

## ON THE THEORY OF LATTICE SPIN RELAXATION

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A theoretical discussion is given of relaxation in systems containing two types of interacting spins with very different values of their lattice relaxation times. The correlation function method is applied to the fast relaxing spin variables of the system.

## 1. INTRODUCTION

THE lattice relaxation of nuclear spins in diamagnetic crystals and liquids is the result of the modulation by heat motion of the magnetic dipole-dipole interactions between spins or of the interaction of the nuclear quadrupole moment with the non-uniform field of the charges surrounding the nucleus. Waller<sup>1</sup> constructed a theory of relaxation based on the magnetic interaction of particles for cubic crystals. Bloembergen et al.<sup>2</sup> were the first to give a theoretical consideration of relaxation through dipole interactions between particles in liquids. It was later shown that Bloembergen's theory also describes satisfactorily relaxation processes for spins in molecular diamagnetic crystals, for instance, in solid hydrogen.<sup>3</sup>

It is very characteristic for lattice relaxation in liquids that the changes in the coordinates which describe the heat motion of the system are fluctuating in time. If one considers the relaxation through the dipole interactions between particles, such randomly changing coordinates are the distances between the particles and the angles which the radius vector makes with the axes of the laboratory system of coordinates. In the paper<sup>4</sup> by Al'tshuler and the author devoted to the longitudinal relaxation of electron spins of paramagnetic ions which in a solution form octahedral complexes of the form  $XY_6$  ( $X$  is the paramagnetic ion;  $Y$  is a molecule of the solvent or an anion) we considered as such randomly changing functions of the time the normal coordinates for the vibrations of the complex. The theoretical discussion of the relaxation process is facilitated by the fact that only a small number from the vast number of lattice coordinates will interact with each particular spin. Thus, with the spin of the  $X$  ion in the  $XY_6$  complex only the coordinates of the normal vibrations of the complex will interact. The influence of the other "thermal" degrees of freedom of the

system is manifest in producing the random character of the changes in all the other coordinates. The period of correlation for consecutive values for different coordinates must be determined separately and in each case individually.

In this paper we consider the relaxation process for spins of one kind which are connected through exchange of magnetic dipole forces with spins of another kind; the latter are assumed to relax independently of the former and very rapidly. Such a situation is realized in the following cases. The lattice relaxation of nuclei with a quadrupole moment takes place in molecular liquids through the interaction of the quadrupole moment with the electrical field of the surrounding charges, is fast, and is independent of the interaction with the spins of the other nuclei. At the same time, the relaxation of spins of nuclei without a quadrupole moment (protons) goes slowly and may depend strongly on the interaction with the spin of a nucleus with a quadrupole moment. This is confirmed by experiments studying the highly resolved nuclear magnetic resonance spectra: those lines in the spectrum which are caused by the protons which are chemically connected with the  $N^{14}$  nitrogen atoms are appreciably wider than the lines due to the other protons.<sup>5</sup> Another interesting example is the relaxation of the spins of the nuclei of paramagnetic atoms which takes place through the hyperfine interaction with the spins of the electron shells of the same atom. The lattice relaxation of the electron spin takes place independently of its interaction with the nuclear spins and with an appreciably larger speed than the relaxation of the nuclear spin. The situation is similar to the one discussed both in paramagnetic crystals and in liquids: the relaxation of the nuclear spins of diamagnetic atoms in such media takes place due to their coupling with the spins of the paramagnetic atoms, as is found out in the study of proton relaxation.<sup>6</sup>

We consider the fast relaxing spin variables of the system as randomly changing quantities, which can take on a number of discrete values, and treat them in the same way as fluctuating lattice coordinates that interact with relaxing spins. Such a representation of a part of the spin variables of the system simplifies the theoretical study of the relaxation process very greatly by making it very clear. From a thermodynamical point of view such a representation is completely permissible: it simply means assigning to the lattice structure those spins which interact strongly with it and separating into the "spin system" structure the spins that are weakly coupled to the lattice. It is clear that one must consider the lattice relaxation times of those spins which are assigned to the lattice as their correlation times. Since these spin variables are random functions of the time, we apply to them the method of correlation functions — both in the case of liquids and in the case of crystals.

