

Shape of NMR spectra of solids

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A simple physical model proposed in the present paper makes it possible to account qualitatively for the main features of the NMR spectra of solids and to calculate the spectral profile due to the dipole–dipole interactions of nuclear spins with one another. The usefulness of the model is illustrated by calculations of the spectra of CaF₂ (simple cubic lattice), solid molecular hydrogen (hexagonal lattice), and crystalline polyethylene (trans-zigzag conformation). The results of these calculations are in good agreement with experiments.

The spectral profile of an NMR spectrum is one of the fundamental problems in statistical mechanics of spin systems. The first hypotheses on the spectral profile were made back in the pioneering work of Bloembergen, Purcell, and Pound¹ who assumed that the absolute majority of the NMR absorption lines can be described by two types of curve: Lorentzian and Gaussian. The subsequent development of experimental methods^{2,3} let to the discovery^{3,4} that the NMR spectra of ordinary solids are very different from the Gaussian profile: the directly observed time Fourier transformants of the absorption spectra, known as the free-precession signals, include oscillations demonstrating that neither of these functions can provide a correct description of the line profile. Tens of papers have already been published on the problem of the NMR line profile (see, for example, Refs. 5–10), but the problem remains unsolved.

The reasons preventing the successful solution of the problem of the NMR line profile are the many-body nature of the problem and the absence of a small parameter in the Hamiltonian. Most authors therefore are forced to adopt uncontrolled approximations in order to obtain satisfactory results after long and very laborious calculations. Although the results of such calculations do frequently agree with experiments, the absence of clear physical reasons for the assumptions which are made, as well as the absence of linkage to the physical parameters and processes occurring in spin systems, reduces the value of these results. Therefore, the task of developing a reasoned physical model describing NMR spectra of solids and explaining the principal experimental observations still remains urgent. This is particularly important because not only are the NMR spectra of solids highly informative^{11–13} and capable of yielding data on the crystal structure, mobility of molecules and atomic groups, and electronic structure, but they also provide an opportunity for investigating the statistical mechanics of irreversible processes, in view of the fact that nuclear spin systems represent a unique “laboratory” for such investigations. It is these systems that have been used in attainment of “time reversal” (Ref. 14), the result of which is a “magic echo,” etc.

We shall propose a model which is a further development of an earlier model suggested by us.¹⁵ The model discussed below makes it possible to calculate completely all the

components of the free precession signal (FPS) observed for solids.

It is known¹⁶ that the FPS which appears in an equilibrium nuclear spin system subjected to a high static magnetic field H_0 on application of a $\pi/2$ pulse is proportional to the time correlation function, which is defined in a coordinate system rotating at the Larmor frequency:

$$\Gamma(t) = \frac{1}{\text{Sp}(S_x^2)} \text{Sp}\{S_x(t)S_x\}; \quad (1)$$

S_x is the total x component of the spin of the system. It satisfies the Heisenberg equation

$$dS_x/dt = i[H, S_x]. \quad (2)$$

In Eq. (2) and later the energy is measured in frequency units. In this equation we have

$$S_x = \sum_i S_{xi}, \quad (3)$$

$$H = \frac{1}{2} \sum_{i \neq j} b_{ij} \left\{ S_z^i S_z^j - \frac{1}{4} (S_i^+ S_j^- + S_i^- S_j^+) \right\} = H_{zz} + H_{ij}.$$

Here, H is the secular part of the dipole-dipole interaction,¹⁶ where $b_{ij} = \gamma^2 \hbar (1 - 3\cos^2\theta_{ij})/r_{ij}^3$, r_{ij} is a vector linking spins i and j , and θ_{ij} is the angle between r_{ij} and an external magnetic field. Using the operators $S^\pm = S_x \pm iS_y$, we find that the expression (1) can be rewritten in the form

$$\Gamma(t) = \frac{1}{2 \text{Sp}(S_x^2)} \text{Sp}\{S^+(t)S^-\} = \langle S^+(t) \rangle. \quad (4)$$

Since in a regular lattice with one kind of nuclei all the spins are equivalent, we find that

$$\text{Sp}\{S^+(t)S^-\} = \sum_i \text{Sp}\{S_i^+(t)S_i^-\} = N \text{Sp}\{S_0^+(t)S_0^-\} \approx \langle S_0^+(t) \rangle,$$

where N is the number of spins in a sample and 0 is the number of a specific spin.

