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Abstract

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RELAXATION PROCESSES IN A SYSTEM OF INTERACTING SPINS

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It has been noted in the literature ([1]) that the theory of nuclear paramagnetic relaxation in liquids proposed by Bloembergen ([2]) is not rigorous. The relaxation times calculated from this theory and those measured often agree only in order of magnitude. Nevertheless, on the basis of discrepancies between experimental and theoretical values, unjustified assumptions are sometimes made about the structure of the liquid ([3]).

One of the assumptions of ([2]) is that the spin of each nucleus relaxes independently, although the relaxation itself is due to pair dipole-dipole interactions of the nuclear magnetic moments. Bearing in mind the mechanism of "internal" relaxation (caused by the interaction of the spins of nuclei of one molecule), we shall consider the processes of thermal relaxation of systems of several equivalent* spins 1/2 situated in an external magnetic field $\mathbf{H}_0$ (the field is directed along the z axis). It is assumed that the dipole-dipole interaction of the nuclear magnetic moments, which provides the coupling between the spin system and the thermal motion of the molecules (the heat bath), is small in comparison with the interaction of the spin system with the external field (the dipole-dipole interaction is of order μ^2/r^3, where μ is the magnetic moment of the nucleus and r is the internuclear distance; the interaction with the external field is of order μH_0). Therefore the former may be regarded as a perturbation, and the relaxation processes may be described with the aid of transition probabilities between the levels of a system of noninteracting spins situated in the external field $\mathbf{H}_0$.

Let the unperturbed system consist of n spins 1/2 with magnetic moments μ, placed in the field $\mathbf{H}_0$; the index i will denote the number of the level, and the index ξ the number of one of the degenerate states of this level.

Denote by $N_{i\xi}(t)$ the number of systems in the state i, ξ. We shall consider a representation in which the diagonal component of the total spin $\mathbf{I}$ of the system along the z axis is diagonal. Then the index i has the meaning I_z, while ξ may denote the orientation of the spins m_k of the individual nuclei m_{zk}, with

$$\sum_k m_{zk} = I_z.$$

Since the nuclei are assumed to be equivalent,

$$N_{i\xi} = N_{i\xi'} = N_i.$$

As in ([4]), one may consider orthogonal states with definite values of I_x and m_{xk} (although they are not states with a given energy) and speak of the number of systems in state i with a definite I_x.

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* That is, spins of nuclei each of which is at the same distance from every other.

Transitions between levels are caused by the interaction

$$\begin{aligned} V = \sum_{k>l} V_{kl}; \qquad V_{kl} = \mu^2 \left\{ \frac{3(\mathbf{m}_k \mathbf{r}_{kl})(\mathbf{m}_l \mathbf{r}_{kl})}{r_{kl}^5} - \frac{\mathbf{m}_l \mathbf{m}_k}{r_{kl}^3} \right\} = \\ = \left[\dot{m}_{zk} m_{zl} - \frac{1}{4} \left(m_k^+ m_l^- + m_k^- m_l^+ \right) \right] F_0^{kl} + \left[m_k^+ m_{zl} + m_{zk} m_l^+ \right] F_1^{kl} + \\ + \left[m_k^- m_{zl} + m_{zk} m_l^- \right] \left(F_1^{kl} \right)^* + m_k^+ m_l^+ F_2^{kl} + m_k^- m_l^- \left(F_2^{kl} \right)^*, \end{aligned} \tag{1}$$

where k, l are the numbers of the nuclei, and the remaining notation is the same as in ([4]).

It is seen from this that transitions with $|\Delta I_z| > 2$ are forbidden, as are those transitions for which $|\Delta I_z| \leq 2$, but the orientation Δm_{zk} of more than two individual spins changes. The same selection rule also holds for $\Delta I_x, \Delta m_{xk}$, if one considers the representation in which I_x is diagonal.

