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Relaxation Processes in a System of Two Spins*

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Abragam and Pound's method for the calculation of the longitudinal relaxation time T_1 has been extended to the transverse relaxation time T_2. Explicit calculations have been carried out for a pure dipole-dipole interaction, showing that for an interacting pair of like spins, or for nuclei in paramagnetic solution, T_1 is exactly equal to T_2 in the extreme narrow case. For a pair of interacting unlike spins, it is shown that the longitudinal components of the magnetic moments do not have simple exponential decays. This gives rise to a steady and transient Overhauser effect. The transverse components, however, have in all cases, simple exponential decay defined by a single relaxation time T_2. A set of modified Bloch's equations is found, giving the correct equation of motion of the macroscopic magnetic moments of such a system of pairs of unlike spins.

The equality of T_1 and T_2 has been verified in paramagnetic solutions, and a nuclear Overhauser effect has been observed in anhydrous hydrofluoric acid. If one assumes that the extreme narrow case corresponds to the actual motion, the experimental results are not consistent with the picture of a pure dipole-dipole interaction between the hydrogen and fluorine nuclei of a molecule without taking into account the effect of the other molecules.

I. INTRODUCTION

We consider a particle of spin **I** interacting with another particle of spin **S**. The Hamiltonian of such an interacting pair, in a magnetic field H_0 along the z direction is

$$\mathcal{H}=\mathcal{H}_M-\hbar\gamma_I H_0 I_z-\hbar\gamma_S H_0 S_z+\mathcal{H}'. \qquad (1)$$

$\mathcal{H}_M$ is the Hamiltonian of the motion of the particles and commutes with the spin operators. The next two terms are the Zeeman energies of the spins in the constant magnetic field H_0. $\mathcal{H}'$ is the spin-spin interaction term considered as a perturbation. All the explicit calculations will be performed in the case of a dipole-dipole type interaction:

$$\mathcal{H}'=-(\hbar^2\gamma_I\gamma_S/b^3)[3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})-\mathbf{I}\cdot\mathbf{S}], \qquad (2)$$

but any other type of interaction, e.g., electron-coupled interaction $A\mathbf{I}\cdot\mathbf{S}$, can be treated in the same way.

We will consider only spins of value $\frac{1}{2}$ so that there is no quadrupole interaction. Larger values for the spins would make computations more complicated without fundamental changes.

II. TRANSITION PROBABILITIES

If $|m_i\rangle$ and $|m_j\rangle$ are two eigenstates of the unperturbed Hamiltonian with the corresponding energies E_i and E_j, the transition probability per unit time between these two states is, in the first order, given by

$$w_{ij}=\frac{1}{t}\frac{1}{\hbar^2}\left|\int_0^t \langle m_j|\mathcal{H}'(t')|m_i\rangle e^{-i\omega_{ij}t'}dt'\right|^2, \qquad (3)$$

with

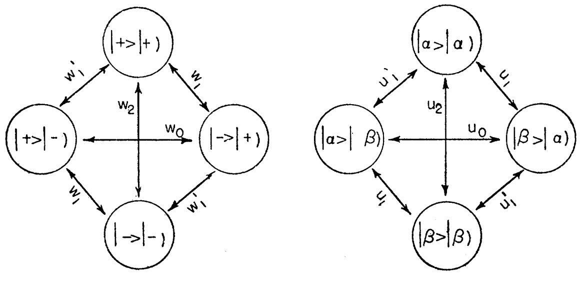
$$\omega_{ij}=(E_j-E_i)/\hbar.$$

In the case of a randomly fluctuating perturbing Hamiltonian $\mathcal{H}'(t)$, this integral has been calculated by Abragam and Pound.[1] When the fluctuations are rapid, as in liquids and gases, the result is a time-independent transition probability per unit time. In the present case of spin $\frac{1}{2}$, we define four eigenstates of the spins by the following relations:

$$\begin{aligned} I_z|+\rangle&=+\tfrac{1}{2}|+\rangle,\\ I_z|-\rangle&=-\tfrac{1}{2}|-\rangle,\\ S_z|+)&=+\tfrac{1}{2}|+),\\ S_z|-)&=-\tfrac{1}{2}|-), \end{aligned} \qquad (4)$$

so that the four unperturbed eigenstates of a pair are $|+\rangle|+)$, $|+\rangle|-)$, $|-\rangle|+)$, and $|-\rangle|-)$ with the respective occupation numbers N_{++}, N_{+-}, N_{-+}, and N_{--}.

The transition probabilities per unit time w_0, w_1, w_1', and w_2 between these four states, which we are going to use in the discussion of the motion of the longitudinal component of the magnetic moment are indicated in diagram (A) of Fig. 1.



(A) (B)

Fig. 1. (A) Transition probabilities between the eigenstates of the longitudinal components of the spin operators. (B) Transition probabilities between the eigenstates of the transverse components of the spin operators.

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[1] A. Abragam and R. V. Pound, Phys. Rev. 92, 953 (1953).

