NQR in the Effective Fields of a Multiple-Pulse Sequence *

G. B. Furman, G. E. Kibrik, A. Yu. Poljakov, and I. G. Shaposhnikov
Radiospectroscopy Laboratory, Perm University, Perm 614005, USSR

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We discuss a new form of resonant response for a quadrupolar nuclear spin system subjected to applied alternating magnetic fields.

Key words: NQR, Multiple-pulse, Effective field.

Let a quadrupolar nuclear spin system be acted on by two magnetic fields: a sequence of pulses (frequency ω, amplitude H_1) along the Y-axis of the electric field gradient (EFG) tensor, and a continuous low frequency (l.f.) field (frequency $\Omega \ll \omega$, amplitude H_2) along a unit vector $\boldsymbol{a}$. In the representation used in [1, 2], the equation of motion for the density operator $\varrho(t)$ is

$$i\,\mathrm{d}\varrho(t)/\mathrm{d}t \qquad (1)$$
$$= [\Delta S_z + \varphi_y f(t)\, S_y + \omega_2\, \boldsymbol{a}\,\boldsymbol{S} \cos(\Omega t) + H_d, \varrho(t)],$$

where

(i) $\Delta = \omega_Q - \omega$, with ω_Q denoting the NQR frequency,

(ii) $\varphi_y = \gamma H_1 t_w$, γ being the gyromagnetic ratio and t_w is the pulse duration,

(iii) $f(t) = \sum_{k=0}^{\infty} \delta(t - k t_c - t_c/2)$, where t_c is the multiple-pulse sequence period,

(iv) $\omega_2 = \gamma H_2$, and

(v) $H_d = \sum_{m=-2}^{2} H_d^m$ is the secular part of the dipole-dipole interaction term of the spin Hamiltonian (see [2]).

To solve (1) we apply a unitary transformation to all operators according to

$$\tilde{\alpha} = R^+(t)\, \alpha\, R(t) \qquad (2)$$

with

$$R(t) = P(t) \exp(-2\pi i k t \boldsymbol{n}\boldsymbol{S}/t_c), \quad k = 0, \pm 1, \pm 2, \ldots, \qquad (3)$$

where $P(t)$ is the solution of the equation

$$i\,\mathrm{d}P(t)/\mathrm{d}t = \{\Delta S_z + \varphi_y f(t)\, S_y\}\, P(t) - \omega_e\, P(t)\, \boldsymbol{n}\boldsymbol{S},$$
$$P(0) = 1 \qquad (4)$$

with

$$\omega_e = 2 \cos^{-1}[\cos(\varphi_y/2)\cos(\Delta t_c/2)]/t_c \qquad (5)$$

and

$$n_1 = \sin(\varphi_y/2)/\sin(\omega_e t_c/2), \quad n_2 = 0,$$
$$n_3 = \cos(\varphi_y/2)\sin(\Delta t_c/2)/\sin(\omega_e t_c/2). \qquad (6)$$

Then (1) may be rewritten in the form

$$i\,\mathrm{d}\tilde{\varrho}(t)/\mathrm{d}t = [\Omega_k\, \boldsymbol{n}\boldsymbol{S} + \omega_2\, \widetilde{\boldsymbol{a}\boldsymbol{S}} \cos(\Omega t) + \tilde{H}_d, \tilde{\varrho}(t)], \qquad (7)$$

where

$$\Omega_k = \omega_e + 2\pi k/t_c, \qquad (8)$$

$$\widetilde{\boldsymbol{a}\boldsymbol{S}} = \sum_{q \neq k} A_q \exp(2\pi q t i/t_c) + A_k, \qquad (9)$$

and

$$\tilde{H}_d = \sum_{q \neq k} B_q \exp(2\pi q t i/t_c) + B_k + H_d^0. \qquad (10)$$

A_q and B_q are the Fourier coefficients.

Analysis of (7) with expressions (8)–(9) reveals a resonant absorption of the l.f. field energy by the spin system in the case $\Omega \cong \Omega_k$, $k = 0, \pm 1, \pm 2, \ldots$. To take into account the role played by the corresponding resonance terms of the right-hand side of (7), we use the unitary transformation

$$\varrho^*(t) = \exp(i\Omega\, \boldsymbol{n}\boldsymbol{S} t)\, \tilde{\varrho}(t) \exp(-i\Omega\, \boldsymbol{n}\boldsymbol{S} t). \qquad (11)$$

After this transformation the evolution of the density operator is determined by the equation

$$i\,\mathrm{d}\varrho^*(t)/\mathrm{d}t = [H_{\mathrm{eff}} + V(t), \varrho^*(t)], \qquad (12)$$

where the time-independent term H_{eff} is given by $H_{\mathrm{eff}} = H_0 + H_d^0$ with H_d^0 following from $H_d = \sum_{m=-2}^{2} H_d^m$.