Since the nuclear spins are equivalent, for the probabilities of transitions between the states $i\xi, i'\xi'$ we have

$$W_{i\xi \to i'\xi'} = W_{i\xi'' \to i'\xi'''} = W_{i \to i'},$$

provided that both transitions are allowed by the selection rules. Using this circumstance and the selection rules, one can write the kinetic equations for the number of systems N_i that are in the state $i\xi$ (where $i = I_z, I_x$, $\xi = m_{zk}, m_{xk}$):

$$
\begin{aligned}
\frac{dN_i}{dt} = & -N_i\left[\left(\frac{n}{2}-i\right)W_{i\to i+1}+\frac{1}{2}\left(\frac{n}{2}-i\right)\left(\frac{n}{2}-i-1\right)W_{i\to i+2}\right.\\
& \left.+\left(\frac{n}{2}+i\right)W_{i\to i-1}+\frac{1}{2}\left(\frac{n}{2}+i\right)\left(\frac{n}{2}+i-1\right)W_{i\to i-2}\right]+\\
& +N_{i-1}\left(\frac{n}{2}+i\right)W_{i-1\to i}+\frac{1}{2}N_{i-2}\left(\frac{n}{2}+i\right)\left(\frac{n}{2}+i-1\right)W_{i-2\to i}+\\
& +N_{i+1}\left(\frac{n}{2}-i\right)W_{i+1\to i}+\frac{1}{2}N_{i+2}\left(\frac{n}{2}-i\right)\left(\frac{n}{2}-i-1\right)W_{i+2\to i},
\end{aligned}
\tag{2}
$$

$i = I,\ I-1, \ldots, -I;$ n is the number of spins in the system.

If i is understood as I_x, then, as in ([4]), we assume that

$$W_{I_x\to I'_x} = W_{I'_x\to I_x} = u_{I_x\to I'_x},$$

since these transitions are not connected with the absorption of energy from the heat bath. If, however, i has the meaning I_z, then, analogously to ([2]), we shall take

$$W_{I_z\to I'_z} = w_{I_z\to I'_z}e^{\varkappa(I'_z-I_z)}, \qquad \varkappa = \frac{\mu H_0}{kT},$$

where $w_{I_z\to I'_z} = w_{I'_z\to I_z}$ and $\varkappa \ll 1$. Restricting ourselves to terms of order $\varkappa$, we find that system (2) becomes in this case

$$
\begin{aligned}
\frac{dN_{I_z}}{dt} = & -N_{I_z}\left[\left(\frac{n}{2}-I_z\right)w_{I_z\to I_z+1}+\frac{1}{2}\left(\frac{n}{2}-I_z\right)\left(\frac{n}{2}-I_z-1\right)w_{I_z\to I_z+2}\right.\\
& \left.+\left(\frac{n}{2}+I_z\right)w_{I_z\to I_z+1}+\frac{1}{2}\left(\frac{n}{2}+I_z\right)\left(\frac{n}{2}+I_z-1\right)w_{I_z\to I_z-2}\right]+\\
& +N_{I_z-1}\left(\frac{n}{2}+I_z\right)w_{I_z\to I_z-1}+\frac{1}{2}N_{I_z-2}\left(\frac{n}{2}+I_z\right)\left(\frac{n}{2}+I_z-1\right)w_{I_z\to I_z-2}+\\
& +N_{I_z+1}\left(\frac{n}{2}-I_z\right)w_{I_z\to I_z+1}+\\
& +\frac{1}{2}N_{I_z+2}\left(\frac{n}{2}-I_z\right)\left(\frac{n}{2}-I_z-1\right)w_{I_z\to I_z+2}+C_{I_z};
\end{aligned}
\tag{3}
$$

