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A study of the spin–echo spin-locking effect in multi-pulse sequences in ^{14}N nuclear quadrupole resonance

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Abstract

Experimental evidence of observing a rather unusual spin-locking spin echo (SLSE) effect in the fields of two multi-pulse sequences $(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$ and $(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_n$ in ^{14}N nuclear quadrupole resonance is presented. It was demonstrated that the SLSE effect is observed only in the even pulse intervals of both sequences. All experiments were carried out at room temperature on a powder sample of $NaNO_2$. A theoretical description of the effect is given.

Keywords: Nuclear quadrupole resonance; Multi-pulse sequence; Spin-locking; Spin–echo; Solid echo

1. Introduction

The discovery of the multi-pulse spin-locking spin–echo (SLSE) effect in the nuclear quadrupole resonance (NQR) spectroscopy [1] greatly stimulated the development of this area of spectroscopy. The possibility presented by the SLSE effect to accumulate multiple signals radically increased the range of compounds that could be studied as it permitted to detect directly even the weak signals in nitrogen-containing substances. The practical significance of this was recently confirmed by a whole new range of NQR applications [2–6].

Therefore, the great interest of researchers in the SLSE effect reflected in numerous publications of both experimental and theoretical nature [1,7–18], is justified.

Until now the SLSE effect in NQR has been observed experimentally in the fields of only three multi-pulse sequences:

MW-4 [1]

$$(\varphi_0)_y - (\tau - \varphi_x - \tau)_n, \tag{1}$$

MW-2 [7]

$$(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_{-x} - \tau)_n \tag{2}$$

and [18]

$$(\varphi_0)_{\pi/4} - (\tau - \varphi_x - 2\tau - \varphi_y - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-y} - \tau)_n. \tag{3}$$

(φ_0 and φ are the flip angles of the preparatory pulse and the other pulses of the sequence, respectively).

In the case of the quadrature detection the signals observed after all the three sequences do not display any significant differences. This becomes obvious if we consider the equations for the spin system magnetisation obtained for each of the three sequences [14,18] which vary only by the value of the resonance offset of the effective field of the sequence.

This communication presents data on a rather unusual SLSE effect that is generated by sequences of the following type:

$$(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n \tag{4}$$

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and

$$(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_n, \qquad (5)$$

where ϕ is the preparatory pulse phase.

The peculiarity of the effect consists in its being observed only in the even pulse intervals of each of the sequences and whatever the phase of the preparatory pulse ϕ is set, it is never observed in the odd intervals.

A theoretical analysis given in the paper confirms that the focusing properties of the spin-system with homonuclear dipole interactions can only be observed in the even pulse intervals of sequences (4) and (5). The analysis was carried out on the basis of a two-particle model.

All experimental data presented in this communication was obtained for powder $NaNO_2$ at room temperature.

2. Theory

2.1. Preliminaries

To display the principal peculiarities of the formation of the echo signal to sequences (4) and (5) we will use a two-particle model and a detailed formalism of two-particle operators (TO) [19]. The relations between TO and ordinary one-particle operators of a fictitious spin-1/2 are presented in Tables 1–3.