The equations of motion of the transverse components of the magnetic moment involve the operators I_x (or I_y) and S_x (or S_y). So, in similarity to set (4) we define four eigenstates of the spins by

$$\begin{aligned} I_x|\alpha\rangle &= +\tfrac{1}{2}|\alpha\rangle, \\ I_x|\beta\rangle &= -\tfrac{1}{2}|\beta\rangle, \\ S_x|\alpha\rangle &= +\tfrac{1}{2}|\alpha\rangle, \\ S_x|\beta\rangle &= -\tfrac{1}{2}|\beta\rangle. \end{aligned}$$

The four states of a pair $|\alpha\rangle|\alpha\rangle$, $|\alpha\rangle|\beta\rangle$, $|\beta\rangle|\alpha\rangle$, and $|\beta\rangle|\beta\rangle$ are not eigenstates of the energy. However, these four states are orthogonal, so it is still meaningful to speak of the occupation numbers $N_{\alpha\alpha}$, $N_{\alpha\beta}$, $N_{\beta\alpha}$, $N_{\beta\beta}$ and of the transition probabilities per unit time u_0, u_1, u_1', and u_2 between these states as indicated on Fig. 1(B).

To calculate the transition probabilities, we proceed as follows:

Consider two orthogonal states $|a\rangle$ and $|b\rangle$ that are not eigenstates of the energy. They can always be expanded in eigenvectors of the energy.

$$\begin{aligned} |a\rangle &= \textstyle\sum_i a_i|m_i\rangle, \\ |b\rangle &= \textstyle\sum_j b_j|m_j\rangle. \end{aligned} \tag{5}$$

For example, in the present case of spin $\frac{1}{2}$ we have:

$$\begin{aligned} |\alpha\rangle &= (1/\sqrt{2})[|+\rangle+|-\rangle], \\ |\beta\rangle &= (1/\sqrt{2})[|+\rangle-|-\rangle]. \end{aligned} \tag{5$'$}$$

Using the expansion (5) and the fact that $\langle a|b\rangle=0$, we get a formula generalizing (3). The transition probability per unit time between the states $|a\rangle$ and $|b\rangle$ is

$$u_{ab}=\frac{1}{t}\frac{1}{\hbar^2}\left|\int_0^t \sum_{ij}\langle m_j|\mathcal{H}'(t')|m_i\rangle a_i b_j e^{-i\omega_{ij}t'}dt'\right|^2.$$

This integral can be calculated in the same technique as Abragam and Pound[1] used and will be shown to be time independent in the case of rapid motion.

III. EQUATIONS OF MOTION OF THE MAGNETIC MOMENT

From the definition of the w's, it follows that

$$\begin{aligned} dN_{++}/dt &= -(w_1+w_1'+w_2)N_{++}+w_1'N_{+-} \\ &\qquad +w_1N_{-+}+w_2N_{--}+\text{constant}, \\ dN_{+-}/dt &= w_1'N_{++}-(w_0+w_1+w_1')N_{+-} \\ &\qquad +w_0N_{-+}+w_1N_{--}+\text{constant}, \\ dN_{-+}/dt &= w_1N_{++}+w_0N_{+-}-(w_0+w_1+w_1')N_{-+} \\ &\qquad +w_1'N_{--}+\text{constant}, \\ dN_{--}/dt &= w_2N_{++}+w_1N_{+-}+w_1'N_{-+} \\ &\qquad -(w_1+w_1'+w_2)N_{--}+\text{constant}. \end{aligned} \tag{6}$$

The constants are obtained by considering the system at temperature equilibrium by inserting the proper Boltzman's factor, and are unimportant in the computation of the relaxation times.

The experimentally observable quantities are the macroscopic magnetic moments $\bar{I}_z$ and $\bar{S}_z$, distinguishable by their different Larmor frequencies and proportional to:

$$\begin{aligned} (N_{++}+N_{+-})-(N_{-+}+N_{--}) &= K\bar{I}_z, \\ (N_{++}+N_{-+})-(N_{+-}+N_{--}) &= K\bar{S}_z. \end{aligned} \tag{7}$$

Inserting the values (7) in (6) we get:

$$\begin{aligned} d\bar{I}_z/dt &= -(w_0+2w_1+w_2)\bar{I}_z \\ &\qquad -(w_2-w_0)\bar{S}_z+\text{constant} \\ d\bar{S}_z/dt &= -(w_2-w_0)\bar{I}_z \\ &\qquad -(w_0+2w_1'+w_2)\bar{S}_z+\text{constant}. \end{aligned} \tag{8}$$

These equations along with the results of identical calculations for the transverse components I_x and S_x lead finally to the following set of equations:

$$\begin{aligned} d\bar{I}_z/dt &= -(w_0+2w_1+w_2)(\bar{I}_z-I_0) \\ &\qquad -(w_2-w_0)(\bar{S}_z-S_0), \\ d\bar{S}_z/dt &= -(w_2-w_0)(\bar{I}_z-I_0) \\ &\qquad -(w_0+2w_1+w_2)(\bar{S}_z-S_0), \end{aligned} \tag{9}$$

$$\begin{aligned} d\bar{I}_x/dt &= -(u_0+2u_1+u_2)\bar{I}_x-(u_2-u_0)\bar{S}_x, \\ d\bar{S}_x/dt &= -(u_2-u_0)\bar{I}_x-(u_0+2u_1'+u_2)\bar{S}_x. \end{aligned} \tag{10}$$