Rivkind<sup>6</sup> and slightly later Bloembergen<sup>7</sup> have stated some of the methods used in our paper for the nuclear relaxation process to explain the experimental results on proton relaxation in liquid solutions of paramagnetic salts. Rivkind assumed that in a certain volume around the paramagnetic ion (in the solvate atmosphere of the ion) the mobility of the molecules of the solvent is limited and that in that volume the "change in quantization of the electron spin relative to an external static magnetic field" is a very fast process. Rivkind succeeded in explaining qualitatively his own experimental results by substituting in the formulae of Bloembergen et al.<sup>2</sup> for the electron spin relaxation time  $\tau_e$  the correlation time for the thermal motion of the particles in the liquid  $\tau_c$ . Bloembergen<sup>7</sup> assumed the existence of an exchange interaction of the form  $A(\mathbf{I} \cdot \mathbf{S})$  between the spin of a proton in the first hydrate shell of the ion and the spin of the paramagnetic ion; such an assumption makes it possible to explain the difference between the times  $T_1$  and  $T_2$  for protons in solutions of  $Mn^{2+}$ ,  $Gd^{3+}$ , and  $Fe^{3+}$  ions.

## 2. PROTON-RESONANCE QUADRUPOLE LINE BROADENING IN LIQUIDS

The indirect interaction between spins  $\mathbf{I}_i$  and  $\mathbf{I}_j$  belonging to nuclei in the structure of one molecule arises from taking into account the exchange overlap of the electron shells of atoms  $i$  and  $j$ . The energy of the resulting spin-spin interaction can be written in the form

$$\mathcal{H} = \hbar \sum_{i < j} A_{ij} \mathbf{I}_i \mathbf{I}_j \quad (1)$$

The Hamiltonian (1) is invariant under rotations of the system of coordinates since a rotation of the molecule does not change its energy and therefore does not produce relaxation. We pick out from among all the nuclear spins in one separate molecule the spin  $\mathbf{I}_k$  of the nucleus  $k$  which relaxes through quadrupole interaction with an appreciably greater speed than the spins of the other nuclei of the molecule. In accordance with what we have said a moment ago we can assume the spin  $\mathbf{I}_k$  to be a variable which varies randomly with time; we can then take from (1) the part which depends on time and which leads to the relaxation of the spins  $\mathbf{I}_j$ :

$$\mathcal{H}'(t) = \hbar \sum_i A_{ik} [I_{zi} I_{zk}(t) + I_{xi} I_{xk}(t) + I_{yi} I_{yk}(t)]. \quad (2)$$

The correlation times of the quantities  $I_{zk}$  and  $I_{xk}$ ,  $I_{yk}$  will be equal to the longitudinal ( $\tau_z$ ) and transverse ( $\tau_x$ ,  $\tau_y$ ) relaxation times of the spin  $\mathbf{I}_k$ , respectively. For a liquid  $\tau_x = \tau_y = \tau_z = \tau_k$  because of the fast thermal motion of the particles.

We shall denote the wave functions of the proton spin in a strong magnetic field by  $\varphi_i(I_z = \frac{1}{2}) = |+\rangle$  and  $\varphi_i(I_z = -\frac{1}{2}) = |-\rangle$ ; the wave functions of  $\mathbf{I}_{xi}$  corresponding to the eigenvalues  $I_{xi} = \frac{1}{2}$  and  $-\frac{1}{2}$  can then be written in the  $I_z$  representation in the form of linear combinations

$$\begin{aligned} \psi_i(\alpha) &= (|+\rangle + |-\rangle) / \sqrt{2}, \\ \psi_i(\beta) &= (|+\rangle - |-\rangle) / \sqrt{2}. \end{aligned} \quad (3)$$

The probability that the system makes during 1 sec a transition from the state  $l$  to a state  $k$  under the action of the perturbation  $\mathcal{H}'(t)$  can then be evaluated from the equation<sup>8</sup>

$$W_{lk} = \frac{1}{i\hbar^2} \left| \int_0^t \langle l | \mathcal{H}'(t') | k \rangle e^{-i\omega_{lk}t'} dt' \right|^2. \quad (4)$$

