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THE INFLUENCE OF TUNNEL TRANSITIONS ON THE LINE SHAPE OF A NUCLEAR MAGNETIC RESONANCE SIGNAL IN CRYSTALS

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The theory of the nuclear magnetic resonance (NMR) line shape in crystals was developed by Van Vleck (^{1}) (determination of the line moments by the method of diagonal sums) for the case of an absolutely rigid crystal lattice. In the papers of Pake (^{2}) and Gutowsky and Pake (^{3}) it was shown that, when rapid rotations of molecular groups containing the nuclei under study are present in the sample, a decrease occurs in the second moment of the NMR signal line, corresponding to a narrowing of the line under the influence of internal molecular motions (in accordance with the general theory (^{4})). On the other hand, it is easy to see that the second moment of the NMR spectrum does not depend on the character of the motions of the molecules of the sample (^{5}). This means that the motion of molecules, occurring with some characteristic frequency ω_m, modulates the Larmor precession of the nuclear spins (frequency ω_L), as a result of which satellites arise in the NMR spectrum at frequencies of the order of $\omega_L \pm n\omega_m,\ n = 1, 2 \ldots$. The appearance of satellites also explains the invariance of the second moment of the entire NMR spectrum with respect to internal motions of the molecules, whereas the second moment of the "main" line (i.e., the line observed at the frequency ω_L) decreases in comparison with the case of an absolutely rigid lattice (line narrowing). For free rotation and random reorientation of a pair of nuclei possessing magnetic dipole moments, the question of the appearance of satellites was quantitatively investigated in the work of Andrew and Newing (^{6}) by semiclassical methods under the assumption (not mentioned explicitly by the authors) that the frequency of rotation (or reorientation) is considerably smaller than the Larmor precession frequency ω_L. As for other works devoted to the study of the influence of internal motions on the NMR signal line shape (for example (^{2,3,5})), they consider only the limiting cases $\omega_m \gg \Delta\omega$ or $\omega_m \ll \Delta\omega$, where $\Delta\omega$ is the line width at the frequency $\omega = \omega_L$. In the present work the quantum-mechanical problem of the NMR line shape is solved for a pair of nuclei undergoing reorientation by the mechanism of the tunnel effect.

We shall consider magnetically dilute substances (i.e., we shall assume that the interactions of our pair of nuclei with the remaining paramagnetic particles of the sample may be neglected and that the spin-lattice relaxation time T_1 is sufficiently large). Then the NMR spectrum (for a single crystal) consists of a set of narrow lines, whose frequencies and intensities we shall determine. If the assumptions made above are not fulfilled sufficiently rigorously, this will lead to a broadening of each of the lines, which in principle can be taken into account in exactly the same way as in (^{5}). Further, the problem is formulated as follows (see Fig. 1).

Nuclei 1 and 2 are capable of carrying out simultaneous motions in a plane whose normal makes an angle α with the direction of the constant magnetic field H_0 (the z-axis), the vector $\mathbf{r}$ connecting them at all times passing through the origin and remaining constant in absolute value. For the angle φ, which describes the position of the vector $\mathbf{r}$ in the plane, the potential energy has the form of a symmetric potential ···

pits (Fig. 1b), whose two minima correspond to positions I and II of the vector $\mathbf{r}$; δ is the angular distance between the minima; φ_0 is the angle corresponding to the top of the barrier between the minima. Nuclei 1 and 2 are assumed to be magnetically equivalent. The picture presented above corresponds, for example, to two protons in dimers of carboxylic acids.

We shall write the Hamiltonian of the system under consideration in the form

$$\mathscr{H} = \mathscr{H}_m - \hbar\gamma H_0(S_{z1} + S_{z2}) - W, \tag{1}$$

where $\mathscr{H}_m = \mathscr{H}_m(\varphi)$ is the Hamiltonian describing the collective motion of both nuclei; the second term is the interaction of the magnetic moments of the nuclei with the field H_0 (γ is the gyromagnetic ratio), and

$$W = \frac{\hbar^2\gamma^2}{b^3}\left[\frac{3}{2}S_{z1}S_{z2} - \frac{1}{2}\mathbf{S}_1\mathbf{S}_2\right][1 - 3\cos^2\theta] \tag{2}$$

is the secular part of the dipole-dipole interaction of nuclei 1 and 2 (1); θ is the polar angle of the vector $\mathbf{r}$; $b = |\mathbf{r}|$.

In what follows we shall consider the influence on the NMR spectrum of the tunneling transition of the nuclei from state I to state II. Correspondingly, we shall assume that the spectrum of $\mathscr{H}_m$ consists of two close levels E_1^0 and E_2^0, with $E_1^0 - E_2^0 = \Gamma$, while all the remaining levels of $\mathscr{H}_m$ lie sufficiently far from $E_{1,2}^0$: $\Gamma \ll |E_{1,2}^0 - E_n^0|$, $n \neq 1, 2$. Obviously, the probability of transition from state I to II is equal to $\Gamma/\hbar$. Let the wave functions corresponding to the levels E_1^0 and E_2^0 be, respectively, $\chi_1(\varphi)$ and $\chi_2(\varphi)$. Then the complete system of functions Φ_i is obtained, for example, by multiplying each of the functions χ by each of the eigenfunctions ξ_k of the operators $(S_{z1} + S_{z2})$ and $(\mathbf{S}_1 + \mathbf{S}_2)^2$. Restricting ourselves, for simplicity, to the case of spins 1/2, we

Fig. 1

Figure 1: Fig. 1

consider the secular equation for Hamiltonian (1). If it is assumed that the magnetic dipole-dipole interaction of nuclei 1 and 2 is much smaller than the interaction of their magnetic moments with the constant magnetic field H_0, then it is easy to show that the eighth-order secular equation splits into 4 second-order equations; by solving them one can determine the energy eigenvalues E_n and the eigenfunctions ψ_n of the system under consideration.