I_0 and S_0 are the equilibrium values of the magnetic moments of the spins **I** and **S**, and make explicit the values of the constants of Eqs. (8). These equations show that, in general, the decay of the observed quantities is not a simple exponential, but rather a linear combination of two exponentials. There are two cases that can easily be seen to give simple exponential decays:

(a) The two spins **I** and **S** are alike ("alike" meaning that $\gamma_I=\gamma_S$). Then the only observable quantities are $\bar{I}_z+\bar{S}_z$ and $\bar{I}_x+\bar{S}_x$. From the definition it follows that $w_1'=w_1$ and $u_1'=u_1$; thus the equation of motion of the two observable quantities is

$$\begin{aligned} \frac{d}{dt}(\bar{I}_z+\bar{S}_z) &= -2(w_1+w_2)(\bar{I}_z+\bar{S}_z-I_0-S_0), \\ \frac{d}{dt}(\bar{I}_x+\bar{S}_x) &= -2(u_1+u_2)(\bar{I}_x+\bar{S}_x). \end{aligned} \tag{11}$$

These are the usual decays with the relaxation times

$$\begin{aligned} 1/T_1 &= 2(w_1+w_2), \\ 1/T_2 &= 2(u_1+u_2). \end{aligned} \tag{12}$$

(b) Nuclei relaxed in a paramagnetic solution. The relaxation of such a nuclear spin **I** will be almost entirely the result of the dipole-dipole interaction $\mathcal{H}'$, when paired with an electronic spin **S** of a paramagnetic ion. On the other hand, this interaction $\mathcal{H}'$ is a negligible relaxation process for the electronic spin **S**, so that, in the time scale of observation of the nuclear magnetic moment, we may consider to have $\bar{S}_z=S_0$ and $\bar{S}_x=0$. Then Eqs. (9) and (10) show that the nuclear spins **I** have simple decays with relaxation times:

$$\begin{aligned} 1/T_1&=w_0+2w_1+w_2,\\ 1/T_2&=u_0+2u_1+u_2. \end{aligned} \tag{13}$$

IV. BLOCH'S EQUATIONS FOR A TWO-SPIN SYSTEM

Equations (9), which we will rewrite for convenience as

$$\begin{aligned} d\bar{I}_z/dt&=-\rho(\bar{I}_z-I_0)-\sigma(\bar{S}_z-S_0),\\ d\bar{S}_z/dt&=-\rho'(\bar{S}_z-S_0)-\sigma(\bar{I}_z-I_0), \end{aligned} \tag{14}$$

with

$$\begin{aligned} \rho&=w_0+2w_1+w_2,\\ \rho'&=w_0+2w_1'+w_2,\\ \sigma&=w_2-w_0 \end{aligned} \tag{15}$$

are the usual macroscopic Bloch equations[2] in which we have added a term representing the spin **I**—spin **S** interaction.

It is less straightforward to compare the equation of motion (10) for the transverse components with Bloch's equations because our Eqs. (10) are the equation of motion of the expectation values of the time independent spin operators, and therefore describe the motion of I_x and S_x in coordinates rotating respectively with angular velocity $\omega_I=\gamma_I H_0$ and $\omega_S=\gamma_S H_0$. Nevertheless, let us try to represent the motion of the transverse components of the macroscopic magnetic moment by a set of Bloch's equations similarly modified by adding a spin-spin interaction term. These equations will be in the laboratory coordinates:

$$\begin{aligned} dI_+'/dt&=-i\omega_I I_+'-\nu I_+'-\mu S_+',\\ dS_+'/dt&=-i\omega_S S_+'-\nu' S_+'-\mu I_+', \end{aligned} \tag{16}$$

with

$$\begin{aligned} I_+'&=I_x'+iI_y',\\ S_+'&=S_x'+iS_y'. \end{aligned}$$

Now to compare with Eqs. (10) we shall write Eqs. (16) in the rotating coordinates ($I_+=I_+'e^{i\omega_I t}$ and $S_+=S_+'e^{i\omega_S t}$):

$$\begin{aligned} dI_+/dt&=-\nu I_+-\mu e^{-i(\omega_S-\omega_I)t}S_+,\\ dS_+/dt&=-\nu' S_+-\mu e^{-i(\omega_I-\omega_S)t}I_+. \end{aligned} \tag{17}$$

(a) In the case of like spins, $\omega_S=\omega_I$ and Eqs. (17) give simply: (ν and ν' are obviously equal by symmetry considerations)

$$\frac{d}{dt}(I_++S_+)=-(\nu+\mu)(I_++S_+).$$

That is exactly the second of Eq. (11) with

$$\nu+\mu=2(u_1+u_2). \tag{18}$$

(b) In the case of unlike spins, "unlike" meaning that

$$|\omega_I-\omega_S|\gg\nu,\quad |\omega_I-\omega_S|\gg\nu',$$

the last term of Eq. (17) will average out so that the transverse components have simple exponential decays:

$$\begin{aligned} dI_+/dt&=-\nu I_+,\\ dS_+/dt&=-\nu' S_+. \end{aligned} \tag{19}$$