The matrix elements corresponding to a transition between states of the spins  $\mathbf{I}_i$  and  $\mathbf{I}_k$  are equal to  $\langle + | \mathcal{H}'(t') | - \rangle = \frac{1}{2} A\hbar [I_{kx}(t') - i I_{ky}(t')]_{m_k, m_k+1}$ ,

$$\omega_{lk} = \omega_i - \omega_k; \quad (5)$$

$$\langle \alpha | \mathcal{H}'(t') | \beta \rangle = \frac{1}{2} A\hbar I_{zk}(t'), \quad \omega_{lk} = 0. \quad (6)$$

The matrix element (5) corresponds to a simultaneous change in orientation of the proton spin and the spin of the nucleus  $k$ ; the generalized kinetic moment of the system is then conserved.

The lifetime of the proton spin in a state characterized by a well determined value of  $I_z$  is commonly called the longitudinal relaxation time  $T_1$ , and the life time in a state with a well defined value of  $I_x$ —the transverse relaxation time  $T_2$ .

Using the well known relation between transition probabilities and relaxation times<sup>2</sup> we get from (4), (5), and (6):

$$\frac{1}{2T_1} = W_{+-} = \frac{A^2}{4t} \left| \int_0^t [I_{kx}(t') - iI_{ky}(t')]_{m_k, m_k+1} e^{-i(\omega_i - \omega_k)t'} dt' \right|^2, \quad (7)$$

$$\frac{1}{2T_2} = W_{\alpha, \beta} = \frac{A^2}{4t} \left| \int_0^t I_{zk}(t') dt' \right|^2 \quad (8)$$

We shall perform the further evaluations of the integrals by taking an exponential law for the change of the correlation functions of the quantities  $I_{zk}$ ,  $I_{xk}$ ,  $I_{yk}$  with the same correlation time  $\tau_k$ :

$$\langle I_{zk}(t') I_{zk}(t' + \tau) \rangle = \frac{1}{3} I_k(I_k + 1) \exp(-\tau / \tau_k); \quad (9)$$

$$\langle I_{xk}(t') I_{xk}(t' + \tau) + I_{yk}(t') I_{yk}(t' + \tau) \rangle = \frac{2}{3} I_k(I_k + 1) \exp(-\tau / \tau_k). \quad (10)$$

The relaxation times  $T_1$  and  $T_2$  obtained in this way are quantities which are averaged over all the protons in the specimen:

$$T_1^{-1} = \frac{2}{3} A^2 I_k(I_k + 1) \tau_k / [1 + (\omega_i - \omega_k)^2 \tau_k^2]; \quad (11)$$

$$T_2^{-1} = A^2 I_k(I_k + 1) \tau_k / 3. \quad (12)$$

If the condition  $A\tau_k \lesssim 1$  is fulfilled Eqs. (11) and (12) are applicable. This condition is similar to inequality (6.24) from the paper by Kubo and Tomita<sup>9</sup> and is the criterion that one broad line exists instead of a spectrum of discrete lines; if the inequality is strengthened to  $A\tau_k \ll 1$ , a "narrowing of the line by motion" arises. Such a change occurs, for instance, in the spectrum of the hyperfine structure lines of electron resonance under the action of a fast exchange motion in the spin system,<sup>10</sup> and a narrowing of the nuclear resonance lines due to a fast molecular motion in liquids has been theoretically established already in reference 2. Equations (11) and (12) demonstrate a new example of similar changes in a spectrum produced by the fast relaxation of one of the interacting spins. If  $A > \tau_k^{-1}$  the proton line will be split into  $2I_k + 1$  components; if  $A \lesssim \tau_k^{-1}$  the components merge together, forming one line; and if  $A \ll \tau_k^{-1}$  the proton lines narrow because of the fast relaxation of the spin  $I_k$ .