Fig. 1

In view of the unwieldiness of the resulting expressions, we shall give the final results only after further simplifications. For the moment we note only that the functions ψ_n have the form

$$\psi_n = (C_1^{(n)}\chi_1 + C_2^{(n)}\chi_2)\xi_{k_n}, \tag{3}$$

where $C_1^{(n)}, C_2^{(n)}$ are coefficients determined from the secular equation; ξ_{k_n} is one of the basis spin functions (mixing of the functions ξ_k does not occur, since $\mathcal{H}_m$ and W commute with $S_{z1} + S_{z2}$ and $(\mathbf{S}_1 + \mathbf{S}_2)^2$; the functions χ_1 and χ_2, however, are mixed because $[\mathcal{H}_m, W] \neq 0$).

We now show how the matrix elements of the secular equation are calculated under the assumption that a tunneling transition from state I to II takes place. Let us consider, for example, the quantity:

$$(\chi_i\xi_k|W|\chi_j\xi_{k'}) = \frac{\hbar^2\gamma^2}{b^3}\left(\xi_k\left|\frac{3}{2}S_{z1}S_{z2} - \frac{1}{2}\mathbf{S}_1\mathbf{S}_2\right|\xi_{k'}\right)(\chi_i|Q|\chi_j), \tag{4}$$

where $Q = 1 - 3\cos^2\theta$. The calculation of the spin part in (4) presents no difficulty. To calculate $Q_{ij} = (\chi_i|Q|\chi_j)$, we note that for sufficiently

high potential barrier

$$\chi_1 = \frac{1}{\sqrt{2}}(\chi_I + \chi_{II}), \qquad \chi_2 = \frac{1}{\sqrt{2}}(\chi_I - \chi_{II}), \tag{5}$$

where χ_I and χ_{II} describe the states of the nuclei near the minima I and II, respectively. Since the nuclei can, to a sufficient degree of accuracy, be regarded as localized at the points, χ_I and χ_{II} may be approximated by δ-functions. Consequently, from (4) and (5) we find

$$Q_{11} = Q_{22} = \frac{1}{2}(Q_I + Q_{II}) = \frac{1}{2}V;$$

$$Q_{12} = \frac{1}{2}(Q_I - Q_{II}) = \frac{1}{2}U, \tag{6}$$

where Q_I and Q_{II} are the values of Q in positions I and II, respectively. It is easy to see that

$$U = 3\sin^2\alpha \, \sin 2\varphi_0 \, \sin\delta,$$

$$V = 2 + 6\sin^2\alpha \left[\sin^2\varphi_0 \cos^2\frac{\delta}{2} + \cos^2\varphi_0 \sin^2\frac{\delta}{2}\right].$$

Taking also into account the selection rule $\Delta(S_{z1} + S_{z2}) = \pm 1$, we find that the NMR spectrum consists of 8 lines with frequencies

$$\hbar\omega_{1-8} = \hbar\omega_L + \frac{1}{2}\left[\pm\frac{3}{4}kV \pm \sqrt{\Gamma^2 + \frac{1}{4}k^2U^2} \pm \sqrt{\Gamma^2 + \frac{1}{16}k^2U^2}\right], \qquad k = \gamma^2\hbar^2/b^3. \tag{7}$$

(in the square brackets the sign before each term may be chosen independently of the signs before the others). The intensities of these lines are, evidently, proportional to the square of the modulus of the matrix element $(\psi_n|S_x|\psi_{n'})$, and since the ψ_n have the form (3), the relative intensities of the spectral lines are determined by expressions of the form

$$\left|C_1^{(n)}C_1^{(n')} + C_2^{(n)}C_2^{(n')}\right|^2.$$

Thus, for the line with the frequency obtained from (7) in the case where all terms in the bracket are taken with the plus sign, the relative intensity is

$$I = \frac{\left[\frac{1}{8}k^2U^2 - (\Gamma - R_1)(\Gamma + R_2)\right]^2}{\left[(\Gamma - R_1)^2 + k^2U^2/4\right]\left[(\Gamma + R_2)^2 + k^2U^2/16\right]};$$

$$R_1 = \sqrt{\Gamma^2 + \frac{1}{4}k^2U^2}; \qquad R_2 = \sqrt{\Gamma^2 + \frac{1}{16}k^2U^2}.$$

In the limiting case of very rapid transitions ($\Gamma \gg kV$), the relative intensity of the lines corresponding to frequencies for which both of the last terms in (7) are taken with the same signs is a quantity of order k^2V^2/Γ^2; therefore the spectrum practically consists of 2 lines with a frequency difference $\Delta\omega = \frac{3}{4}kV$, as it should be.^(5) In the absence of exchange ($\Gamma = 0$), 4 lines are observed in the spectrum, which corresponds to a single crystal in which there are two types of differently oriented pairs of nuclei.

Let us note, finally, that our treatment does not explicitly include the dependence of the form of the spectrum on temperature. In fact, however, the shape of the potential barrier is determined by the interaction of the pair of nuclei under consideration with the other molecules of the crystal and, consequently, depends on temperature. Thus, the temperature dependence of the formulas obtained must be determined by the temperature dependence of the parameter.

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