Back in the early sixties, Abragam¹⁶ found empirically that the FPS of a CaF₂ single crystal could be described with remarkable accuracy by the following expression valid in the case of reasonably long times:

$$\Gamma(t) = \frac{\sin bt}{bt} e^{-a^2 t^2/2} = \Gamma_0(t) e^{-a^2 t^2/2}. \quad (5)$$

The quantities a and b are selected so as to ensure the correct second and fourth moments of the absorption line. Subsequently it has been demonstrated experimentally¹⁷ that if $t \gtrsim 3T_2$, then the Gaussian component of the FPS of Eq. (5) becomes exponential:

$$\Gamma(t) \propto \frac{\sin bt}{bt} e^{-c't} = \Gamma_0(t) e^{-c't}. \quad (6)$$

The first attempt to explain these simple and surprisingly "physical" results was provided by our model.¹⁵ It was pointed out in Ref. 15 that the whole crystal can be divided, in relation to a certain arbitrarily selected spin labeled 0, into two regions in one of which the motion of spins is correlated with the selected spin and in the other it is not. The region with correlated motion is called a cell. We are speaking here of the time correlations which appear in such a system because of flip-flop processes described by the operator H_{ff} in the Hamiltonian (3). We can estimate the flip-flop probability¹⁵ by employing the Bloembergen formula¹⁸ according to which

$$W_{ij}^{(1)} = \frac{1}{8\sqrt{2}} \hbar^2 \gamma^4 (1 - 3 \cos^2 \theta_{ij})^2 r_{ij}^{-6} T_2 \propto r_{ij}^{-6} T_2. \quad (7)$$

In view of the rapid convergence (in respect of r) of the probability of flip-flop processes, we can expect the radius of such a cell to be of the same order as the lattice constant d and the number of spins in such a cell is not macroscopic. A correct definition of the boundaries of such a cell would require investigation of more complex combined flip-flop processes (see below) capable in principle of expanding the cell. However, we did not discuss the cell boundaries in Ref. 15. We demonstrated¹⁵ that the spins excluded from a cell make a Gaussian contribution to the FPS of Eq. (5), which then becomes exponential in accordance with Eq. (6), and we calculated the argument of the Gaussian and exponential functions. Although an expression obtained for b in Ref. 15 was in agreement with the experimentally determined value of b , the FPS profile governed by the spins in the cell was not calculated. The development of the model proposed below makes it possible to calculate also the contribution made to the FPS by a cell.

The probability of flip-flop processes given by Eq. (7) allows only for the pair process. As pointed out earlier, when the boundaries of a cell are determined, it is necessary to investigate the process of transfer of correlations along chains in which each spin interacts with the nearest neighbors. Nevertheless, we can hope that in the case of crystals with a large number of nearest neighbors, i.e., those with large numbers of z of spins in a cell, such correlations are destroyed because for geometric reasons each of the nearest neighbors has practically its own cell. A calculation of the probability of flip-flop processes given in the Appendix I demonstrates clearly these points. In fact, we have

$$W_{ij}^{(2)} \sim r_{ij}^{-6} r_{ik}^{-6} T_2^3 \quad (8)$$

and $T_2 = M_2^{-1/2}$, where M_2 is the second moment of the absorption line. For large values of z , we have

$$M_2 \approx b_0'^2 z, \quad b_0' = [3/4 S(S+1)]^{1/2} b_0, \quad (9)$$

where b_0 is the coefficient describing the dipole-dipole interaction with the spins in a cell. Hence, it is clear that a large number of neighbors does indeed result in weakening of the correlation by a factor of z in the case of the triple flip-flop process compared with the pair process. A comparison of the probabilities of the two- and three-spin flip-flop processes in a CaF_2 single crystal subjected to an external magnetic field along the [100] axis is given in the Appendix I. For this orientation we have $z = 6$ (Ref. 15). The calculated ratio of the probabilities is

$$W^{(1)}/W^{(2)} \approx 0.07. \quad (10)$$

Consequently, the contribution of the combined flip-flop processes to the transfer of the correlation effects is negligible. It follows that in the case of crystals with a large number of the nearest neighbors the processes of this kind in each pair of spins in a cell occur independently of the flip-flop processes in all the other pairs. Consequently, in order to calculate the non-Gaussian component of the FPS, we must find the contribution made by the flip-flop processes of the zeroth spin interacting with any of the spins in its cell and then, allowing for the statistical independence of the pairs, we must sum the results. Naturally, the flip-flop pairs should be regarded against the background of local z fields acting on each of the spins participating in the elementary process.