Fig. 1. Scheme of transitions in a system of three equivalent spins

Figure 1: Fig. 1. Scheme of transitions in a system of three equivalent spins

$$C_{I_z} = \varkappa \Big\{ \left(\frac{n}{2} + I_z\right) w_{I_z \to I_z - 1} \left(N_{I_z} + N_{I_z - 1}\right) - \left(\frac{n}{2} - I_z\right) w_{I_z \to I_z + 1} \left(N_{I_z} + N_{I_z + 1}\right) + \\ + \left(\frac{n}{2} + I_z\right)\left(\frac{n}{2} + I_z - 1\right) w_{I_z \to I_z - 2} \left(N_{I_z} + N_{I_z - 2}\right) - \\ - \left(\frac{n}{2} - I_z\right)\left(\frac{n}{2} - I_z - 1\right) w_{I_z \to I_z + 2} \left(N_{I_z} + N_{I_z + 2}\right) \Big\}.$$

The solution of system (3) for the case of two spins coincides with Solomon' s result (4), provided only that $N_i(t)$ at the initial instant differs from the equilibrium value by a quantity of order $\varkappa \ll 1$, as is the case under ordinary experimental conditions. But from (3) it is seen that in this case $C_{I_z} = \text{const}$ with accuracy up to terms of order $\varkappa^2$.

The formulation of the problem for three spins is illustrated in Fig. 1, where transitions between states with definite values of I_x are shown. The wave function of the state marked by an asterisk has the form

$$2^{-3/2}[\alpha(1) - \beta(1)][\alpha(2) -$$

$$-\beta(2)][\alpha(3) + \beta(3)].$$

Fig. 1. Scheme of transitions in a system of three equivalent spins

The transition probabilities are denoted in the following way:

$$W_{3/2 \to 1/2} = W_{-3/2 \to -1/2} = u_1; \qquad W_{3/2 \to -1/2} = W_{-3/2 \to 1/2} = u_2; \qquad W_{1/2 \to -1/2} = u_3.$$

In the case of transitions between states with definite I_z, the scheme remains the same; only, instead of u_i, one must write w_i. The wave function of the state marked by an asterisk in this case has the form

$$\beta(1)\beta(2)\alpha(3).$$

Denoting $W_{I_z \to I'_z}$ by w_j and solving system (3) for $C_{I_z} = \text{const}$, we have

$$N_{3/2} - N_{-3/2} = \frac{3}{4}\varkappa N - \frac{3(w_1 - w_2)}{s_1 + 3(w_1 + w_2)}\varkappa N C e^{s_1 t} - \frac{3(w_1 - w_2)}{s_2 + 3(w_1 + w_2)}\varkappa N D e^{s_2 t},$$

$$N_{1/2} - N_{-1/2} = \frac{1}{4}\varkappa N - \varkappa N C e^{s_1 t} - \varkappa N D e^{s_2 t}, \tag{4}$$

where

$$s_{1,2} = -2\left[w_1 + w_2 + w_3 \pm \sqrt{w_1^2 + w_2^2 + w_3^2 - (w_1 w_2 + w_1 w_3 + w_2 w_3)}\right], \tag{5}$$

N is the total number of systems. Hence we find:

$$\langle M_z(t)\rangle = 3\mu\left(N_{3/2} + N_{1/2} - N_{-1/2} - N_{-3/2}\right) =$$

$$= \mu N_0 \varkappa \left\{1 - \frac{s_1 + 6w_1}{s_1 + 3(w_1 + w_2)} C e^{s_1 t} - \frac{s_2 + 6w_1}{s_2 + 3(w_1 + w_2)} D e^{s_2 t}\right\}, \tag{6}$$

$N_0 = nN$ is the total number of nuclei in the sample.

Solving system (2), with the notation for $u_{I_x \to I'_x}$ used in Fig. 1, we obtain for $\langle M_x\rangle$ an expression analogous to (6), with the difference that w_j are everywhere replaced by u_j, and the first term in braces is absent ($\langle M_x(\infty)\rangle = 0$).