So these modified Bloch equations of the transverse components, obtained by analogy with the Eq. (14) for the longitudinal components, predict that, in Eqs. (10), we shall have

$$u_2-u_0=0. \tag{20}$$

This will be proven quantum mechanically in the next section. Then Eqs. (17) represent the correct motion of the transverse components in all the cases with the set of values

$$\begin{aligned} \nu&=u_0+2u_1+u_2,\\ \nu'&=u_0+2u_1'+u_2,\\ \mu&=u_2-u_0. \end{aligned} \tag{21}$$

To summarize, it has been shown in this section, that the Bloch equations do not hold for a two-spin system. However, by a slight modification of these, one can still find a set of equations [Eqs. (14) and (17)] that represent the motion of the macroscopic magnetic moment. It has been seen, too, that unlike the longitudinal components, the transverse components always have a simple exponential decay.

V. STEADY AND TRANSIENT OVERHAUSER EFFECT

In any steady-state condition, the first of Eqs. (14) will give

$$-\rho(\bar{I}_z-I_0)-\sigma(\bar{S}_z-S_0)=0. \tag{22}$$

If we apply an intense rf field at the resonance frequency of the spins S, for example, so that we equalize the populations in state $|+)$ and $|-)$ ("saturation"), we will have

$$S_z=0. \tag{23}$$

Now, inserting the value (23) in Eq. (22) we get the value of I_z, when S_z is saturated:

$$\bar{I}_z=I_0+(\sigma/\rho)S_0. \tag{24}$$

This is the effect first derived by Overhauser,[3] and extended by Bloch[4] to the case of dipole-dipole interaction. It is to be remarked that in the case of nuclear spins, Eq. (24) could be used to determine the relative signs of the gyromagnetic ratios of the two spins: The effect would be an increase of the static magnetic moment if the two signs are the same, and a decrease if the signs are opposite.

A solution of Eqs. (14) of particular interest is the one corresponding to the initial conditions:

$$\begin{aligned} (\bar{I}_z-I_0)_{t=0}&=0,\\ (\bar{S}_z-S_0)_{t=0}&=S_i. \end{aligned} \tag{25}$$

The solution, in the case $\rho=\rho'$, is, (the case $\rho\neq\rho'$ gives more complicated formulas, without any funda-

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[2] F. Bloch, Phys. Rev. **70**, 460 (1946).

[3] A. Overhauser, Phys. Rev. **89**, 689 (1953); **92**, 477 (1953).

[4] F. Bloch, Phys. Rev. **93**, 944 (1954).

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$$\bar{I}_z-I_0=\tfrac{1}{2}S_i[e^{-(\rho+\sigma)t}-e^{-(\rho-\sigma)t}],$$
$$\bar{S}_z-S_0=\tfrac{1}{2}S_i[e^{-(\rho+\sigma)t}+e^{-(\rho-\sigma)t}]. \tag{26}$$

These equations show that the relaxation of the spins **S** changes the difference of populations of spins **I** in time. This could be called a "transient" Overhauser effect and has been studied experimentally. The results will be discussed in Sec. VII.

VI. COMPUTATION OF THE TRANSITION PROBABILITIES

As an illustration of the method given in Sec. II we are going to compute the transition probabilities when the perturbing Hamiltonian $\mathcal{H}'$ is the dipole-dipole interaction (2). This perturbing Hamiltonian will be written as in Bloembergen, Purcell, and Pound's paper[5]:

$$\mathcal{H}'=[I_zS_z-\tfrac{1}{4}(I_+S_-+I_-S_+)]F_0+[I_+S_z+I_zS_+]F_1 +[I_-S_z+I_zS_-]F_1^*+I_+S_+F_2+I_-S_-F_2^*, \tag{27}$$

with

$$F_0(t)=k[1-3\cos^2\theta(t)],$$
$$F_1(t)=-\tfrac{3}{2}k\sin\theta(t)\cos\theta(t)e^{i\varphi(t)},$$
$$F_2(t)=-\tfrac{3}{4}k\sin^2\theta(t)e^{2i\varphi(t)}, \tag{28}$$
$$k=\hbar^2\gamma_I\gamma_S/b^3.$$

We shall assume, as usual, that

$$\langle F(t)F^*(t+\tau)\rangle=\langle|F(0)|^2\rangle e^{-|\tau|/\tau_c},$$

the brackets meaning average among all pairs.