It therefore follows that the Hamiltonian of a given pair is described by the expression

$$H = \gamma \hbar_0 S_{z0} + \gamma \hbar_j S_{zj} + a_{0j} (S_0^+ S_j^- + S_0^- S_j^+). \quad (11)$$

Here, the index 0 labels the selected spin, the index j identifies one of the spins in a cell, and \hbar_0 and \hbar_j are random Gaussian local fields. The second moment of the distribution of the local fields \hbar_0 and \hbar_j (assumed to be statistically independent) is equal to the second moment which is due to the H_{zz} interaction of the Hamiltonian (3) with the cell spins (see the Appendix II). It should be noted that the replacement of the H_{zz} interaction in the Hamiltonian (3) by the interaction with a random Gaussian local field in the Hamiltonian (11) is quite accurate because in crystals with a large number of neighbors it gives rise to a Gaussian profile of an NMR line,^{19,20} in agreement with the Gaussian distribution of the local field. A more accurate allowance for H_{zz} is possible with the aid of the projection operators introduced in Ref. 8. However, these operators would have complicated greatly our calculations without producing any new results.

We can now use the Hamiltonian (11) to obtain quite readily a closed system of equations of motion ($S = 1/2$):

$$d\Gamma_0(t)/dt = i\gamma \hbar_0 \Gamma_0(t) + 2ia_{0j} B_{0j}(t), \quad (12a)$$

$$dB_{0j}(t)/dt = i\gamma \hbar_j B_{0j}(t) - 1/2 ia_{0j} \Gamma_0(t). \quad (12b)$$

Here,

$$\Gamma_0(t) = \langle S_0^+(t) \rangle; \quad B_{0j}(t) = \langle S_{z0}(t) S_j^+(t) \rangle;$$

$$\Gamma_0(0) = 1; \quad B_{0j}(0) = 0; \quad \langle \dots \rangle = A^{-1} \text{Sp} \{ \dots S^- \}.$$

The second term in Eq. (12a) describes the flip-flop processes in a pair of spins. In accordance with the above discussion we should allow for the statistical independence of these processes in different pairs and then sum over the index j in Eq. (12a). We then obtain

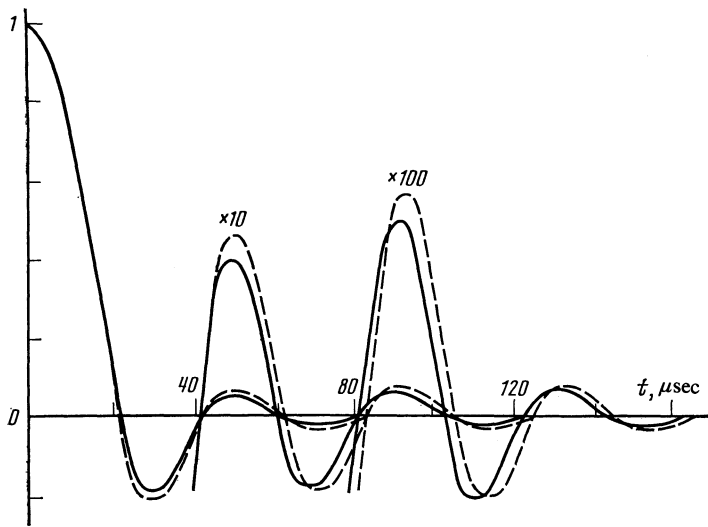


FIG. 1. Free precession signal of CaF_2 . The external field as oriented along the [100] axis. The continuous curve represents the solution of the system (13a)–(13b) multiplied by the function $\Gamma_1(t)$ (see the Appendix II). The dashed curve represents the experimental data taken from Ref. 17.

$$\frac{d\Gamma_0(t)}{dt} = i\gamma h_0 \Gamma_0(t) - 2i \sum_j a_{0j} B_{0j}(t), \quad (13a)$$

$$\frac{dB_{0j}(t)}{dt} = i\gamma h_j B_{0j}(t) - \frac{i}{2} a_{0j} \Gamma_0(t). \quad (13b)$$

The index j labels all the spins in a cell. Therefore, in the case of CaF_2 with the [100] orientation and $z = 6$, we have to solve a system of seven coupled equations, whereas for the [110] orientation (characterized by $z = 14$ —see Ref. 15) we need fifteen equations, etc.

