Shape of NMR spectra in solids. The pair interaction model

A. A. Lundin

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences
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A rigorous numerical solution of the integral equation derived in a preceding paper [Soviet Phys. JETP **60**, 570 (1984)] for the free precession signal of a nuclear spin cell is presented. The results of the calculations are compared with the experimental data for a CaF_2 single crystal.

In a previous paper[1] we derived, by developing a pair-interaction model, an equation for the free-precession signal of a nuclear-spin cell in a solid:

$$\Gamma(t)=G_0(t)-A^2\int_0^t G_0(t-t')\int_0^{t'}G_0(t'-t'')\Gamma(t'')\,dt'\,dt'', \tag{1}$$

where

$$\Gamma(t)\propto \mathrm{Sp}[\exp(-iH_d^0 t)S^+\exp(iH_d^0 t)S^-],$$
$$A^2=k^2\sum_j\frac{1}{16}b_{0j}^2,\qquad G_0(t)=\prod_j\cos\left(k\frac{b_{0j}t}{2}\right). \tag{2}$$

Here $S^{\pm}=S_x\pm iS_y$ are the components of the total spin operator of the system, H_d^0 is the secular part of the dipole-dipole interactions, and b_{0j} is the dipole-dipole interaction coefficient. The coefficient k is chosen to ensure the correct value for the second moment of the absorption spectrum M_2 (sum rule):

$$A^2+B^2=M_2.$$

B^2 being the second moment of the kernel $G_0(t)$. On uniform renormalization of the constants b_{0j}, we have $k=\sqrt{3/2}$ and $A^2/B^2=1/2$.

Equation (1) was solved in Ref. 1 numerically and, in particular, to describe the free-precession signal of a CaF_2 single crystal with an external magnetic field $\mathbf{H}_0$ directed along the [100] axis. The kernel $G_0(t)$ in this case was approximated by the Gaussian function

$$G_0(t)=\exp(-B^2t^2/2). \tag{3}$$

which is valid for a large number z of spins in the cell ($z\to\infty$).

Unfortunately, the numerical solution of Eq. (1) presented in Ref. 1 is wrong because of the method of solution chosen. Thus the integration procedure QUANC-8 (cf. Ref. 2), used in the iteration of Eq. (1), requires interpolation of the integrands. However, since the functions were defined by a small number of points (with intervals of 1.2 μs), the interpolation errors accumulated during the iterations. The correct solution yields a curve that agrees with that in Ref. 1 only within 25 μs and, moreover, satisfactory agreement between the amplitudes is observed only for the first few extrema. On the other hand, all the zeros are equally spaced only beginning with the second one (in the solution presented in Ref. 1 all zeros are virtually equidistant), Furthermore, the solution obtained decays at a higher rate beginning with the fourth extremum (see Table I).

The correct calculation resulted in worse agreement between theory and experiment [although the agreement, nevertheless, remained at least close (see Fig. 1)]. Equation (1) was therefore solved without approximating the kernel by a Gaussian function: with $\mathbf{H}_0$ oriented along the [100] axis there are only six spins in the cell. Consequently, the results are in appreciably better quantitative agreement with the experimental data up to 100 μs (Fig. 1). For longer times, beats in the nucleus begin to exert an effect. It should be mentioned that the beats could easily be smoothed out by slightly "smearing out" the spectrum of the nucleus on the

TABLE I Parameters of free-precession signal of cell in CaF_2. The field $\mathbf{H}_0$ is directed along the [100] axis.

Number of zeros	Position of zeros, μs			Scale of signal (value at extremum points)		
	Ref. 1	$G_0(t)$		Ref. 1	$G_0(t)$	
		Eq. (3)	Eq. (2)		Eq. (3)	Eq. (2)
1	21	22	21	−0,19	−0,188	−0,2
2	43	53	46	0,45	0,375	0,52
3	64	83	69	−0,014	−0,0074	−0,013
4	84	113	89	0,005	0,0015	0,015

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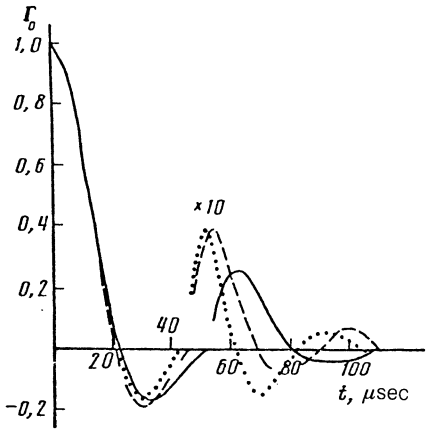

FIG. 1. Curves of free precession signal $\Gamma_0(t)$ in a CaF_2 single crystal. The external field is directed parallel to the [100] axis. The solid line is the solution of Eq. (1) multiplied by a "Gaussian-exponential" function accounting for spins of the remote surroundings;[1,3] the dashes are the solution of the same equation but with a kernel represented by the product of cosines; the points are the experimental results.[3]

basis of some self-evident physical considerations, to obtain in this way very good agreement with the experimental data in a longer time interval. This, however, would somewhat depreciate the absolute simplicity and and clarity of the model.[1] In conclusion, it should be noted that correcting the numerical solution does not affect the physical results or the main conclusions of Ref. 1.

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[1] A. A. Lundin and A. V. Makarenko, Zh. Eksp. Teor. Fiz. **87**, 999 (1984) [Sov. Phys. JETP **60**, 570 (1984)].
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[3] M. Engelsberg and I. G. Lowe, Phys. Rev. **B10**, 822 (1974).

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