It can be seen[5] that

$$\langle F_0^2\rangle=\tfrac{4}{5}k^2,$$
$$\langle|F_1|^2\rangle=\tfrac{3}{10}k^2,$$
$$\langle|F_2|^2\rangle=\tfrac{3}{10}k^2.$$

Now we can calculate the transition probabilities used in the preceding sections. Equation (3) gives

$$w_0=\frac{1}{t\hbar^2}\left|\int_0^t \tfrac{1}{4}F_0(t')e^{-i(\omega_I-\omega_S)t'}dt'\right|^2,$$
$$w_1=\frac{1}{t\hbar^2}\left|\int_0^t \tfrac{1}{2}F_1(t')e^{-i\omega_It'}dt'\right|,$$
$$w_1'=\frac{1}{t\hbar^2}\left|\int_0^t \tfrac{1}{2}F_1(t')e^{-i\omega_St'}dt'\right|^2, \tag{29}$$
$$w_2=\frac{1}{t\hbar^2}\left|\int_0^t \tfrac{1}{2}F_2(t')e^{-i(\omega_I+\omega_S)t'}dt'\right|^2.$$

Equation (6) gives, with the use of the expansion (5′),

$$u_0=\frac{1}{t\hbar^2}\left|\frac{1}{4}\int_0^t\{(1-\tfrac{1}{4}[e^{-i(\omega_I-\omega_S)t'}+e^{i(\omega_I-\omega_S)t'}])F_0(t')-(e^{-i\omega_It'}-e^{-i\omega_St'})F_1(t') +(e^{i\omega_It'}-e^{i\omega_St'})F_1^*(t')-e^{-i(\omega_I+\omega_S)t'}F_2(t')-e^{i(\omega_I+\omega_S)t'}F_2^*(t')\}dt'\right|^2,$$

$$u_1=\frac{1}{t\hbar^2}\left|\frac{1}{4}\int_0^t\{\tfrac{1}{4}(e^{-i(\omega_I-\omega_S)t'}-e^{i(\omega_I-\omega_S)t'})F_0(t')+e^{-i\omega_St'}F_1(t') +e^{i\omega_St'}F_1^*(t')-e^{-i(\omega_I+\omega_S)t'}F_2(t')+e^{i(\omega_I+\omega_S)t'}F_2^*(t')\}dt'\right|^2, \tag{30}$$

$$u_2=\frac{1}{t\hbar^2}\left|\frac{1}{4}\int_0^t\{(1+\tfrac{1}{4}[e^{-i(\omega_I-\omega_S)t'}+e^{i(\omega_I-\omega_S)t'}])F_0(t')+(e^{-i\omega_It'}+e^{-i\omega_St'})F_1(t') -(e^{i\omega_It'}+e^{i\omega_St'})F_1^*(t')+e^{-i(\omega_I+\omega_S)t'}F_2(t')+e^{i(\omega_I+\omega_S)t'}F_2^*(t')\}dt'\right|^2.$$

u_1' is obtained from u_1 by interchanging ω_I and ω_S.

It is seen that, before performing the integration, we must distinguish the cases where $\omega_I=\omega_S$ and $\omega_I\neq\omega_S$. We will assume that the motion is rapid, so that $\tau_cw\ll1$ and $\tau_cu\ll1$.

(a) Pairs of Like Spins: $\omega_I=\omega_S=\omega$

$$w_0=\frac{\tau_c}{8\hbar^2}\langle F_0^2\rangle,$$
$$w_1=w_1'=\frac{\tau_c}{2\hbar^2}\langle|F_1|^2\rangle\frac{1}{1+\omega^2\tau_c^2}, \tag{31}$$
$$w_2=\frac{2\tau_c}{\hbar^2}\langle|F_2|^2\rangle\frac{1}{1+4\omega^2\tau_c^2},$$

$$u_0=\frac{\tau_c}{8\hbar^2}\left[\frac{\langle F_0^2\rangle}{4}+\langle|F_2|^2\rangle\frac{2}{1+4\omega^2\tau_c^2}\right],$$
$$u_1=u_1'=\frac{\tau_c}{8\hbar^2}\left[\langle|F_1|^2\rangle\frac{2}{1+\omega^2\tau_c^2}+\langle|F_2|^2\rangle\frac{2}{1+4\omega^2\tau_c^2}\right], \tag{32}$$
$$u_2=\frac{\tau_c}{8\hbar^2}\left[\frac{9}{4}\langle F_0^2\rangle+\langle|F_1|^2\rangle\frac{8}{1+\omega^2\tau_c^2}+\langle|F_2|^2\rangle\frac{2}{1+4\omega^2\tau_c^2}\right].$$

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[5] Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

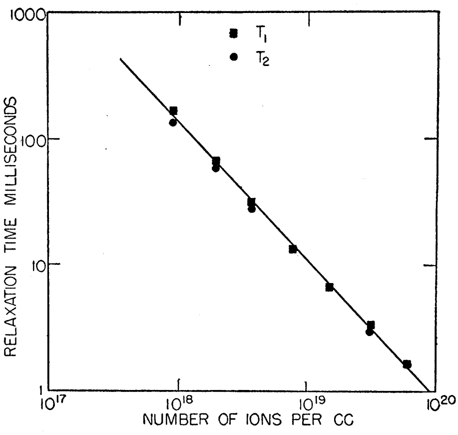

FIG. 2. Longitudinal and transverse relaxation times of protons at room temperature in paramagnetic solutions of ferric ions ($FeNH_4(SO_4)_2+12H_2O$) of different concentrations.

