

ON THE NUCLEAR ORIENTATION ASSOCIATED WITH A SATURATED FORBIDDEN RESONANCE AND WITH DOUBLE RESONANCE

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Parameters f_k , characterizing the degree of nuclear orientation, are calculated for orientation produced by saturating a forbidden resonance and for a double resonance. Modifications of the double resonance method are examined.

1. During 1956 and 1957, Feher and Jeffries proposed two new methods for obtaining polarized nuclei. Jeffries' method¹ is based on the saturation of a forbidden paramagnetic resonance, while Feher's uses double resonance.² Experimentally both methods have led to observable polarizations.³⁻⁸ In this paper we calculate the quantities f_k which characterize the degree of orientation,⁹ and discuss the two methods.

2. Let the sample be a paramagnetic salt or silicon (or germanium) doped with nuclei having valence five or three. We assume that the nuclei of the paramagnetic ions, or of the impurity atoms, have spin, and if the sample is a paramagnetic salt, assume that the electron cloud in the paramagnetic ion has effective spin $\frac{1}{2}$. For silicon or germanium, we assume that the temperature is so low that the impurity atoms are not ionized.

Such a system can be thought of as a set of electron clouds with spin S , and a set of nuclei with spin I , the electron clouds being those of the paramagnetic ions (with an extra electron or hole). In a strong magnetic field, the energy levels of such a system are given by the equation

$$E_{Mm} = Mg\beta H + KMm + O(B^2 j g\beta H, g_I \beta H, P). \quad (1)$$

The notation is standard (in particular, M and m are the projections of the electron and nuclear spins respectively on the axis of quantization).

Figure 1 shows the energy levels when all terms can be neglected, except the Zeeman energy of spin S (as is the case when computing Boltzmann factors). For conciseness, the state $M = \frac{1}{2}$, m will

be denoted by m' , while the state $M = -\frac{1}{2}$, m will be denoted by m .

The ordinary paramagnetic resonance lines induced by the alternating field are due to transitions with selection rules $\Delta M = \pm 1$, $\Delta m = 0$, and energy differences given approximately by $g\beta H + Km$. Those transition which have selection rules $\Delta M = 0$, $\Delta m = \pm 1$ and energy differences $\approx K/2$ correspond to nuclear magnetic resonance (more precisely, there will be correction terms of order $B^2/g\beta H$, $g_I \beta H$, and P).

The forbidden paramagnetic resonance lines correspond to transitions with $\Delta M = \pm 1$, $\Delta m = \pm 1$ and energy differences of about $g\beta H + K(m + \frac{1}{2})$.^{10,11} In particular, if the spin Hamiltonian is axially symmetric about the direction of the magnetic field, then transitions will occur with $\Delta M = -\Delta m = \pm 1$ (provided that the alternating field has a non-zero component along the main field). In other cases, other transitions will be possible, with selection rules $\Delta M = \Delta m = \pm 1$.

There are also relaxation transitions, as follows:

1. Vertical transitions: $\Delta M = \pm 1$, $\Delta m = 0$ (purely electronic relaxation).
2. Horizontal transitions: $\Delta M = 0$, $\Delta m = \pm 1$ (purely nuclear relaxation).
3. Flip-flop transitions: $\Delta M = -\Delta m = \pm 1$.
4. Flip-flip transitions: $\Delta M = \Delta m = \pm 1$.
5. Quadratic transitions: $\Delta M = 0$, $\Delta m = \pm 2$.

We note that the contact interaction between electronic and nuclear spins can give only flip-flop transitions. The dipole-dipole interaction between these spins can give transitions of type 1, 2, 3, and

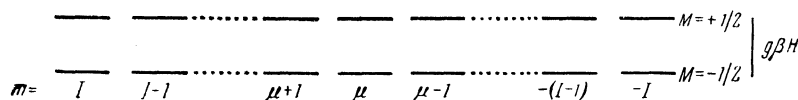


FIG. 1

4. The quadrupole interaction between the nucleus and the electric field of the electron cloud gives rise to transitions of types 5 and 2.