From (5) and (6) it is seen that the relaxation process of each component of the magnetic moment is, generally speaking, described by two exponentials. In the special case when $w_{I_z \to I'_z}$ (if M_z is meant) and $u_{I_x \to I'_x}$ (if M_x is meant) depend only on $\Delta I_{z,x}$ and do not depend on $I_{z,x}$, from (5) and (6) there follows the usual exponential law of relaxation, and moreover—

the longitudinal and transverse relaxation times are determined from the equalities

$$\frac{1}{T_1} = 2(w_1 + 2w_2); \qquad \frac{1}{T_2} = 2(u_1 + 2u_2).$$

For a system of four spins (in the same particular case), equations (2) and (3) again give a simple exponential law, with

$$\frac{1}{T_1} = 2(w_{\Delta I=1} + 3w_{\Delta I=2}); \qquad \frac{1}{T_2} = 2(u_{\Delta I=1} + 3u_{\Delta I=2}).$$

Using the methods proposed in Refs. ([2,5]), Solomon ([4]) calculated the transition probabilities in a system of two spins. It is easy to see that, in an analogous way, one can find w_j, u_j also for systems consisting of a larger number of spins.

Let us write out the results of calculating the transition probabilities for a system of three spins:

$$w_1 = \frac{39}{80}k^2\frac{\tau_c}{1+\omega^2\tau_c^2}; \qquad w_2 = \frac{3}{5}k^2\frac{\tau_c}{1+4\omega^2\tau_c^2}; \qquad w_3 = \frac{9}{80}k^2\frac{\tau_c}{1+\omega^2\tau_c^2};$$

$$u_1 = \frac{39}{160}k^2\left[\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{\tau_c}{1+4\omega^2\tau_c^2}\right];$$

$$u_2 = \frac{k^2}{80}\left[9\tau_c+\frac{12\tau_c}{1+\omega^2\tau_c^2}+\frac{\tau_c}{1+4\omega^2\tau_c^2}\right];$$

$$u_3 = \frac{9}{160}k^2\left[\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{\tau_c}{1+4\omega^2\tau_c^2}\right],$$

where $k=\gamma^2\hbar/b^3$, b is the distance between nuclei.

For $\tau_c\omega \ll 1$ we find $w_j = u_j$, i.e., the relaxation processes of the longitudinal and transverse components of the magnetic moment proceed in the same way, in agreement with the general theory ([1]):

$$u_1 = w_1 = {}^{39}/_{80}\,k^2\tau_c, \qquad u_2 = w_2 = {}^{3}/_{5}\,k^2\tau_c, \qquad u_3 = w_3 = {}^{9}/_{80}\,k^2\tau_c.$$

Substituting these values into (4), (5), and (6), and assuming

$$N_{3/2}(0) = N_{1/2}(0) = N_{-1/2}(0) = N_{-3/2}(0),$$

we find approximately:

$$\langle M_z(t)\rangle = M_0\left(1-0.62e^{-3.2k^2\tau_c t}-0.38e^{-1.6k^2\tau_c t}\right).$$

The contributions of both terms are of the same order, and neither of them can be discarded.

The results obtained must be taken into account in interpreting experiments on the relaxation of nuclear spins of molecules containing the groups CH_3, H_3O^+, etc., in the case when "internal" relaxation plays a noticeable role.

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REFERENCES

1. R. Kubo, K. Tomita, J. Phys. Soc. Japan, **9**, 888 (1954).
2. N. Bloemberger, E. M. Purcell, R. V. Pound, Phys. Rev., **73**, 679 (1948).
3. L. Giulotto, G. Chiarotti, G. Cristiani, J. Chem. Phys., **22**, 1143 (1954).
4. I. Solomon, Phys. Rev., **99**, 559 (1955).
5. A. Abragam, R. V. Pound, Phys. Rev., **92**, 953 (1953).

Note: Figure translations are in progress. See original paper for figures.