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Reprint requests to Prof. Dr. I. Shaposhnikov, Radiospectroscopy Laboratory, Perm University, Bukirev St. 15, Perm 614005, USSR.

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Also,

$$H_0 = (\Omega_k - \Omega)\, \boldsymbol{n S} + \omega_2 (2\omega_e t_c)^{-1} \sin(\omega_e t_c/2)\, \boldsymbol{a S}\,. \quad (13)$$

Now we consider the condition

$$\| H_{\text{eff}} \| \gg \| V(t) \|\,, \quad (14)$$

a case which is experimentally realizable. From (14) it follows that there exists some τ such that for $t \leqq \tau$ the term $V(t)$ on the right-hand side of (12) may be neglected, whereas not for $t > \tau$. The problem to be solved is: given a value $M(0) = M_0$ for the component of the macroscopic magnetic moment $\boldsymbol{M}$ along the direction $\boldsymbol{n}$ (see (6)), what is the value $M(\tau) \equiv M_\tau$ of this component at some later time?

Let M_0 be created by a very short pulse applied to the system at equilibrium. For $t \leqq \tau$ we have

$$i\,\mathrm{d}\varrho^*(t)/\mathrm{d}t = [H_{\text{eff}}, \varrho^*(t)] \quad (15)$$

with the initial condition (in the high-temperature approximation)

$$\varrho^*(0) = 1 - \beta_L\, \omega_Q\, \boldsymbol{n S}\,. \quad (16)$$

Here β_L is the inverse temperature of the lattice. The formal solution is

$$\varrho^*(t) = \exp(-i H_{\text{eff}} t)\, \varrho^*(0) \exp(i H_{\text{eff}} t)\,. \quad (17)$$

Taking $H_{\text{eff}} = f_1 + f_2$ with $f_1 = H_0$, $f_2 = H_d^0$, one obtains

$$[H_{\text{eff}}, f_1] \cong [H_{\text{eff}}, f_2] \cong [f_1, f_2] \cong 0 \quad (18)$$

and

$$\mathrm{Sp}(f_m) = 0, \quad \mathrm{Sp}(f_m f_{m'}) = \delta_{mm'}\, \mathrm{Sp}(f_m)^2; \quad m, m' = 1, 2. \quad (19)$$

From (17)–(19) it follows that

$$\mathrm{Sp}[\varrho^*(t) f_m] = \mathrm{Sp}[\varrho^*(0) f_m], \quad m = 1, 2, \quad (20)$$

and, in particular,

$$\mathrm{Sp}[\varrho^*(\tau) f_m] = \mathrm{Sp}[\varrho^*(0) f_m]\,. \quad (21)$$

Using (16) and (21), we then have

$$M_\tau(\Omega) = M_0 \frac{(\Omega_k - \Omega)^2}{(\Omega_k - \Omega)^2 + \omega_2^2 (2\omega_e t_c)^{-2} \sin^2(\omega_e t_c/2) + \omega_{\text{loc}}^2}\,,$$

where

$$\omega_{\text{loc}}^2 = \mathrm{Sp}(H_d^0)^2 / \mathrm{Sp}(\boldsymbol{n S})^2\,. \quad (23)$$

This is the solution of the problem above mentioned.

To verify the theoretical predictions, a set of some experiments was performed. With a home-made multiple-pulse NQR spectrometer, the ^{35}Cl NQR in polycrystalline $KClO_3$ was observed at 77 K and

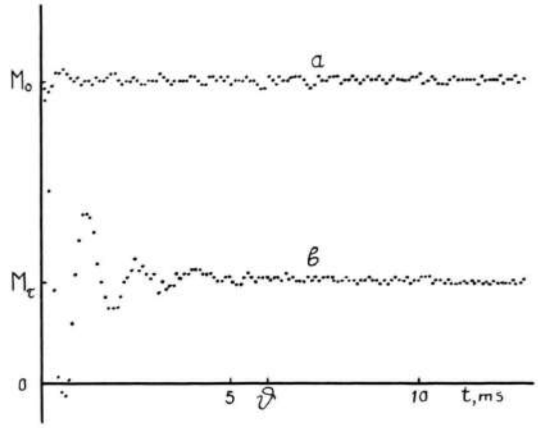

Fig. 1. Time dependence of the magnetization (a) in the absence of the l.f. field; (b) in the presence of the l.f. field.