3. Jeffries' method is based on saturating the forbidden paramagnetic resonance and can be used when the vertical relaxation is predominant over other modes. These conditions are always fulfilled for paramagnetic salts, and also for silicon, doped for example, with As⁷⁶ or Sb¹²². In general, it need not be more difficult to saturate a forbidden resonance than an allowed one. Forbidden transitions are less likely than allowed ones, but on the other hand the relaxation rate of the forbidden transition is usually smaller than that of an allowed one.

Returning to Fig. 1, suppose that one of the transitions $\Delta M = -\Delta m = \pm 1$ is saturated (in particular, the transition $\mu \leftrightarrow \mu - 1'$ where μ can take on values $I, I-1, \dots, -I+1$). Figure 2 shows three pairs of levels from Fig. 1, the levels corresponding to nuclear spin projections $\mu+1, \mu$ and $\mu-1$. Let $W(\mu)$ be the probability (per unit

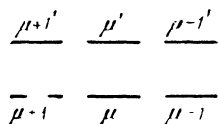


FIG. 2

time) that the alternating field induces the transitions $\mu \leftrightarrow \mu - 1'$. In this case there are three characteristic times: the time $T_r = 1/W(\mu)$ required for the alternating field to cause one transition (on the average), the vertical relaxation time T_e , and the nuclear relaxation time T_n (i.e., the relaxation time associated with changing m).

Suppose these times satisfy the inequalities

$$T_r \ll T_e \ll T_n$$

In this case, in a relaxation time of order T_r , the alternating field will make the populations of the states μ and $\mu - 1'$ equal. In a time of order T_e equilibrium will be established between the states μ and μ' , and also between $\mu - 1$ and $\mu - 1'$. In a time T_n , full equilibrium will be established. We will use indices $r, e,$ and n to distinguish between the orientation parameters corresponding to these three stages.

It is easy to obtain the results*

$$f_1^r = -\frac{\tanh \delta}{2I(2I+1)}, \quad f_2^r = -\frac{3(2\mu-1)}{2I(2I+1)(2I-1)} \tanh \delta; \quad (2)$$

$$f_1^e = -\frac{\tanh \delta}{I(2I+1)}, \quad f_2^e = -\frac{3(2\mu-1)}{I(2I+1)(2I-1)} \tanh \delta, \quad (3)$$

where $\delta = g\beta H/2kT$.

*The f_k are normalized so that their maximum value is 1.⁹

It is also easy to find an expression for the mean value of m^k (where k is an arbitrary, positive integer):

$$\langle m^k \rangle - \langle m^k \rangle_0 = -\alpha \tanh \delta \cdot [\mu^k - (\mu - 1)^k] / (2I + 1), \quad (4)$$

In Eq. (4), the index zero denotes no saturation, α is $\frac{1}{2}$ in the first stage (r), and 1 in the second (e). From this last formula, it is easy to find the values of $f_3, f_4,$ etc in the first two stages. It turns out that

$$f_k^e = 2f_k^r \quad (5)$$

for all k .

Buishvili¹² has obtained the following expressions for f_1^n and f_2^n , on the assumption that the nuclear relaxation is due to the contact interaction only:

$$f_1^n = -\frac{[I(I+1) - \mu(\mu-1)] \sinh \delta}{I[(I+1-\mu)e^{-\delta} + (I+\mu)e^{\delta}]} ;$$

$$f_2^n = -\frac{[I(I+1) - \mu(\mu-1)](2\mu-1) \sinh \delta}{I[(I+1-\mu)e^{-\delta} + (I+\mu)e^{\delta}](2I-1)}. \quad (6)$$

What is the physical meaning of these results? f_1 is negative because the alternating field causes more transitions from μ to $\mu - 1'$ than the other way around (the population of the state μ being larger before saturation), with the result that the mean value of the projection of the nuclear spin decreases. Similarly, it is easy to see why f_2 is proportional to $1 - 2\mu$. Indeed, it can be shown that if $\mu > \frac{1}{2}$, then $\langle m^2 \rangle$ decreases when the resonance $\mu \leftrightarrow \mu - 1'$ is saturated, while if $\mu < \frac{1}{2}$, then $\langle m^2 \rangle$ increases.