Table 1
Definitions of two-particle operators

$$K_1^p = I_{p,e}I_{p,1} + I_{p,1}I_{p,e},\ K_2^p = I_{p,2}I_{p,3} + I_{p,3}I_{p,2}$$
$$K_3^p = I_{p,3}I_{p,3} - I_{p,2}I_{p,2},\ K_1^q = I_{p,e}I_{p,2} + I_{p,2}I_{p,e},$$
$$K_2^q = I_{p,3}I_{p,1} + I_{p,1}I_{p,3},\ K_3^q = I_{p,1}I_{p,1} - I_{p,3}I_{p,3},$$
$$K_1^r = I_{p,e}I_{p,3} + I_{p,3}I_{p,e},\ K_2^r = I_{p,1}I_{p,2} + I_{p,2}I_{p,1},$$
$$K_3^r = I_{p,2}I_{p,2} - I_{p,1}I_{p,1},\ K_e^p = I_{p,1}I_{p,1} + I_{p,e}I_{p,e},$$
$$K_e^q = I_{p,2}I_{p,2} + I_{p,e}I_{p,e},\ K_e^r = I_{p,3}I_{p,3} + I_{p,e}I_{p,e},$$
$$K_E = I_{p,1}I_{p,1} + I_{p,2}I_{p,2} + I_{p,3}I_3 + 3I_{p,e}I_{p,e},$$
$$L_1 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,1} + I_{p,1}(I_E - 2I_{p,e}) + I_{q,1}I_{r,2} + I_{r,1}I_{q,2} + I_{q,2}I_{r,1} + I_{r,2}I_{q,1}],$$
$$L_2 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,2} + I_{p,2}(I_E - 2I_{p,e}) + I_{q,1}I_{r,1} + I_{r,1}I_{q,1} - I_{q,2}I_{r,2} - I_{r,2}I_{q,2}],$$
$$L_3 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,3} + I_{p,3}(I_E - 2I_{p,e}) - I_{q,1}I_{q,1} - I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2}],$$
$$L_e = \tfrac{1}{2}(I_{q,1}I_{q,1} + I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2}) - 2I_{p,2}I_{p,1} + \tfrac{1}{2}(I_EI_{p,e} + I_{p,e}I_E),$$
$$M_1 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,1} + I_{p,1}(I_E - 2I_{p,e}) - I_{q,1}I_{r,2} - I_{r,1}I_{q,2} - I_{q,2}I_{r,1} - I_{r,2}I_{q,1}],$$
$$M_2 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,2} + I_{p,2}(I_E - 2I_{p,e}) - I_{q,1}I_{r,1} - I_{r,1}I_{q,1} + I_{q,2}I_{r,2} + I_{r,2}I_{q,2}],$$
$$M_3 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,3} + I_{p,3}(I_E - 2I_{p,e}) + I_{q,1}I_{q,1} + I_{q,2}I_{q,2} - I_{r,1}I_{r,1} - I_{r,2}I_{r,2}],$$
$$M_e = -\tfrac{1}{2}(I_{q,1}I_{q,1} + I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2}) - 2I_{p,2}I_{p,e} + \tfrac{1}{2}(I_EI_{p,e} + I_{p,e}I_E),$$
$$N_1 = I_{p,e}I_{p,e},\ N_2 = I_{q,1}I_{q,1} + I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2} = L_e - M_e,$$
$$N_3 = \tfrac{1}{2}[(I_{q,3} - I_{p,3})I_E + I_E(I_{q,3} - I_{p,3})] = -\tfrac{2}{3}E + (I_EI_{p,e} + I_{p,e}I_E) = -\tfrac{2}{3}E + L_e + M_e + 4N_1,$$
$$E = I_EI_E,\ I_{p,e} = 2I_{p,i}^2$$

Table 2
The commutation, anticommutation, and trace relations

$$[K_1^p, K_1^q] = -[K_2^p, K_2^q] = \tfrac{1}{2}\mathrm{i}K_1^r,\ [K_1^p, K_2^q] = -[K_2^p, K_1^q] = -\tfrac{1}{2}\mathrm{i}K_2^r,$$
$$[K_1^p, K_1^q]^+ = -[K_2^p, K_2^q]^+ = \tfrac{1}{2}K_2^r,\ [K_1^p, K_2^q]^+ = [K_2^p, K_1^q]^+ = \tfrac{1}{2}K_1^r,$$
$$[K_1^p, K_3^q] = [K_1^p, K_3^r] = [K_1^p, K_e^q] = -[K_1^p, K_e^r] = \tfrac{1}{2}\mathrm{i}K_2^p,$$
$$[K_1^p, K_3^q]^+ = [K_1^p, K_3^r]^+ = [K_1^p, K_e^q]^+ = [K_1^p, K_e^r]^+ = \tfrac{1}{2}K_1^p,$$
$$[K_2^p, K_3^q] = [K_2^p, K_3^r] = [K_2^p, K_e^q] = -[K_2^p, K_e^r] = -\tfrac{1}{2}\mathrm{i}K_1^p,$$
$$[K_2^p, K_3^q]^+ = -[K_2^p, K_3^r]^+ = [K_2^p, K_e^q]^+ = [K_2^p, K_e^r]^+ = \tfrac{1}{2}K_2^p,$$
$$[K_3^p, K_3^q] = [K_e^p, K_e^q] = [K_3^p, K_e^q] = [K_e^p, K_3^q] = [K_e^p, K_a^p] = [K_a^p, K_b^p]^+ = 0,$$
$$[K_e^p, K_3^q]^+ = [K_e^p, K_e^q]^+ = -[K_3^p, K_3^q]^+ = -[K_3^p, K_3^q]^+ = \tfrac{1}{2}(K_E - 2K_e^r),$$
$$[K_a^p, K_a^p]^+ = [K_e^p, K_e^p]^+ = K_e^p,\ [K_a^p, K_e^p]^+ = K_a^p,\ [K_a^p, K_b^p] = \mathrm{i}K_c^p,$$
$$[K_E, K] = 0,\ [K_E, K]^+ = 2K,\ \mathrm{Tr}(K_E, K) = \mathrm{Tr}(K);$$