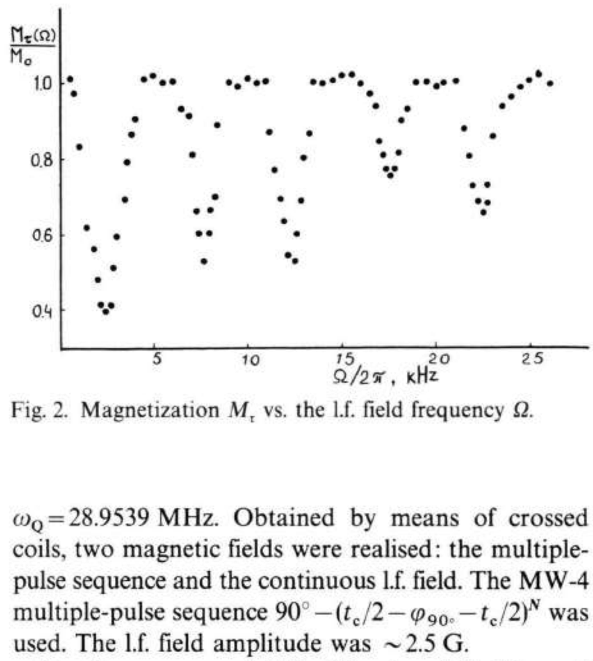

Fig. 2. Magnetization M_τ vs. the l.f. field frequency Ω.

$\omega_Q = 28.9539$ MHz. Obtained by means of crossed coils, two magnetic fields were realised: the multiple-pulse sequence and the continuous l.f. field. The MW-4 multiple-pulse sequence $90^\circ - (t_c/2 - \varphi_{90^\circ} - t_c/2)^N$ was used. The l.f. field amplitude was ~ 2.5 G.

Results are presented in Figs. 1 and 2. Figure 1 shows $M(t)$ for $t < T_1$ under the multiple-pulse sequence, after the preparation pulse, both in the absence of the l.f. field (Fig. 1a) and in the presence of this field with $\Omega = \omega_e$ (Fig. 1b). One sees here that the l.f. field clearly influences the spin system behavior. Figure 2 shows the dependence on Ω of the value M_ν of M at time ν (see Fig. 1b): $M_\nu(\Omega)$. This curve was obtained for the following pulse sequence parameters: $\varphi_y = \pi/2$, $t_c = 100$ ms, $\Delta = 0$. The values of Ω for which the curve has minima are $\Omega_0/2\pi = 2.4$ kHz, $|\Omega_{-1}/2\pi| = 7.6$ kHz, $\Omega_1/2\pi = 12.4$ kHz, $|\Omega_{-2}/2\pi| = 17.6$ kHz,

$\Omega_2/2\pi = 22.4$ kHz. For these Ω values the absorption of the l.f. field energy by the spin system becomes maximum. This is a new resonance phenomenon for nuclear quadrupole spin systems.

The experimental results are in good agreement with the theoretical curve (22), which suggests that the supposition $\nu \sim \tau$ is plausible.

A problem, similar to that studied in this paper was considered in [3, 4]. Our approach, however, is more general both theoretically and experimentally. Relaxation phenomena also can be examined in the framework of the problem in question, and the results of such investigations can be used for the study of slow molecular motions in solids.

We conclude with a remark concerning terminology. In [3, 4] the term "effective field" was used for the quantity $\omega_e \boldsymbol{n}$ (see (5), (6)). From the point of view of our results it would be more fitting to use "effective fields" for the quantities $\omega_e^{(k)} \boldsymbol{n}$, with

$$\omega_e^{(k)} = \frac{2}{t_c} \cos^{-1}[\cos(\varphi_y/2)\cos(\Delta t_c/2)] + 2\pi k/t_c, \quad k = 0, \pm 1, \pm 2, \ldots \quad (24)$$

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