Let us now make a numerical estimate of the relaxation times  $T_1$  and  $T_2$ . The relaxation time  $\tau_k$  of the spins which are coupled with the thermal motion through the nuclear quadrupole moment is in liquids  $\sim 10^{-4}$  sec,  $|\omega_i - \omega_k| = 10^7$  cps. The value of the spin-spin coupling constant depends

on the number of chemical bonds which separate the nuclei and is of the order of 200, 50, and 10 cps if the proton and the nucleus  $k$  are separated by one, two, and three chemical bonds, respectively.<sup>11</sup> If the proton is directly joined to an atom, the nucleus of which possesses a quadrupole moment, the values calculated with Eq. (11) are  $T_1 = 10^5$  sec and  $T_2 = 0.3$  sec. The contribution from the spin-spin coupling of the protons and the other nuclei to the longitudinal relaxation is thus extremely small compared to the contribution to this relaxation from the dipole-dipole interaction of the nuclei. It is clear that the broadening of the "spread out" proton lines is caused by the strengthening of the transverse relaxation of the proton spins, i.e., by the occurrence of an unresolved structure due to the spins of nuclei which possess a quadrupole moment; this broadening is of the order  $1/T_2 \approx 10$  cps which agrees well with the observed line width. Since the longitudinal relaxation of the protons which give a broad line takes place through magnetic dipole interactions, the ratio  $T_1/T_2$  for them must differ considerably from unity.

Equation (12) makes it possible to determine the value of the spin-spin coupling constant  $A_{jk}$  from the broadening of the proton lines produced by this coupling. This method is possibly unique since the spin-spin coupling with a fast relaxing spin does not produce a splitting of the lines. We must note that the produced broadening depends essentially on the relaxation time of the spins  $I_k$ .

### 3. RESONANCE PHENOMENA IN SPIN-LATTICE RELAXATION

The systems considered by us contain two kinds of spins: the spins of the first kind have a long lattice relaxation time, and the spins of the second kind have an appreciably shorter time. In such systems the relaxation time of the first spins is shortened when the energy intervals between the sublevels of these and of the other spins are the same. This experimental fact can be explained using Eq. (11). We shall put  $\omega_i = \omega_k$ ; we have then:

$$T_1^{-1} = \frac{2}{3} A^2 I_k(I_k + 1) \tau_k. \quad (18)$$

The quantity  $A$  characterizes the interaction energy of spins with different relaxation times. In this way we get for the case of a coupling between protons and nuclei with a quadrupole moment, which we considered above, for the same values of the parameters,  $T_1 \approx 0.1$  sec. The value of  $T_1$  which characterizes the relaxation of protons through dipole interactions is in molecular liquids about 10 sec. The time  $T_1$  can thus be decreased

by a factor 100 in the case of "relaxation resonance" for a proton and a nucleus relaxing through a quadrupole moment.

From this example the nature of relaxation resonance is clear although it is apparently not possible to realize it, because in liquids the quadrupole interaction of a nucleus does not lead to a constant contribution in the splitting of the spin levels and the intervals between those are determined by the Zeeman energy of the spins. The intervals  $\Delta E(m_i, m_i \pm 1)$  and  $\Delta E(m_k, m_k \pm 1)$  between pairs of levels of two spins  $I_i$  and  $I_k$  belonging to nuclei of the foregoing two kinds, which are unequal for one value of the field, may become equal for another value of the field only if there is already a splitting of the levels: the quadrupole splitting of nuclear spin levels in diamagnetic crystals or the electrical splitting of electron spin levels in paramagnetic crystals. It is clear that the strongest interaction between the nuclear spins in diamagnetic crystals will be the magnetic dipole interactions. The latter, and also an exchange interaction of the form (1), can provide a transfer of energy absorbed by one kind of spins to spins of the other kind which are strongly coupled to the thermal motion in the lattice. The absorbed energy goes over from the latter into the thermal motion of the particles in the system.

If such a mechanism is present resonance phenomena can arise in relaxation processes. Such an occurrence was observed experimentally in crystals of paradichlorobenzene.<sup>12</sup> In these crystals the proton lattice relaxation time  $T_{1p}$  was greatly decreased at the moment when the proton resonance frequency  $\nu_p$  became the same as the interval  $\nu_Q$  between a pair of nuclear spin levels of chlorine. We can estimate the proton relaxation time  $T_{1p}$  when there is relaxation resonance with the chlorine nucleus:  $\nu_p = \nu_Q$ . The matrix element corresponding to the transition ( $m_p = \frac{1}{2}$ ,  $m_k$ ;  $m_p = -\frac{1}{2}$ ,  $m_k + 1$ ) which is produced by the dipole interaction is equal to<sup>2</sup>

$$\langle \frac{1}{2}, m_k | V_{ik} | -\frac{1}{2}, m_k + 1 \rangle = -\frac{1}{4} g_i g_k \beta_N^2 r_{ik}^{-3} (1 - 3 \cos^2 \theta_{ik}) \times \sqrt{(I_k - m_k)(I_k + m_k + 1)}. \quad (19)$$