The system (13a)–(13b) can be solved by the Laplace transformation

$$\Gamma(\lambda) = \left[\lambda - i\gamma h_0 + \sum_j \frac{a_{0j}^2}{\lambda - i\gamma h_j} \right]^{-1}, \quad (13c)$$

where λ is a complex variable. The expression (13c) is averaged (integrated numerically) over the Gaussian distributions of statistically independent local fields $\{h_j\}$ and then a computer is used to carry out the inverse Laplace transfor-

mation. The results of such calculations and a comparison with the experimental results can be found in Figs. 1 and 2. In addition to the values plotted in these figures, we calculated also the FPS of CaF_2 for the [110] and [111] orientations, the FPS of an hexagonal close-packed lattice, and the FPS of polyethylene subjected to an external magnetic field directed at right-angles to its molecular axes. In all cases a good agreement was obtained between the theory and experiment. Calculations carried out for the hexagonal lattice were compared (after averaging over grain particles) with the results of Metzger and Gaines²¹ for polycrystalline solid molecular hydrogen.

The internal self-consistency of the model can be tested by generalizing it. The simplest way to generalize the model is to allow exactly for the flip-flop processes in a triplet of spins and to find the FPS of a cell by a suitable summation over all the triplets. Although in principle such a direct procedure is possible, it is extremely difficult to carry out: even for an isolated triplet we must solve a system of fifteen coupled differential equations. Therefore, before considering

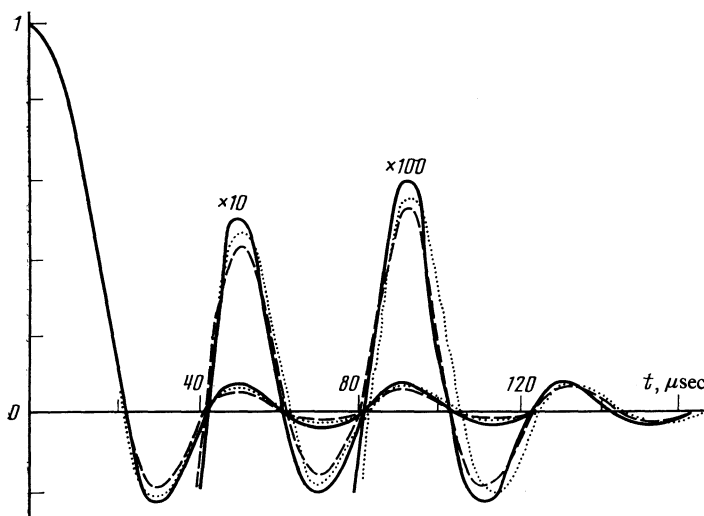


FIG. 2. Free precession signal of CaF_2 . The external field is oriented along the [100] axis. The continuous curve is a solution of the system (13a)–(13b), the dashed curve is the solution of Eq. (16), and the dots are the solution of a system of equations for a triplet of spins.

triplets, we shall simplify somewhat the system (13a)–(13b). Multiplying both equations by an integrating factor and then calculating the integral, we obtain

$$\Gamma_0(t) = \exp(i\omega_0 t) - 2i \sum_j a_{0j} \int_0^t \exp\{i\omega_0(t-t')\} B_{0j}(t') dt', \quad (14a)$$

$$B_{0j}(t) = -\frac{i}{2} a_{0j} \int_0^t \exp\{i\omega_j(t-t')\} \Gamma_0(t') dt', \quad (14b)$$

$$\omega_0 = \gamma h_0, \quad \omega_j = \gamma h_j.$$

Substituting Eq. (14a) into Eq. (14b), we obtain

$$\Gamma_0(t) = \exp(i\omega_0 t) - \sum_j a_{0j}^2 \int_0^t \exp\{i\omega_0(t-t')\} \times \int_0^{t'} \exp\{i\omega_j(t'-t'')\} \Gamma_0(t'') dt'' dt'. \quad (15)$$