Using these values in Eqs. (12) we get the relaxation times:

$$\frac{1}{T_1}=\frac{6}{20}\frac{\hbar^2\gamma^4}{b^6}\left[\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right],$$
$$\frac{1}{T_2}=\frac{3}{20}\frac{\hbar^2\gamma^4}{b^6}\left[3\tau_c+\frac{5\tau_c}{1+\omega^2\tau_c^2}+\frac{2\tau_c}{1+4\omega^2\tau_c^2}\right].\tag{33}$$

These results are identical to Kubo and Tomita's.[6] In the extreme narrow case ($\omega^2\tau_c^2\ll 1$), we can see that $T_1=T_2$.

$$1/T_1=1/T_2=\tfrac{3}{2}(\hbar^2\gamma^4/b^6)\tau_c.\tag{34}$$

(b) Pairs of Unlike Spins

The w's give the straightforward generalization

$$w_0=\frac{\tau_c}{8\hbar^2}\langle F_0^2\rangle\frac{1}{1+(\omega_I-\omega_S)^2\tau_c^2},$$
$$w_1=\frac{\tau_c}{2\hbar^2}\langle|F_1|^2\rangle\frac{1}{1+\omega_I^2\tau_c^2},$$
$$w_1'=\frac{\tau_c}{2\hbar^2}\langle|F_1|^2\rangle\frac{1}{1+\omega_S^2\tau_c^2},\tag{35}$$
$$w_2=\frac{2\tau_c}{\hbar^2}\langle|F_2|^2\rangle\frac{1}{1+(\omega_I+\omega_S)^2\tau_c^2}.$$

In computing the u's, if we suppose that $|\omega_I-\omega_S|\gg 1/T$, so that any integral of the form:

$$\frac{1}{T}\frac{1}{\hbar^2}\int_0^T\int_0^T F^*(t')e^{-i\omega_It'}F(t'')e^{i\omega_St''}dt'dt''$$

averages out for any macroscopic time of observation T ($1/T$ is of order of magnitude of the u's) we get

$$u_0=u_2=\frac{\tau_c}{8\hbar^2}\left\{\left(1+\frac{1}{8}\frac{1}{1+(\omega_I-\omega_S)^2\tau_c^2}\right)\langle F_0^2\rangle+\left(\frac{2}{1+\omega_I^2\tau_c^2}+\frac{2}{1+\omega_S^2\tau_c^2}\right)\langle|F_1|^2\rangle+\frac{2}{1+(\omega_I+\omega_S)^2\tau_c^2}\langle|F_2|^2\rangle\right\},$$
$$u_1=\frac{\tau_c}{8\hbar^2}\left\{\frac{1}{8}\frac{1}{1+(\omega_I-\omega_S)^2\tau_c^2}\langle F_0^2\rangle+\frac{2}{1+\omega_S^2\tau_c^2}\langle|F_1|^2\rangle+\frac{2}{1+(\omega_I+\omega_S)^2\tau_c^2}\langle|F_2|^2\rangle\right\},\tag{36}$$
$$u_1'=\frac{\tau_c}{8\hbar^2}\left\{\frac{1}{8}\frac{1}{1+(\omega_I-\omega_S)^2\tau_c^2}\langle F_0^2\rangle+\frac{2}{1+\omega_I^2\tau_c^2}\langle|F_1|^2\rangle+\frac{2}{1+(\omega_I+\omega_S)^2\tau_c^2}\langle|F_2|^2\rangle\right\}.$$

In the extreme narrow conditions ($\omega_I^2\tau_c^2\ll 1$ and $\omega_S^2\tau_c^2\ll 1$), the above formulas are considerably simplified:

$$w_0=\tfrac{1}{10}\delta,$$
$$w_1=w_1'=(3/20)\delta,\tag{37}$$
$$w_2=\tfrac{3}{5}\delta,$$

$$u_0=u_2=27/80,$$
$$u_1=u_1'=13/80,\tag{38}$$

with $\delta=\hbar^2\gamma_I^2\gamma_S^2\tau_c/b^6$.

With these values, the equation of motion (14) and (17) become

$$\frac{d}{dt}(\bar{I}_z-I_0)=-\delta[(\bar{I}_z-I_0)+\tfrac{1}{2}(\bar{S}_z-S_0)],$$
$$\frac{d}{dt}(\bar{S}_z-S_0)=-\delta[\tfrac{1}{2}(\bar{I}_z-I_0)+(\bar{S}_z-S_0)],\tag{39}$$
$$dI_+/dt=-\delta I_+,$$
$$dS_+/dt=-\delta S_+.$$

And the solution (26) for the longitudinal components is,

$$\bar{I}_z-I_0=\tfrac{1}{2}S_i[\exp(-\tfrac{3}{2}\delta t)-\exp(-\tfrac{1}{2}\delta t)],$$
$$\bar{S}_z-S_0=\tfrac{1}{2}S_i[\exp(-\tfrac{3}{2}\delta t)+\exp(-\tfrac{1}{2}\delta t)].\tag{40}$$

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[6] R. Kubo and K. Tomita, J. Phys. Soc. (Japan) **9**, 888 (1954).

