Spin dynamics in multipulse NMR experiments

Yu. N. Ivanov, B. N. Provotorov, and E. B. Fel'dman

Institute of Chemical Physics, USSR Academy of Sciences

(Submitted 9 December 1977)
Pis'ma Zh. Eksp. Teor. Fiz. 27, No. 3, 164–168 (5 February 1978)

A new theoretical approach is proposed to explain the narrowing of multipulse NMR spectra in a solid. The results differ substantially from those obtained by the average-Hamiltonian method.

PACS numbers: 76.60.Es, 75.10.Dg

Recent experimental investigations[1,2] have yielded results that contradict strongly the existing theory of multipulse experiments–the theory of the average Hamiltonian.[3] We therefore propose in the present article another approach to the multipulse narrowing of NMR lines.

By way of example we consider the simplest pulse sequence $90^0_y-\tau-(\phi_x-2\tau-)^n$, where ϕ_x denotes the pulse that rotates the spins through an angle ϕ around the x axis; 2τ is the distance between pulses.

In a coordinate system rotating at the Larmor frequency around the z axis, the equation for the density matrix of the spin system $\rho(t)$ is of the form

$$i\frac{d\rho}{dt}=[-f(t)\hat{S}_x-\hat{\mathcal{H}}^z_d,\ \rho(t)], \tag{1}$$

where $f(t)$ is an impulse function defined by the formula

$$f(t)=\phi\sum_{k=0}^{\infty}\delta(\tau+2k\tau-t) \tag{2}$$

and $\hat{\mathcal{H}}^z_d$ is the secular part of the dipole-dipole interaction

$$\hat{\mathcal{H}}^z_d=-(1/2)\hat{\mathcal{H}}^x_d+\hat{\mathcal{H}}^2_d+\hat{\mathcal{H}}^{-2}_d, \tag{3}$$

where $\hat{\mathcal{H}}^x_d$ and $\hat{\mathcal{H}}^{\pm 2}_d$ are the operators of the secular and the nonsecular parts of $\hat{\mathcal{H}}^z_d$.

It is convenient next to change over to a new coordinate frame, where

$$\rho^*(t)=\exp\{-i(\int_0^t f(t')dt'-\omega_1 t)\hat{S}_x\}\,\rho\,\exp\{i(\int_0^t f(t')dt'-\omega_1 t)\hat{S}_x\},$$

$$i\frac{d\rho^*}{dt}=[\hat{\mathcal{H}}_0+\tilde{g}(t)\hat{\mathcal{H}}^2_d+\tilde{g}^*(t)\hat{\mathcal{H}}^{-2}_d,\ \rho^*(t)],$$

$$\hat{\mathcal{H}}_0 = -\omega_1 \hat{S}_x - (1/2)\hat{\mathcal{H}}_d^x + (\sin\phi/\phi)(\hat{\mathcal{H}}_d^2 + \hat{\mathcal{H}}_d^{-2}), \qquad \omega_1 = \phi/2\tau,$$

$$g(t) = \tilde{g}(t) + (\sin\phi/\phi) = \sum_{n=-\infty}^{\infty} C_n \exp\{-in\pi t/\tau\},$$

$$C_n = (-1)^n \sin\phi/(n\pi + \phi).$$

Let initially $\omega_1 \sim \omega_{loc}$. Since it is assumed that $\omega_{loc}\tau < 1$, this case corresponds to angles $\phi < 1$. We carry out for each nonzero harmonic $g(t)$ a canonical transformation

$$\tilde{\rho} = \exp\{(-in\pi t/\tau)\hat{S}_x\}\exp\{i\hat{R}_n\}\exp\{(in\pi t/\tau)\hat{S}_x\}\rho^* \exp\{(-in\pi t/\tau)\hat{S}_x\}$$
$$\times \exp\{-i\hat{R}_n\}\exp\{(in\pi t/\tau)\hat{S}_x\}, \tag{5}$$

where

$$\hat{R}_n = i\tau(C_n\hat{\mathcal{H}}_d^2 - C_n^* \hat{\mathcal{H}}_d^{-2})/(n\pi + \phi). \tag{6}$$