It is known²² that the z components of a local field vary more slowly than the transverse components of the spins. The characteristic time of such slowing down is $(3-4)T_2$. Hence, we can assume that averaging of the exponential functions in Eq. (15) over the distribution of local fields, independent of $\Gamma_0(t)$ and $B_{0j}(t)$, does not result in a significant error in the calculations. Such averaging gives

$$\langle \exp(i\omega t) \rangle = \frac{1}{X} \int_{-\infty}^{\infty} e^{i\omega t} \exp\left\{-\frac{\omega^2}{M_2'}\right\} d\omega$$

$$= \exp\left\{-\frac{M_2' t^2}{2}\right\} = G_0^{(4)}(t),$$

where M_2' is the second moment of the distribution of the z components of a local field of spins in a cell. In this way we obtain

$$\Gamma_0(t) = G_0^{(4)}(t) - \sum_j a_{0j}^2 \int_0^t G_0^{(4)}(t-t') \int_0^{t'} G_0^{(4)}(t'-t'') \Gamma_0(t'') dt'' dt'. \quad (16)$$

The above approximation has made it possible to reduce the system of coupled differential equations to a fairly simple integral equation. A comparison of the solution of the system (13) with a solution of Eq. (16), made in Fig. 2, shows that such an approximation has practically no influence on the results, at least in the case when the ratio of the parameters M_2' and a_{0j} is typical of ordinary solids. Independent averaging of the exponential functions in the system of equations for spin triplets allows us to consider only a solution of fifteen coupled equations. It is clear from Fig. 2 that the change from pairs to triplets also has little effect on the results, which provides an additional evidence of this adequacy of the model. It remains to establish the relationship between this model and a chain of equations of motion. We shall do this by considering the Hamiltonian

$$H = \sum_j \omega_j S_{zj} + \frac{1}{2} \sum_{i \neq j} a_{ij} (S_i^+ S_j^- + S_i^- S_j^+). \quad (17)$$

The notation used in Eq. (17) is similar to that adopted

above. If we use the Heisenberg equations of motion, we obtain

$$\frac{d\Gamma_0(t)}{dt} = i\omega_0 \Gamma_0(t) - 2i \sum_j a_{0j} B_{0j}(t), \quad (18a)$$

$$\frac{dB_{0j}(t)}{dt} = i\omega_j B_{0j}(t) - \frac{1}{2} i a_{0j} \Gamma_0(t) - \sum_k a_{0k} \langle (S_0^+(t) S_k^-(t) S_i^+(t) + S_0^-(t) S_k^+(t) S_i^+(t)) \rangle - 4 \sum_{k \neq j} a_{kj} \langle S_{z0}(t) S_{zj}(t) S_k^+(t) \rangle. \quad (18b)$$

We can easily see that the equations of motion in the model (13a) and (13b) are obtained if we drop the three-particle (three-body) terms from Eq. (18b). We shall clarify the reasons why termination of the chain of equations of motion is permissible by assuming that

$$\omega_j \approx \alpha z b_0' \sim z b_0', \quad \alpha = \text{const} \approx 1. \quad (19)$$

This representation is acceptable for crystals with a large number of neighbors. We can also obtain equations of motion for three-particle contributions to Eq. (18b). However, they are cumbersome and we shall not reproduce them here. We nevertheless should point out that the general structure of the Laplace transforms of equations of motion is

$$\dots \dots \dots$$

$$(\lambda + z b_0') F_n(\lambda) = F_{n-1}(\lambda) + z b_0' F_{n+1}(\lambda), \quad (20)$$

$$(\lambda + z b_0') F_{n+1}(\lambda) = F_n(\lambda) + z b_0' F_{n+2}(\lambda),$$

where λ is a complex variable, $F_0 = 0$, $F_1(\lambda) = \Gamma_0(\lambda)$, $F_2(\lambda) = B_{0j}(\lambda)$, etc. Dropping of the term $F_{n+2}(\lambda)$ from Eq. (20), we obtain

$$F_{n+1}(\lambda) = F_n(\lambda) (\lambda + z b_0')^{-1}. \quad (21)$$

Therefore, termination of the chain of equations of motion introduces an error of the order of $\sim 1/z$, which is unimportant in the case of large values of z .