The linear relations

$$K_e^p = \tfrac{1}{2}(K_E - K_e^q + K_3^q) = \tfrac{1}{2}(K_E - K_e^r - K_3^r) = K_E - K_e^q - K_e^r = \tfrac{1}{3}(K_E + K_3^q - K_3^r),$$
$$K_3^p = \tfrac{1}{2}(K_E - 3K_e^q - K_3^q) = \tfrac{1}{2}(-K_E + 3K_e^r - K_3^r) = -K_e^q + K_e^r = -K_3^q - K_3^r,$$
$$K_3^p + K_3^q + K_3^r = 0,\ K_e^p + K_e^q + K_e^r = K_E;$$

The trace relations

$$\mathrm{Tr}(K_E) = 3,\ \mathrm{Tr}(K_e^p) = 1,\ \mathrm{Tr}(K_a^p) = 0,\ \mathrm{Tr}[(K_E)^2] = 3,$$
$$\mathrm{Tr}[(K_a^p)^2] = \mathrm{Tr}[(K_e^p)^2] = \tfrac{1}{2},$$
$$\mathrm{Tr}(K_a^pK_b^p) = \mathrm{Tr}(K_a^pK_e^p) = \mathrm{Tr}(K_a^pK_b^q) = \mathrm{Tr}(K_1^pK_1^q) = \mathrm{Tr}(K_2^pK_2^q) = 0,$$
$$\mathrm{Tr}(K_e^pK_3^p) = \mathrm{Tr}(K_e^pK_e^q) = -\mathrm{Tr}(K_3^pK_3^q) = -\mathrm{Tr}(K_3^pK_3^q) = -\mathrm{Tr}(K_3^pK_e^q) = \tfrac{1}{4},$$

Here, a, b, $c = x, y, z$, and K denotes any operators of the set; these relations hold also after cyclic permutations of p, q, r, and/or a, b, c.

Table 3
The relations among two-particle operators

$$[K, L] = [K, L]^+ = [K, M] = [K, M]^+ = [L, M] = [L, M]^+ = 0,$$
$$[N, K] = [N, L] = [N, M] = [N_1, N_2] = [N_2, N_3] = 0,$$
$$\mathrm{Tr}(KL) = \mathrm{Tr}(KM) = \mathrm{Tr}(LM) = 0,$$
$$[L_a, L_b] = iL_c,\ [L_a, L_b]^+ = 0,\ [L_a, L_b]^+ = [L_e, L_e]^+ = L,\ [L_a, L_e] = L_a,$$
$$\mathrm{Tr}(L_a) = 0,\ \mathrm{Tr}(L_e) = 1,\ \mathrm{Tr}(L_a, L_b) = 0,\ \mathrm{Tr}[(L_a)^2] = \tfrac{1}{2},$$

Here, $a, b, c = x, y, z$ or cyclic permutations; K, L, M or N denote any operator of the K, L, M or N sets, respectively.

Similarly to [19] we use the following system of notations. The place of the operator in the product of two one-particle fictitious spin-1/2 operators corresponds to the number of the spin to which this operator refers. Thus, if we are considering a system consisting of two spins 1 and 2, than for example operator $I_{p,1}$ for spin 1 can be presented as $I_{p,1}^{(1)} = I_{p,1}^{(1)}I_E^{(2)} = I_{p,1}I_E$ (I_E is a unit operator for spin 2).