From the formulas for f_1 it follows that

$$|f_1^r| < |f_1^e| < |f_1^n|,$$

which is also not difficult to understand. After the populations of the states μ and $\mu - 1'$ have become equal, vertical relaxation occurs between the states μ' and μ , as well as $\mu - 1'$ and $\mu - 1$, followed by transitions $\mu \rightarrow \mu - 1'$ induced by the alternating field. When nuclear relaxation enters the picture, there will be transitions between the levels on the left in Fig. 1 to those on the right. All this increases the population of states with small m .

If the inequality $T_r \ll T_e$ does not hold, equilibrium under the alternating field and under vertical relaxation will be established simultaneously, and formulas (2) will not be applicable. If the inequality $T_e \ll T_n$ is violated, vertical and nuclear relaxations will establish equilibrium at the same time, and formula (3) will no longer hold.

The equations (6) remain valid in all cases, except that if the transitions $\mu \leftrightarrow \mu - 1'$ are not completely saturated (which will be the case if T_r

$\sim T_N$), then the right hand sides must be multiplied by a factor $s(\mu)$ which tells how saturated is the transition.¹²

At first sight it would appear that to get maximum polarization, T_N should be as small as possible. However, this is not the case because when the nuclei relax quickly it is hard to saturate the forbidden transition.

Finally, it is easy to show that if the forbidden transition $\mu \leftrightarrow \mu + 1'$ is saturated, the minus sign in formulas (2) and (3) has to be replaced* by a plus sign, and $2\mu - 1$ replaced by $2\mu + 1$. The formulas for f_1^n and f_2^n become much more complicated because in this case the alternating field and the nuclear relaxation cause different transitions.

4. We now consider the double resonance method of orienting nuclei. Bloch has shown¹³ that an adiabatic fast passage through a resonance results in an inversion of the two populations, provided the resonance is swept through quickly enough. In the following, the inverted pair of levels i and k will be denoted by the symbol $[i, k]$.

In Fig. 1 (or 2), let the pair of levels $[\mu, \mu']$ be inverted. The nuclei will not be polarized as a consequence of this, and so the amount of polarization will remain small. Now let us invert one of the pairs $[\mu, \mu - 1]$, $[\mu, \mu + 1]$, $[\mu', \mu - 1']$, or $[\mu', \mu + 1']$. This will result in a significant nuclear polarization.

For example, the two inversions $[\mu, \mu']$ and $[\mu', \mu - 1']$ are equivalent to exchanging the populations of the levels μ and $\mu - 1'$. As a result, the number of nuclei with spin projection $\mu - 1$ will increase, while the number with spin μ will decrease. This leads to a negative nuclear polarization ($f_1 < 0$).

The final expressions for f_1 and f_2 in the four possible cases are given below:

$$f_1 = \pm \frac{\tanh \delta}{I(2I+1)}, \quad f_2 = \pm \frac{3(2\mu-1)}{I(2I+1)(2I-1)} \tanh \delta, \quad (7)$$

the upper sign corresponding to inverting first the pair $[\mu, \mu']$ and then $[\mu, \mu - 1]$, while the lower sign corresponds to inverting first $[\mu, \mu']$ and then $[\mu', \mu - 1']$. Furthermore,

$$f_1 = \mp \frac{\tanh \delta}{I(2I+1)}, \quad f_2 = \mp \frac{3(2\mu+1)}{I(2I+1)(2I-1)} \tanh \delta, \quad (8)$$

where the upper sign corresponds to the inversion $[\mu, \mu + 1]$ after $[\mu, \mu']$ while the lower one corresponds to $[\mu', \mu + 1']$ after $[\mu, \mu']$.