Finally, we note that although all the analyses were carried out so far for the $S = 1/2$ spin, this is unimportant in the case of crystals with a large number of spins in a cell and the model proposed above can be generalized by a trivial procedure to the case of an arbitrary value of S : when z is large, the spin alters only the time scale, but it does not alter the FPS profile.²³

We shall conclude by noting an interesting feature of our results. Our calculations indicate that the FPS of a crystal with a large number of neighbors has a profile which is described very satisfactorily by the relationships (5) and (6) irrespective of the dependence on the crystallographic structure. This FPS profile applies to all the materials mentioned above and to the model system representing a two-dimensional simple cubic lattice, which is subjected to a magnetic field at right-angles to the plane of the lattice. In the case of polyethylene the results obtained within the framework of our model (Fig. 3) agree with the experimental data²⁴ and earlier rigorous calculations.²⁵ It is interesting to note that in the case of polyethylene we have $z = 3$ for the orientation in question. Therefore, already the number "3" is "large" in the problem under discussion because calculations of the FPS for a quasi-one-dimensional fluorine apatite character-

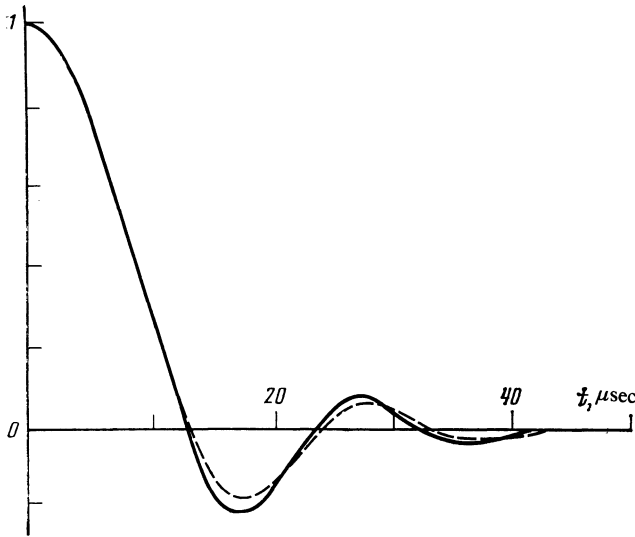


FIG. 3. Free precession signal of crystalline polyethylene. The external field is oriented along the molecular axes. The continuous curve is theoretical and the dashed curve is based on the results of Ref. 25.

ized by $z = 2$ fail to ensure agreement with the experimental data.

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APPENDIX I.

Calculation of the flip-flop probability in the second order of perturbation theory

We shall follow calculations of the probability of flip-flop processes^{18,26} and estimate the probability of a three-spin process by calculating the average (over the initial and final states) the probability of a transition from a state

$$\langle \Psi_1^{(\alpha)} | = \left\langle \{ \alpha \}; \frac{1}{2}(i); -\frac{1}{2}(k); -\frac{1}{2}(j) \right| \quad (\text{A.1})$$

to a state

$$\langle \Psi_1^{(\alpha)} | = \left\langle \{ \alpha \}; -\frac{1}{2}(i); -\frac{1}{2}(k); \frac{1}{2}(j) \right|. \quad (\text{A.2})$$

The indices i, j , and k label crystal lattice sites and $\{ \alpha \}$ is the set of projections along the z axis with the other spins in a sample. Clearly, the vector with the intermediate value is

$$\langle \Psi_3^{(\alpha)} | = \left\langle \{ \alpha \}; -\frac{1}{2}(i); \frac{1}{2}(k); -\frac{1}{2}(j) \right|. \quad (\text{A.3})$$

Therefore, we have to calculate²⁷

$$W_{ijk}^{(2)} = \frac{2\pi}{\hbar} \sum_{\{\alpha\}} |\langle \Psi_1^{(\alpha)} | H_{ff} | \Psi_3^{(\alpha)} \rangle \langle \Psi_3^{(\alpha)} | H_{ff} | \Psi_2^{(\alpha)} \rangle|^2 (E_i^{(\alpha)} - E_k^{(\alpha)} + i\varepsilon)^{-1} \times \delta(E_i^{(\alpha)} - E_j^{(\alpha)}). \quad (\text{A.4})$$