Further on we will also use the ordinary notation of operators of a fictitious spin-1/2 for designating the sum of the corresponding one-particle operators:

$$I_{p,1} = I_{p,1}^{(1)} + I_{p,1}^{(2)} = I_{p,1}I_E + I_EI_{p,1} = 2K_1^p + L_1 + M_1;$$
$$I_{p,2} = I_{p,2}^{(1)} + I_{p,2}^{(2)} = I_{p,2}I_E + I_EI_{p,2} = 2K_1^q + L_2 + M_2;$$
$$I_{p,3} = I_{p,3}^{(1)} + I_{p,3}^{(2)} = I_{p,3}I_E + I_EI_{p,3} = 2K_1^r + L_3 + M_3. \qquad (6)$$

The total quadrupole Hamiltonian of the two-spin system in terms of two-particle operators looks as follows:

$$
\begin{aligned}
H_Q &= H_Q^{(1)} + H_Q^{(2)} \\
&= \omega_p I_{p,3} + \tfrac{1}{3}(\omega_q - \omega_r)(I_{q,3} - I_{r,3}) \\
&= \omega_p(2K_1^r + L_3 + M_3) + (\omega_q - \omega_r)N_3.
\end{aligned} \tag{7}
$$

There with,

$$
\omega_p = \frac{e^2qQ}{4}(\eta+3), \quad \omega_q = \frac{e^2qQ}{4}(\eta-3),
$$

$$
\omega_r = -\frac{e^2qQ}{2}\eta;
$$

$\omega_p = \omega_+$, $\omega_q = -\omega_-$, $\omega_r = -\omega_0$; ω_+, ω_-, ω_0 are three resonance frequencies of the nitrogen nucleus.

As demonstrated in papers [7,11], heteronuclear dipole interactions do not influence the behaviour of the spin system in multi-pulse fields and can be left out of this consideration. Therefore, our further analysis will be undertaken on the basis of the solution of Liouville equation for the density matrix ρ, which besides the quadrupole Hamiltonian includes the Hamiltonian of the interaction of the spins with a RF field H_{rf}, the Hamiltonian of the homonuclear interactions H_d, and that of inhomogeneous broadening, or resonance offset, H_Δ:

$$
\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mathrm{i}[H_Q + H_{\mathrm{rf}}(t) + H_d + H_\Delta, \rho]. \tag{8}
$$

Let us assume that the RF carrier frequency of the pulses corresponds to the resonance frequency ω_p. Then the RF Hamiltonian is

$$
\begin{aligned}
H_{\mathrm{rf}}(t) &= H_{\mathrm{rf}}^{(1)}(t) + H_{\mathrm{rf}}^{(2)}(t) \\
&= -2\gamma \cdot H_1[\cos\vartheta_L I_{p,1} + \sin\vartheta_L \cos\varphi_L I_{q,1} \\
&\quad + \sin\vartheta_L \sin\varphi_L I_{r,1}]\cos(\omega_p t + \phi) \\
&= -2\cos(\omega_p t + \phi) \sum_{m=p,q,r} \omega_{1,m} I_{m,1}.
\end{aligned}
$$

Here, $\omega_{1,p} = \gamma H_1 \cos\vartheta_L$, $\omega_{1,q} = \gamma H_1 \sin\ \vartheta_L \cos\varphi_{\mathrm{L}}$, $\omega_{1,r} = \gamma H_1 \sin\vartheta_L \sin\varphi_L$, γ is the gyromagnetic ratio of the nucleus; H_1 is the amplitude of the RF field; ϕ is the initial phase of the RF field; θ_L and φ_L represent the orientation of the RF field in the principal axis of the electric field gradient tensor.

In the interaction representation ($\tilde{\rho}(t) = \exp(\mathrm{i}tH_Q)$ $\rho(t)\exp(-\mathrm{i}tH_Q)$) the part of the RF Hamiltonian independent of time looks as follows:

$$
\begin{aligned}
\tilde{H}_{\mathrm{rf}}(t) &= \tilde{H}_{\mathrm{rf}}^{(1)}(t) + \tilde{H}_{\mathrm{rf}}^{(2)}(t) \\
&= -\omega_1 I_{p,1}\cos\phi + \omega_1 I_{p,2}\sin\phi \\
&= -\omega_1(2K_1^p + L_1 + M_1)\cos\phi \\
&\quad + \omega_1(2K_1^q + L_2 + M_2)\sin\phi \quad (\omega_1 \equiv \omega_{1,p}).
\end{aligned} \tag{9}
$$