We then arrive at the equation

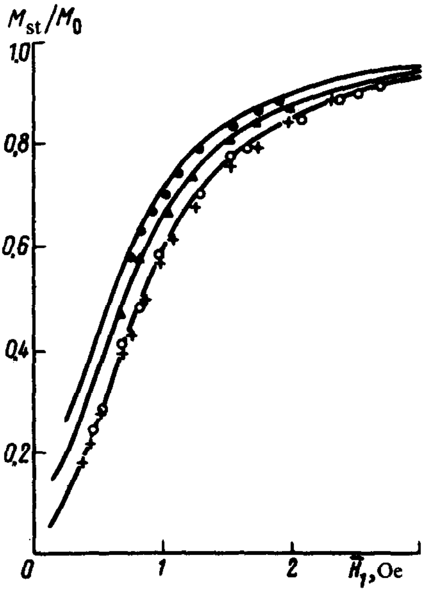

FIG. 1. Dependence of M_{st}/M_0 on the average field H_1 for a CaF_2 crystal whose [111] axis is oriented along H_0. The solid lines were calculated from formula (9) with $H_{loc} = 0.86$ Oe. The experimental points for different ϕ are marked as follows: +: 22.5°; ○: 30°; ▲: 45°; ●: 60°.

$$i\frac{d\tilde{\rho}}{dt} = [\hat{\mathcal{H}}_o + a(t)[\hat{\mathcal{H}}^{-2}_d, \hat{\mathcal{H}}^2_d] + b(t)[\hat{\mathcal{H}}^{-2}_d, \hat{\mathcal{H}}^x_d] + c(t)[\hat{\mathcal{H}}^2_d, \hat{\mathcal{H}}^x_d] + \hat{V}(t), \tilde{\rho}], \tag{7}$$

$$a(t), b(t), c(t) \sim \phi\tau/\pi, \quad \hat{V}(t) \sim (\phi\omega_{loc}\tau/\pi)^2.$$

We see therefore that the time-dependent part of the Hamiltonian decreases by a factor $\epsilon=\phi\omega_{loc}\tau/\pi$, and can be accounted for by perturbation theory. It is also obvious from (7) [4] that after a time $\sim T_2$ there should be established a quasistationary state with a density matrix ρ_{st} and

$$\rho_{st} = 1 - a_{st}\hat{\mathcal{H}}_o, \quad \mathrm{Sp}\,\rho_{st}\hat{\mathcal{H}}_o = \mathrm{Sp}\,\tilde{\rho}(0)\hat{\mathcal{H}}_o, \quad \mathrm{Sp}\,\rho_{st} = 1, \tag{8}$$

where $\tilde{\rho}(0)$ is the density matrix $\tilde{\rho}$ at the instant of time $t=0$.

From (8) we get

$$\frac{M_{st}}{M_o} = \frac{a_{st}}{a(0)} = \frac{(\phi/2\tau)^2 - 0.75\{\cos\phi - (\sin^2\phi/\phi^2)\}\omega^2_{loc}}{(\phi/2\tau)^2 + \{0.25 + 0.75(\sin^2\phi/\phi^2)\}\omega^2_{loc}}. \tag{9}$$

Here $\omega^2_{loc}=\mathrm{Sp}(\hat{\mathcal{H}}^z_d)^2/\mathrm{Sp}(\hat{S}_z)^2$.

Comparison of formula (9) with the experimental results is shown in Fig. 1 and demonstrate the good agreement between theory and experiment.[1,2] We note also that formula (9) $\omega_{loc}\tau \ll 1$ coincides with the analogous formula of[1], and that the average-Hamiltonian theory is incapable at all to deal with the establishment of the stationary state.