Formulas (7) and (8) are applicable only in the

*On the right hand side of formula (4), $\mu - 1$ must be replaced by $\mu + 1$.

case where the time between the two inversions is significantly smaller than the vertical relaxation time T_e . If this inequality does not hold, less orientation will result because partial equilibrium between the levels μ and μ' will have been established by the time the second inversion occurs.

The orientation obtained by Feher's method will decay away with the nuclear relaxation time T_N . Although vertical relaxation transitions occur between the two inversions, they do not change the projection of the nuclear spin.

From the results given above, it follows that the values of the f_k obtained by Feher's method are the same as those in the second stage of Jeffries' method. For example, inverting the two pairs $[\mu, \mu']$ and $[\mu', \mu - 1']$ gives the same result as saturating the forbidden transition $\mu \leftrightarrow \mu - 1'$. Clearly, the two inversions can be replaced by one — the one being an inversion of the two levels in the forbidden transition. For example, instead of inverting the pairs $[\mu, \mu']$ and $[\mu', \mu - 1']$, it is sufficient to invert the pair $[\mu, \mu - 1']$.

5. Different variations have been proposed on the method discussed above.^{14,15} For example, we could saturate the transition $\mu \leftrightarrow \mu'$, and then either saturate or invert one of the horizontal pairs (see Fig. 2). It is easy to see that if we were to saturate the transition $\mu \leftrightarrow \mu'$ and then invert one of the pairs $[\mu, \mu + 1]$, $[\mu, \mu - 1]$, $[\mu', \mu + 1']$, or $[\mu', \mu - 1']$, the resulting orientations f_k would be half as big as those given by formulas (7) and (8). In other words, the values of f_k so obtained would be those corresponding to the first stage in Jeffries' method. The orientation would decay to its equilibrium value with a relaxation time of order T_N .

The values of the f_k would not change if the saturating field were to be removed after the horizontal pair of levels was inverted. When the saturating field goes off, vertical transitions between the levels μ and μ' take place, but these do not change the projection of the nuclear spin.

6. Another possibility is to saturate one of the vertical and also one of the horizontal pairs of levels. It is not difficult to show that

$$\langle m^k \rangle - \langle m^k \rangle_0 = -\frac{1}{2I+1} \left\{ [\mu^k + (\mu-1)^k] - \frac{2}{3+e^{-2\delta}} [2\mu^k + (\mu-1)^k(1+e^{\pm 2\delta})] \right\}, \quad (9)$$

where k is any positive integer and the upper sign in the exponents corresponds to saturating the transitions $\mu \leftrightarrow \mu'$ and $\mu' \leftrightarrow \mu - 1'$, while the lower one corresponds to $\mu \leftrightarrow \mu'$ and $\mu \leftrightarrow \mu - 1$. The

index zero denotes no saturation. Furthermore,

$$\langle m^k \rangle - \langle m^k \rangle_0 = -\frac{1}{2I+1} \left\{ [\mu^k + (\mu+1)^k] - \frac{2}{3+e^{\pm 2\delta}} [2\mu^k + (\mu+1)^k (1+e^{\pm 2\delta})] \right\}, \quad (10)$$

where the upper sign in the exponents corresponds to saturating the transitions $\mu \leftrightarrow \mu'$ and $\mu' \leftrightarrow \mu+1'$ while the lower one refers to $\mu \leftrightarrow \mu'$ and $\mu \leftrightarrow \mu+1$. As in the preceding cases, the polarization decays away with the relaxation time T_n .

If both saturating fields are turned off, the degree of nuclear orientation will not change for times less than T_n . When the field saturating the transition $\mu \leftrightarrow \mu'$ is turned off, vertical transitions will occur, but these do not change the projection of the nuclear spin. When the field saturating the horizontal transitions is turned off, transitions will occur with relaxation time T_n .

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