The quantity ε represents homogeneous broadening of states

because of mutual flip of spins interacting with other spins in a sample. In the subsequent estimates we shall assume that $\varepsilon = \sqrt{M_2''}$, where M_2'' is the contribution made to the second moment of the NMR profile by the H_{ff} Hamiltonian of Eq. (3). Since the separate states in the sum (A.4) determine uniquely the z component of a local field acting on each of the spins, we can follow the procedure of Refs. 18 and 26 and replace the sum over the states in Eq. (A.4) with the integral over the energies (precession frequencies) of a spin in a local field. We shall assume that the distribution of frequencies for each of the spins is described by Gaussian functions and the local fields at different spins are not correlated. We then obtain

$$W_{ijk}^{(2)} = \frac{2\pi}{\hbar} \frac{T_2^3}{(2\pi)^{3/2}} |\langle \Psi_1 | H_{ff} | \Psi_3 \rangle|^2 \times |\langle \Psi_3 | H_{ff} | \Psi_2 \rangle|^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dE_i dE_k dE_j \times \exp\left(-\frac{E_i^2 T_2^2}{2}\right) \exp\left(-\frac{E_j^2 T_2^2}{2}\right) \times \exp\left(-\frac{E_k^2 T_2^2}{2}\right) \frac{\delta(E_i - E_j)}{(E_i - E_k)^2 + \varepsilon^2} = \frac{2\pi}{\hbar} V_{ik}^2 V_{jk}^2 J. \quad (\text{A.5})$$

Bearing in mind the presence of the δ function, we obtain

$$J = \frac{T_2^3}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} dE_i \exp(-T_2^2 E_i^2) \int_{-\infty}^{\infty} \frac{dE_k \exp(-T_2^2 E_k^2/2)}{(E_i - E_k)^2 + \varepsilon^2}. \quad (\text{A.6})$$

Multiplying now the numerator and denominator in Eq. (A.6) by T_2^2 , we have

$$J = \frac{T_2^3}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} dy e^{-y^2} \int_{-\infty}^{\infty} \frac{dz e^{-z^2/2}}{(z-y)^2 + \alpha^2}. \quad (\text{A.7})$$

Here, $y = T_2 E_i$, $z = T_2 E_k$, and $\alpha^2 = \varepsilon^2 T_2^2$. Substituting $x = z - y$, we find that

$$J = \frac{T_2^3}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} dy \exp\left(-\frac{3}{2}y^2 - xy\right) \int_{-\infty}^{\infty} \frac{dx \exp(-x^2/2)}{x^2 + \alpha^2}. \quad (\text{A.8})$$

The integral of the variable y in Eq. (A.8) is easily found,²⁸ which gives

$$J = \frac{T_2^3}{2\pi\sqrt{3}} \int_{-\infty}^{\infty} \frac{dx e^{-x^2/3}}{x^2 + \alpha^2} = \frac{T_2^3}{2\alpha\sqrt{3}} \left[1 - \Phi\left(\frac{\alpha}{\sqrt{3}}\right) \right] \exp\left(\frac{\alpha^2}{\sqrt{3}}\right), \quad (\text{A.9})$$

where $\Phi(x)$ is the error integral tabulated in Ref. 29. We finally obtain

$$W_{ijk}^{(2)} = 0,88 \frac{2\pi\gamma^4\hbar^8}{256} T_2^3 \sum_k r_{ik}^{-6} r_{jk}^{-6} (1 - 3 \cos^2 \theta_{ik})^2 \times (1 - 3 \cos^2 \theta_{jk})^2. \quad (\text{A.10})$$

By way of example, we shall find the probability of flip-flop processes in a triple of the nearest neighbors located along a straight line parallel to an external magnetic field and oriented along the [100] direction. This probability is

$$W_{012}^{(2)} = 0,88 \frac{2\pi\gamma^4 \hbar^8}{256} \frac{16T_2^3}{d^{12}} \approx 0,35 \frac{\gamma^4 \hbar^8}{d^{12}} T_2^3, \quad (\text{A.11})$$

where d is the lattice constant. The probability of the pair flip-flop process of Eq. (7) is

$$W_{01}^{(1)} = \frac{1}{8\sqrt{2}} \frac{\hbar^2 \gamma^4}{d^6} \frac{4T_2}{d^6} = 0,354 \frac{\hbar^2 \gamma^4}{d^6}. \quad (\text{A.12})$$

Hence, the ratio of the probabilities for a triple and a pair is

$$W_{012}^{(2)} / W_{01}^{(1)} \approx 0,07.$$

If in addition to spin No. 1, we use intermediate spins separated by a distance $2^{1/2}d$ from the spin 0, the above correction becomes just $\approx 0.25\%$ of $W_{012}^{(2)}$.