The secular part of the dipolar Hamiltonian with respect to H_Q according to [19] can be expressed in one of the following three forms:

$$
\begin{aligned}
\tilde{H}_d &= \Omega_p(K_E + K_e^p - K_3^p - 4N_1 - N_2) \\
&\quad + (\Omega_q - \Omega_r)(M_3 - L_3), &\text{(10a)} \\
&= \Omega_p(K_E + K_e^q + K_3^q - 4N_1 - N_2) \\
&\quad + (\Omega_q - \Omega_r)(M_3 - L_3), &\text{(10b)} \\
&= \Omega_p(K_E + 2K_e^r - 4N_1 - N_2) \\
&\quad + (\Omega_q - \Omega_r)(M_3 - L_3). &\text{(10c)}
\end{aligned}
$$

According to [11]

$$
\Omega_p = \frac{\gamma^2}{r_{ij}^3}(1 - 3\cos^2\psi_p);
$$

ψ_p is the angle, constituting internuclear vector with principal axis p, along which resonance transition ω_p is excited.

The inhomogeneous line broadening is mostly determined by the deviation of the resonance frequency of the nuclei from the average value due to the scatter of the quadrupole interaction constants inside the sample. Let us introduce offsets $\Delta\omega_i$ ($i = p, q, r$), corresponding to the average deviation from the resonant frequencies of the sample ω_i. It is obvious that the values of $\Delta\omega_i$ are limited by the half-width of the corresponding resonance lines. The Hamiltonian of inhomogeneous broadening H_Δ in presenting the interaction can be written down as [19]:

$$
\begin{aligned}
\tilde{H}_\Delta &= \Delta\omega_p I_{p,3} + \tfrac{1}{3}(\Delta\omega_q - \Delta\omega_r)(I_{q,3} - I_{r,3}) \\
&= \Delta\omega_p(2K_1^r + L_3 + M_3) + (\Delta\omega_q - \Delta\omega_r)N_3 \\
&= \Delta(2K_1^r + L_3 + M_3) + (\Delta\omega_q - \Delta\omega_r)N_3, \quad \Delta \equiv \Delta\omega_p.
\end{aligned} \tag{11}
$$

Components defined by operators K_E and N in equations (10) and (11), do not have any influence on the evolution of the spin system at least at times shorter than the spin-lattice relaxation time T_1, and therefore can be left out without detriment to this consideration.

Under condition $\|\tilde{H}_{\mathrm{rf}}\| \gg \|\tilde{H}_d\|$, $\|\tilde{H}_\Delta\|$ the equation for the density matrix $\tilde{\rho}(t)$ in the interaction representation is

$$
\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = -\mathrm{i}[\tilde{H}_{\mathrm{rf}}, \tilde{\rho}] \tag{12}
$$

during the period of the RF field existence, and

$$
\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = -\mathrm{i}[\tilde{H}_T, \tilde{\rho}] \tag{13}
$$

between pulses.

In (13) notation

$$
\tilde{H}_T = \tilde{H}_d + \tilde{H}_\Delta \tag{14}
$$

is introduced.

Further on, we will omit the tilde sign.

2.2. Two pulse sequence $(\varphi_0)_y - \tau - (\varphi)_x - (t - \tau)$

Let us consider the effect of two-pulse sequence $(\varphi_0)_y - \tau - (\varphi)_x - (t - \tau)$ on the spin system on condition that the carrier frequency of the pulses coincides with the average value of the resonance frequency ω_p (further on we will call it the exact resonance condition). Therewith, we will assume that the resonance frequency of the two spin system under consideration differs from the value of ω_p by the value of Δ. The purpose of this consideration is determining the conditions for the solid echo formation.

The initial equilibrium density matrix equals

$$\rho_{\mathrm{eq}} = \tfrac{1}{9}\{E - \alpha_0\omega_p I_{p,3}\} = \tfrac{1}{9}\{E - \alpha_0\omega_p(2K_1^r + L_3 + M_3)\}. \quad (15)$$

α_0 is the inverse spin temperature corresponding to the equilibrium state.

The unit operator E obviously can be excluded from the consideration.

