. \quad (40b)$$

The signal intensities of the two resonance lines are proportional to $(\sigma_{++}-\sigma_{00})$ and $(\sigma_{00}-\sigma_{--})$, as can be seen from Eqs. (38). In the important special case that only one of the radio-frequency amplitudes is of saturating strength, e.g., $S_{0-}=0$, $w_1 S_{+0} \rightarrow \infty$, one obtains for the Overhauser effect, i.e., the factor f_{Ov} by which the line at ν_{0-} is changed on application of a very strong field at ν_{+0} ,

$$f_{Ov}^{(\infty)}=\frac{w_1+2w_2}{w_1+w_2}. \quad (41)$$

The very good approximation has been made that

$$\sigma_{++}^{(T)}-\sigma_{--}^{(T)}\approx 2(\sigma_{00}^{(T)}-\sigma_{--}^{(T)}).$$

The Overhauser effect depends on the orientation ψ_0 through Eqs. (25) and (26). There is no Overhauser effect, if $w_2=0$. The enhancement factor reaches a maximum value 2 for $w_1=0$. Equations (39) are, of course, much more general than the special case, Eq. (41). They describe in conjunction with Eqs. (38) the intensity of both signals and include completely all saturation effects on the application of two radio-frequency fields.

Similar considerations apply to any system with three unequally spaced levels, in particular to a nucleus with $I=1$ and quadrupole interaction, or a magnetic ion $S=1$ in a crystalline field. Whereas the case that both fields are of saturating strength is not of particular interest for a proton pair, it is very important in the analysis of the operation of a recently proposed solid-

state Maser.¹⁵ In general, transitions between the $+$ and $-$ level could also occur. They can readily be incorporated in the analysis.

The treatment presented here has to be modified if one of the radio-frequency fields becomes larger than the intrinsic line width, $\gamma H_1 > T_2^{-1}$. A rigorous discussion has been given for the case than one radio-frequency field is very large, while the other is relatively weak. Transform to a rotating coordinate system to eliminate the explicit time dependence of the strong field. Redfield¹⁶ has discussed the transformation of the dipolar interaction and relaxation terms in the rotating system. The magnetic resonance response to the weak field is split into components. Their spacing and relative amplitudes depend on the value of the effective field in the rotating system.^{17,18}

For dipolar pairs in a solid lattice, an integration over a distribution of local fields must be carried out. The individual components will not be resolved. The smoothed-out absorption will follow at least qualitatively the equations derived in this section, unless the condition (36) is violated and the saturating field spans both lines.

IV. DISCUSSION AND COMPARISON WITH EXPERIMENT

The ideal situation of an isolated spin pair with hindered rotation cannot be found in actual solids. There will be interaction with neighboring pairs or other dipole moments in the crystalline lattice. This interaction can cause transitions between the singlet and the triplet states and its rigorous inclusion into the theory would be quite cumbersome. Its influence is most prominent, however, on the observed line width, since it produces a wide distribution of resonant frequencies. The observation of T_2 calculated above is only possible if the effect of the static fields from neighboring pairs is eliminated. This can be done in principle by applying a radio-frequency field which is strong enough to produce complete saturation of an individual component, but does not span both components of the pair of resonance lines simultaneously. One moves into the center of resonance of one component in an adiabatic rapid passage variation of the external magnetic field and then stops, while leaving the radiofrequency field on. The magnetization will then decay to zero with a characteristic time T_2 . Its signal may be picked up, for example, in a second crossed coil. The presence of the focusing radio-frequency field prevents loss of phase memory due to a distribution in static local fields. If the external magnetic field is modulated with a frequency $\omega_m \approx T_2^{-1}$ in the presence of a strong radio-frequency field,¹⁶ the phase shift of

¹⁵ N. Bloembergen, Phys. Rev. **104**, 324 (1956).

¹⁶ A. G. Redfield, Phys. Rev. **98**, 1787 (1955). The T_2 in this paper corresponds to T_{2s} in this reference, if a small contribution of time-dependent interaction with outside neighbors is neglected.

¹⁷ F. Bloch, reference 8, Sec. VII.