Here  $g_i$  and  $g_k$  are the  $g$ -factors of the nuclei  $i$  and  $k$ , while  $\beta_N$  is the nuclear magneton. The angle  $\theta_{ik}$  and the distance  $r_{ik}$  between the nuclei are constant quantities since the crystal retains its orientation in a static magnetic field. If  $\omega_i = \omega_k$  we get instead of Eq. (18) the equation

$$W_{+-} = \hbar^{-2} (g_i g_k \beta_N^2 r_{ik}^{-3})^2 (1 - 3 \cos^2 \theta_{ik})^2 I_k (I_k + 1) / 12. \quad (20)$$

The energy of the dipole interaction between two nuclear spins is of the order of  $10^{-23}$  erg and the lattice relaxation time of Cl nuclei at room temperature is of the order  $10^{-2}$  sec. Substituting these quantities into (20) we get  $T_{1p} = 10^{-1}$  sec for the proton relaxation time under the conditions of relaxation resonance, while  $T_{1p}$  would be of the order of a minute if there were no resonance. The relaxation resonance observed in crystals containing two kinds of paramagnetic ions with different lattice relaxation times is apparently caused also by the dipole-dipole interaction between them (the effect is observed in crystals containing the ions<sup>13</sup>  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  and the ions<sup>14</sup>  $\text{Gd}^{3+}$  and  $\text{Ce}^{3+}$ ). The matrix element of the energy of the dipole interaction between two particles is in that case  $|V_{ij}| \sim 10^{-17}$  erg; we can take  $\tau_e = 10^{-11}$  sec for the lattice relaxation time of spins tightly coupled to the lattice. We then get for relaxation times of spins, which under normal conditions have a long time  $T_1$ , under resonance conditions,

$$T_{1\text{res}}^{-1} \sim |V_{ij}|^2 \hbar^{-2} \tau_e \sim 10^9 \text{ sec}^{-1} \quad (20a)$$

It is clear that one can estimate using Eq. (20a) very short relaxation times  $\tau_e$  which cannot be measured by other methods; to do this it is necessary to determine the very long time  $T_{1\text{res}}$  and to estimate the magnitude of the matrix element (19). We note that the applicability of Eqs. (20) and (20a) is determined by criteria which are similar to those stated when we discuss Eqs. (11) and (12).

#### 4. LATTICE RELAXATION OF NUCLEI CONNECTED WITH PARAMAGNETIC ATOMS

One can study also the lattice relaxation of spins of nuclei of paramagnetic atoms in a way similar to the one above. This problem was considered by perturbation theory methods in the papers by the author<sup>15</sup> and Bashkirov.<sup>16</sup> The electron spin of paramagnetic ions in condensed media relaxes with a velocity  $1/\tau_e$  which is appreciably larger than the velocity of the relaxation of the nuclear spin of the paramagnetic ion. The relaxation of the latter takes place through a hyperfine interaction with electron spins. The components of the electron spin entering into the hyperfine interaction energy can be considered to be quantities which change rapidly and in a random fashion:

$$H'(t) = A I_z S_z(t) + B [I_x S_x(t) + I_y S_y(t)]. \quad (21)$$

The probability for a relaxation transition between the sublevels of the nuclear spin energy can be expressed through a formula analogous to (7):

$$W_{m, m-1} = \frac{B^2}{4\hbar^2 t} \left| \int_0^t [S_x(t') - iS_y(t')]_{M-1, M} e^{-i(\omega_N - \omega_S)t'} dt' \right|^2 \times (I+m)(I-m+1). \quad (22)$$