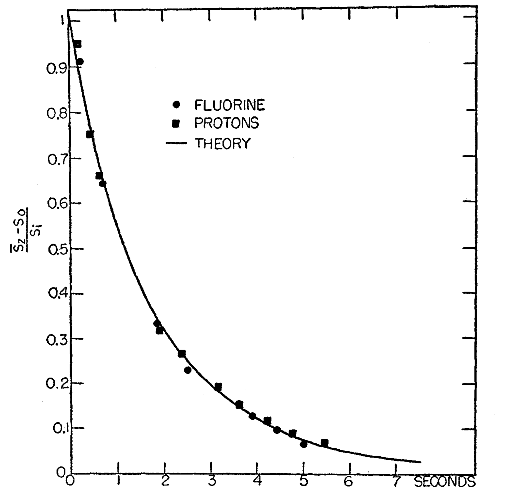

FIG. 3. Motion of the longitudinal component of the magnetic moment of one kind of nuclei toward its equilibrium value in hydrofluoric acid. The equation of the solid curve is

$$(\bar{S}_z-S_0)/S_i=\tfrac{1}{2}[\exp(-t/D_1)+\exp(-t/T_1)],$$

with $T_1=1.27$ sec and $D_1=2.25$ sec.

(c) Relaxation of Nuclei in Paramagnetic Solution

Inserting the values (35) and (36) in the Eqs. (13) one gets:

$$\frac{1}{T_1}=\frac{1}{10}\frac{\hbar^2\gamma_I^2\gamma_S^2}{b^6}\left[\frac{\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2}+\frac{\tau_c}{1+\omega_I^2\tau_c^2}+\frac{\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\right],$$
$$\frac{1}{T_2}=\frac{\hbar^2\gamma_I^2\gamma_S^2}{20b^6}\left[4\tau_c+\frac{\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2}+\frac{3\tau_c}{1+\omega_I^2\tau_c^2}+\frac{6\tau_c}{1+\omega_S^2\tau_c^2}+\frac{6\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\right]. \qquad (41)$$

In the extreme narrow case, as expected, $T_1=T_2$:

$$1/T_1=1/T_2=(\hbar^2\gamma_I^2\gamma_S^2/b^6)\tau_c. \qquad (42)$$

We have measured the relaxation times of protons in paramagnetic solutions containing different concentrations of ferric ions. As it is shown in Fig. 2, the predicted equality between T_1 and T_2 has been verified within about 2.5 percent.

VII. EXPERIMENTAL RESULTS

The most sensitive test of the theory outlined above appears to be the Overhauser effect discussed in Sec. V. This effect has been observed in anhydrous hydrofluoric acid HF at room temperature. The boiling point of the acid, at atmospheric pressure, is 19.4°C. As a result, the commercially obtained acid is stored in steel cylinders, necessitating subsequent distillation. After triple distillation in transparent Kel-F plastic tubes, the acid became colorless. The resonance studies were carried out in small samples of acid sealed in Kel-F tubes.[7]

Free precession techniques[8,9] ("spin echo") were used, permitting a direct measurement of $\bar{S}_z$, $\bar{I}_z$, $\bar{I}_x$, and $\bar{S}_x$.

The initial conditions (25) were obtained by applying at the time $t=0$ a "180° pulse" at the resonance frequency of the spins S. Then at $t=0$,

$$(\bar{S}_z)_{t=0}=-S_0.$$

So the initial conditions (25) are in this case:

$$(\bar{I}_z-I_0)_{t=0}=0,$$
$$S_i=(\bar{S}_z-S_0)_{t=0}=-2S_0. \qquad (43)$$

In the extreme narrow case, we have in Eqs. (14) $\rho=\rho'$. Even if we are not in the extreme narrow case, this equality will hold approximately in hydrofluoric acid, for the Larmor frequencies of hydrogen and fluorine differ by less than 6 percent. In this condition, solution (26) with the initial condition (43) is

$$\bar{I}_z-I_0=S_0[e^{-(\rho-\sigma)t}-e^{-(\rho+\sigma)t}],$$
$$\bar{S}_z-S_0=-S_0[e^{-(\rho-\sigma)t}+e^{-(\rho+\sigma)t}]. \qquad (44)$$

Figures 3 and 4 show the experimental results, that are, as expected from our simple theory, symmetrical with respect to the hydrogen and fluorine nuclei. The figures show that the experimental points can be fitted very

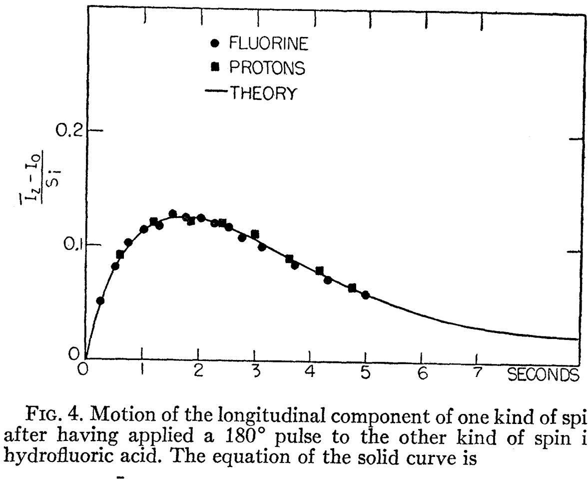

FIG. 4. Motion of the longitudinal component of one kind of spin after having applied a 180° pulse to the other kind of spin in hydrofluoric acid. The equation of the solid curve is

$$(\bar{I}_z-I_0)/S_i=\tfrac{1}{2}[\exp(-t/D_1)-\exp(-t/T_1)],$$

where T_1 and D_1 are the same as in Fig. 3.