¹⁸ S. H. Autler and C. H. Townes, Phys. Rev. **100**, 703 (1955)

the observed signal with respect to the modulation will also make a measurement of T_2 possible. No such experimental data are available at present.

Steady-state saturation effects should be modified according to Redfield's theory¹⁶ to take into account the distribution of local fields. This is especially important for the dispersive, "in-phase" part of the radio-frequency magnetization. Longitudinal relaxation times can be measured by steady-state saturation experiments or by direct observation of the recovery of magnetization after saturation. The interaction with the other spin of a proton pair, undergoing hindered rotation, may very well be the dominant factor for longitudinal relaxation. Equations (30) and (31) show a marked angular dependence. An important special case will now be considered in more detail.

$\theta' = \pi/2$, $\psi_0 = 0$. The pair rotates around a perpendicular axis, which is parallel to the external magnetic field. In this case one has $w_1 = 0$, $w_2 > 0$. Steady-state saturation of each of the components should occur very readily according to Eqs. (39). In practice the field intensity required for saturation will not be zero, as relaxation by outside interactions will take over. The field required for saturation will, however, go through a minimum for $\psi_0 = 0$. It follows from Eqs. (10) that this orientation corresponds to a maximum splitting of the two lines. In a polycrystalline sample, the tails will correspondingly saturate more readily than the center of the resonance absorption. This argument holds not only for a pair, but for any planar configuration of spins rotating around a perpendicular axis. For every individual dipolar interaction has the angles $\theta' = \pi/2$ and $\psi_0 = 0$, and consequently $w_1 = 0$. The tails of the absorption by proton triangles in a polycrystalline specimen also correspond dominantly to the orientation $\psi_0 = 0$. Richards¹⁹ has observed preferential saturation of the tails. Saturation of the tails could also account for too small values of the second moment of the absorption line reported by Andrew³ and by Powles and Gutowski.²⁰

¹⁹ R. E. Richards (private communication). The author is indebted to Dr. Richards for discussions on the experimental situation, which led to this work.

²⁰ J. G. Powles and H. S. Gutowski, *J. Chem. Phys.* **21**, 1695 (1953).

A detailed investigation of the angular dependence ψ_0 of the saturation for a proton pair in a single crystal rotating with $\theta' = \pi/2$, would provide a complete analysis of the intra- and intermolecular contributions to the relaxation time. The relaxation time should reach a maximum for $\psi_0 = 0$. For the same orientation the intensity of the other line would become a maximum through the Overhauser effect. The theoretical increase of a factor two will not be reached because other neighbors will prevent w_1 from becoming exactly zero. The detailed nature of motion around the preferred axis is irrelevant for the angular dependence of the relaxation mechanism. It could be a hindered rotation, torsional oscillations interrupted by tunneling, etc.

The case $\theta' = 0$ is trivial. When the axis of rotation is parallel to the radius vector, there is essentially no relative motion in the pair: $w_1 = w_2 = 0$. Relaxation can only arise from interaction with outside neighbors.

If the correlation time τ_c becomes long and the condition (18) is invalidated, the splitting will not be given by Eq. (14). In the limit of the quasi-static case,¹ where the correlation time is much longer than the inverse dipolar interaction, $(3 \cos^2 \psi_0 - 1)$ has to be replaced by $2(3 \cos^2 \theta - 1)$. There will be a pair of resonance lines for each occurring value of θ . For $\psi_0 = 0$ and $\theta' = \pi/2$, one has $\theta = \pi/2$.

It is still possible that the slow angular variation around the equilibrium θ , or the occasional jump between two equilibrium values of θ , provides the dominant relaxation mechanism. Then Eqs. (30) and (31) for the angular dependence of w_1 and w_2 still hold. The relaxation times would become long in view of the very large value of τ . It is more probable that in the case of slow motion, other relaxation mechanisms based on interactions with other neighbors, take over. Then there would be no Overhauser effect and the angular dependence of saturation would be different. Experiments on the proton resonance in a gypsum single crystal could confirm whether intra- or intermolecular relaxation is the more important.

ACKNOWLEDGMENTS

The author is indebted to Professor E. M. Purcell and Dr. A. G. Redfield for reading the manuscript and making valuable suggestions for improvement.