If we consider a medium with a small concentration of magnetic particles we can neglect the dipole-dipole and exchange effects and assume the correlation times of the quantities  $S_x$ ,  $S_y$ , and  $S_z$  to be the spin-lattice relaxation time of the electron spin  $\tau_e$ . We get then from (22), similar to (11):

$$W_{m, m-1} = B^2 (I+m)(I-m+1) \times S(S+1) \tau_e / 3\hbar^2 (1 + (\omega_N - \omega_S)^2 \tau_e^2). \quad (23)$$

In the practically important case  $\omega_S = g_e \beta H_0 / \hbar > \tau_e^{-1}$ ,  $\omega_S \gg \omega_N$  we have

$$W_{m, m-1} = B^2 (I+m)(I-m+1) \times S(S+1) / 3\hbar^2 (g_e \beta H_0)^2 \tau_e, \quad (24)$$

which agrees with the result of the calculation by the perturbation-theory method.<sup>13,14</sup> We can also use Eqs. (23) and (24) to evaluate the relaxation of the nuclei of paramagnetic atoms in liquids. The evaluation of  $\tau_e$  for that case was given in reference 4.

In paramagnetic media at high temperatures the condition  $\omega_e < \tau_e^{-1}$  is also often realized, when it becomes impossible to observe magnetic resonance. Under those conditions

$$W_{m, m-1} = B^2 (I+m)(I-m+1) \times S(S+1) \tau_e \hbar^{-2} / 3 \sim 10^7 \text{ sec}^{-1}, \quad (25)$$

( $B = 3 \times 10^{-3} \text{ cm}^{-1}$ ,  $\tau_e = 3 \times 10^{-11} \text{ sec}$ ). Such a fast nuclear relaxation can show up when one studies angular correlations of the radioactivity from nuclei: the angular correlation between the directions of two consecutive processes of emission by the nucleus will occur within a time interval<sup>8</sup>  $\tau \leq W_{m-1, m}^{-1}$ .

The transverse relaxation time of the spins of the nuclei of paramagnetic ions is determined by a formula similar to (12):

$$T_{2N}^{-1} \approx 4A^2 \hbar^{-2} S(S+1) I(I+1) \tau_e / 9. \quad (26)$$

One can interpret this quantity as follows. The nuclear resonance line for paramagnetic atoms has a fine structure of  $2I(2S+1)$  components in accordance with the fact that for each of the  $2S+1$  electron spinlevels of each atom there are  $2I$  energy intervals  $\Delta E_{m, m-1}$  between which nuclear magnetic dipole transitions are allowed. Due to the fast relaxation of the electron spin in this

spectrum there occurs a change which is similar, for instance, to the change in the hyperfine structure of the electron resonance lines caused by the fast exchange motion of the spins: if  $A/\hbar \gg \tau_e^{-1}$  all lines will be observed to be separate (the conditions for Eq. (26) are then, generally speaking, not fulfilled); if  $\hbar^{-1} A \approx \tau_e^{-1}$ , the components of the line merge together giving a line of width  $\Delta\nu \sim T_{2N}^{-1} + T_{1N}^{-1}$ ; finally, if  $A/\hbar \ll \tau_e^{-1}$ , a strong narrowing of the nuclear resonance line sets in, owing to the fast lattice relaxation of the electron spin. It would be very interesting to carry out an experiment on nuclear resonance in paramagnetic atoms under the conditions of a strong relaxation narrowing. Such experiments, in our opinion, are most easily carried out on impurity paramagnetic atoms in crystalline silicon. It is clear that the experiments can be successful if the relaxation times of the nuclear spins  $T_{1N}$  and  $T_{2N}$  are not shorter than  $10^{-5} \text{ sec}$ . For a Li atom in silicon<sup>17</sup>  $A/\hbar = B/\hbar = 0.85 \text{ Mcs}$ . We then get from Eqs. (24) and (26) the values  $T_{1N} = 2 \times 10^{-2} \text{ sec}$  and  $T_{2N} = 1.4 \times 10^{-5} \text{ sec}$ , if  $\omega_S = 10^{10} \text{ cps}$  and  $\tau_e = 10^{-8} \text{ sec}$  (the time  $\tau_e$  can be decreased by increasing the temperature of the crystal).

We can similarly establish the conditions for a strong narrowing of the magnetic resonance line for nuclei of paramagnetic atoms (ions) of the iron group and of the rare earths in crystals of salts.

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