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[7] The first experiments were performed in Teflon. But after a few days in Teflon, the liquid acid becomes colored and the relaxation times drop considerably, showing that commercial Teflon is not completely inert to hydrofluoric acid.

[8] E. L. Hahn, Phys. Rev. 80, 580 (1950).

[9] H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).

well by (44) with the values:

$$T_1 = 1/(\rho+\sigma) = 1.27 \text{ sec},$$

$$D_1 = 1/(\rho-\sigma) = 2.55 \text{ sec}.$$

The estimated error in these times is about 20 percent. These results show a ratio $\sigma/\rho = \frac{1}{3}$. The same ratio is obtained directly from the steady Overhauser effect: Saturation of protons (or fluorine nuclei) increases the magnetization due to fluorine (or to protons if fluorine has been saturated) by a factor of about 30 percent. The static magnetic moments of hydrogen and fluorine being approximately equal, Eq. (24) gives $\sigma/\rho \cong \frac{1}{3}$.

This ratio of $\frac{1}{3}$ is, however, in disagreement with the value $\frac{1}{2}$ calculated for a pure dipole-dipole interaction in the extreme narrow case [Eqs. (39) and (40)].

The decay of the transverse component is, within experimental errors, simply exponential with the same time constant T_2 for protons and fluorine nuclei:

$$T_2 = 0.43 \pm 0.015 \text{ sec}.$$

This again is in disagreement with Eq. (39), showing that either the effect of neighboring molecules needs to be taken into account, or that the interaction is not a pure dipole-dipole one, or both. It has been possible to remove the discrepancy by adding to the pure dipole-dipole interaction an electron-coupled exchange interaction $A\mathbf{I}\cdot\mathbf{S}$ of reasonable amplitude. Further experiments on purer hydrofluoric acid are being carried out to investigate this effect.

Figure 5 is an example of the signals obtained: It shows the increase of the magnetization due to fluorine, following a 180° pulse for protons. The magnitude of the longitudinal magnetic moment of fluorine is indicated by the amplitude of the tail following a 90° pulse for fluorine.

On the same photograph are superimposed: (a) the thermal equilibrium value of the magnetic moment of the fluorine obtained by simply applying a 90° pulse for fluorine (tails *a* and *b*). (b) the value of the magnetic moment of the fluorine when the protons are saturated (tail *c*). Similar photographs have been obtained by interchanging the role of hydrogen and fluorine.

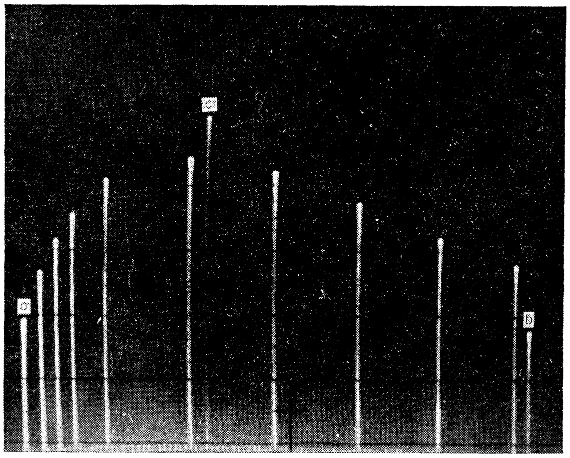

FIG. 5. Amplitude of tails of 90° pulses at fluorine frequency after having applied a 180° pulse at hydrogen frequency in hydrofluoric acid. *a* and *b* represent the amplitude of the tail when no 180° pulse has been applied; *c* represents the amplitude of the tail when the proton resonance has been saturated (steady Overhauser effect).

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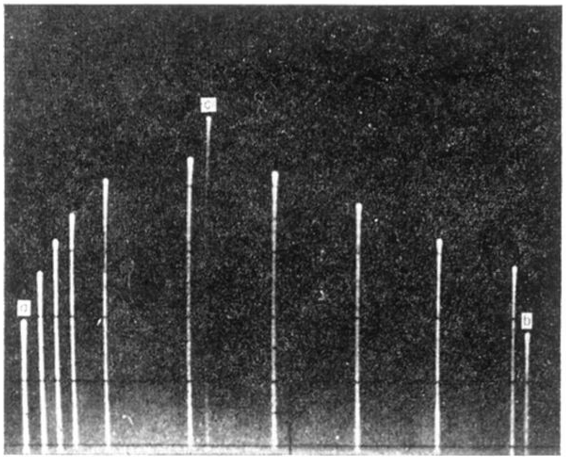

FIG. 5. Amplitude of tails of 90° pulses at fluorine frequency after having applied a 180° pulse at hydrogen frequency in hydrofluoric acid. *a* and *b* represent the amplitude of the tail when no 180° pulse has been applied; *c* represents the amplitude of the tail when the proton resonance has been saturated (steady Overhauser effect).