Calculations of the experimentally observed[2] dependence of the magnetization $M_x(t)$ in the intervals between the pulses yields

$$M_x(t) = M_x(t+2\tau),$$

$$M_x(t)/\mathrm{Sp}(S_x)^2 = a_{st}(\phi/2\tau) - a_{st}\frac{3\sin\phi}{2\phi}\tau\omega^2_{loc}\Big\{(t-\tau)\sin 2(\omega_1 t - \phi) + \tau\sin\phi\left[\frac{\cos(\phi - 2\omega_1 t)}{\sin^2\phi} - \frac{1}{\phi^2}\right]\Big\}. \tag{10}$$

At small ϕ the amplitude of this magnetization is proportional to $\phi\tau$, in agreement with experiment.[2] the relation (10) cannot be obtained within the framework of the average-Hamiltonian theory.

Different results are obtained when $\omega_1 \gg \omega_{loc}$. In this case the canonical transformations (5) must be supplemented by a canonical transformation for the zeroth harmonic of $g(t)$, which has an amplitude π/ϕ times larger than the remaining harmonics and was previously taken into account exactly. The spin system is characterized now by two integrals of motion, and its density matrix is of the form

$$\rho_{st} = 1 + a\omega_1 \hat{S}_x + 0{,}5\,\beta \hat{\mathcal{H}}_d^x, \qquad \mathrm{Sp}\,\rho_{st} = 1. \tag{11}$$

The condition for the conservation of $\hat{\mathcal{H}}_d^x$ at $t \sim T_2$ leads to $\beta=0$. For M_{st}/M_0 we then obtain a formula similar to (9) in which the coefficient $(0.25+0.75 \sin^2\phi/\phi^2)$ is replaced by $0.75 \sin^2\phi/\phi^2$. Then at $\phi=\pi/2$ we obtain $M_{st}=M_0$. The formula for $M_x(t)$ is obtained with the aid of the density matrix (11) and is characterized by an amplitude $\sim\tau^2$.

A discussion of the question of the damping decrements of the magnetization in the stationary regime is best started by considering the case $\phi \sim \pi/2$. The damping is due to absorption of the quanta produced by pulse-modulated dipole-dipole interaction. The absorption of these quanta leads to heating of the Zeeman part of the reservoir of the interactions and to a decrease of the magnetization. The largest contribution to this process is made by the nonzero harmonics with the lowest frequency. Applying to Eq. (7) two successive canonical transformations specified by the operators R_0 and R_{-1}, we find that at $\phi \sim \pi/2$ the main contribution to the absorption is made by a four-spin process, and the absorption probability is equal to

$$\frac{1}{T_{2e}} = \frac{\tau^4}{(T_2^{\bullet})^5} \exp\left\{-2\left(\frac{\pi}{2} - \phi\right)^2 / 3\,\omega_{\mathrm{loc}}^2\,\tau^2\right\}, \qquad T_2^{\bullet} \sim T_2\,. \tag{12}$$

This formula agrees well with the experimental data.[2] It is seen also from (12) that $1/T_{2e}(\tau)$ contains an essential singularity in τ. Therfore the average-Hamiltonian theory, which starts out from the assumption that the function $1/T_{2e}(\tau)$ can be expanded in powers of τ at $\phi \neq \pi/2$ is in principle incorrect.

We note in conclusion that for small ϕ, in second order of perturbation theory in ϵ, we obain for the damping decrement $1/T_{2e}=[\phi^4\tau^6/(T''_2)^7]\exp(-\pi^2/36\omega_{\mathrm{loc}}^2\tau^2)$ and $T''_2 \sim T_2$. This expression agrees satisfactorily with experiment.[1,2]

The authors are sincerely grateful to G.B. Manelis for interest in the work and to L.N. Erofeev and B.A. Shumm for useful discussions.

[1]W.-K. Rhim, D.P. Burum, and D.D. Elleman, Phys. Rev. Lett. 37, 1764 (1976).
[2]L.N. Erofeev and B.A. Shumm, Pis'ma Zh. Eksp. Teor. Fiz. this issue, preceding article.
[3]J.S. Waugh, C.H. Wang, L.M. Huber, and R.L. Vold, J. Chem. Phys. 48, 662 (1968); P. Mansfield and D. Ware, Phys. Lett. 22, 133 (1966)
[4]M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids. Oxford, 1970.