APPENDIX II.

Influence of spins in the distant environment on the free precession profile

Strictly speaking, the local fields h_0 and h_j in the Hamiltonian (11) are time-dependent because of flip-flop processes and they represent sums of two contributions. One of them is created by a cell, whereas the other by all remaining spins:

$$h_0(t) = h_0^{(1)}(t) + h_0^{(2)}(t), \quad h_j(t) = h_j^{(1)}(t) + h_j^{(2)}(t). \quad (\text{A.13})$$

However, we can show that a consistent allowance for both components of a local field is equivalent to a simple multiplication of the calculated contribution to the FPS from a cell by the FPS component due to distant spins.

In fact, since $T_2^* \approx (3-4)T_2$ and the cell spins ensure over 90% of the total second moment, the components $h_0^{(1)}(t)$ and $h_j^{(1)}(t)$ may be regarded as static. Direct calculations readily show that since $h_0^{(2)}(t)$ and $h_j^{(2)}(t)$ are random Gaussian functions of time,¹⁵ the kernel $G_0(t)$ in Eq. (16) should be written in the form

$$G_0(t) = G_0^{(1)}(t) G_0^{(2)}(t) \\ = \exp\left\{-\frac{M_2' t^2}{2}\right\} \exp\left\{-a^2 \int_0^t (t-\tau) k(\tau) d\tau\right\}. \quad (\text{A.14})$$

Here, a^2 is the contribution made to the second moment by the spins outside the selected cell, and $k(\tau)$ is the correlation function of the z components of a local field. We shall assume that $t \gtrsim T_2^*$. We then obtain

$$G_0^{(2)}(t) = e^{-ct}. \quad (\text{A.15})$$

Equation (16) solved using the Laplace transformation is multiplied by the FPS component due to distant spins:

$$\Gamma(t) = \Gamma_0(t) e^{-ct} \\ = e^{-ct} \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} d\lambda G_0^{(1)}(\lambda) e^{i\lambda t} \left[1 + \left(\sum_j a_{0j}^2 \right) G_0^{(1)2}(\lambda) \right]^{-1} \\ = \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} d\lambda_1 G_0(\lambda_1 + c) e^{i\lambda_1 t} \left[1 + \left(\sum_j a_{0j}^2 \right) G_0^2(\lambda_1 + c) \right]^{-1}, \quad (\text{A.16})$$

where λ is a complex variable and $\lambda_1 = \lambda - c$. We can readily obtain³⁰ the following equation with the necessary kernel:

$$\Gamma(t) = G_{0(t)}^{(1)} e^{-ct} - \sum_j a_{0j}^2 \int_0^t G_0^{(1)}(t-t') e^{-c(t-t')} \\ \times \int_0^{t'} G_0^{(1)}(t'-t'') e^{-c(t'-t'')} \Gamma(t'') dt' dt''. \quad (\text{A.17})$$

If $t < T_2^*$, we can use a small [compared with $G_0^{(1)}(t)$ and $\Gamma(t)$] change in the function $G_0^{(2)}(t)$ on this time scale and we can then demonstrate directly the validity of the required relationship:

$$\Gamma(t) = \Gamma_0(t) \exp\left(-\frac{a^2 t^2}{2}\right). \quad (\text{A.18})$$

It should be stressed that this procedure, demonstrating the possibility of representing the FPS in the form

$$\Gamma(t) = \Gamma_0(t) \exp\left\{-a^2 \int_0^t (t-\tau) k(\tau) d\tau\right\}, \quad (\text{A.19})$$

is a formal reflection of a basic physical fact pointed out in Ref. 15: the local fields created by a cell and by the remaining (distant) spins in a sample are statistically independent because of the absence of correlations.

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