After the impact of sequence $\varphi_{0y} - \tau - \varphi_x - (t - \tau)$ the density matrix of the spin system equals

$$\rho = U\rho_{\mathrm{eq}}U^+, \quad (16)$$

$$\begin{aligned} U = {} & \exp(-\mathrm{i}H_T\cdot(t-\tau))\exp(\mathrm{i}\varphi I_{p,1}) \\ & \times\exp(-\mathrm{i}H_T\cdot\tau)\exp(\mathrm{i}\varphi_0 I_{p,2}) \\ = {} & \exp(-\mathrm{i}(\Omega_p(t-\tau)(K_E+K_e^p-K_3^p)+2\Delta K_1^r)) \\ & \times\exp(\mathrm{i}2\varphi_0K_1^p)\times\exp(-\mathrm{i}(\Omega_p\tau(K_E+K_e^p-K_3^p)+2\Delta K_1^r)) \\ & \times\exp(\mathrm{i}2\varphi K_1^q)\times\exp(-\mathrm{i}(\Omega_q-\Omega_r)(t-\tau)M_3)\exp(\mathrm{i}\varphi M_1) \\ & \times\exp(-\mathrm{i}(\Omega_q-\Omega_r)\tau M_3)\exp(\mathrm{i}\varphi_0 M_2) \\ & \times\exp(\mathrm{i}(\Omega_q-\Omega_r)(t-\tau)L_3)\exp(\mathrm{i}\varphi L_1) \\ & \times\exp(\mathrm{i}(\Omega_q-\Omega_r)\tau L_3)\exp(\mathrm{i}\varphi_0 L_2). \end{aligned} \quad (17)$$

In expression (17) $\varphi_0 = \varphi_{M0}\cos\theta_L$, $\varphi = \varphi_M\cos\theta_L$, $\varphi_{M0} = \gamma H_1 t_{w0}$ and $\varphi_M = \gamma H_1 t_w$, t_{w0} and t_w are the durations of the first and second pulse, respectively.

The in-phase and quadrature components of the observed signals are determined by respective equations

$$\begin{aligned} S_1 &= \mathrm{Tr}(\rho I_{p,1}\cos\theta_L) = \mathrm{Tr}(\rho(2K_1^p + M_1 + L_1))\cos\theta_L, \\ S_2 &= \mathrm{Tr}(\rho I_{p,2}\cos\theta_L) \\ &= \mathrm{Tr}(\rho(2K_1^q + M_2 + L_2))\cos\theta_L. \end{aligned} \quad (18)$$

It is only the part of the density matrix (17) that contains operators K_1^p, K_1^q, M_i and L_i $(i = 1, 2)$ that determines the observed signals.

The part of the density matrix corresponding to the observed echo equals:

$$\begin{aligned} \rho_{\mathrm{echo}} = {} & -\tfrac{1}{18}\alpha_0\omega_p[K_1^p\cos\Delta(t-2\tau)\{(\cos 2\varphi - 1) \\ & \times\cos\Omega_p(t-2\tau) - \cos\varphi\cdot\sin\Omega_p(t-2\tau)\} \\ & + K_1^q\sin\Delta(t-2\tau)\{(\cos 2\varphi - 1)\cos\Omega_p(t-2\tau) \\ & - \cos\varphi\cdot\sin\Omega_p(t-2\tau)\}] + M_1(\cos\varphi - 1) \\ & \times\cos((\Delta+\Omega_q-\Omega_r)(t-2\tau)) \\ & + M_2(\cos\varphi - 1)\sin((\Delta+\Omega_q-\Omega_r)(t-2\tau)) \\ & + L_1(\cos\varphi - 1)\cos((\Delta-\Omega_q+\Omega_r)(t-2\tau)) \\ & + L_2(\cos\varphi - 1)\sin((\Delta-\Omega_q+\Omega_r)(t-2\tau))]\sin\varphi_0. \end{aligned} \quad (19)$$

According to equations (18) the quadrature and the in-phase components of the echo signal equal

$$\begin{aligned} S_{1\mathrm{echo}} = {} & -\tfrac{1}{18}\alpha_0\omega_p[(\cos 2\varphi - 1)\cos\Delta(t-2\tau) \\ & \times\cos\Omega_p(t-2\tau) - \cos\varphi\cos\Delta(t-2\tau) \\ & \times\sin\Omega_p(t-2\tau) + (\cos\varphi - 1)\cos(\Delta(t-2\tau)) \\ & \times\cos((\Omega_q-\Omega_r)(t-2\tau))]\sin\varphi_0\cos\theta_L, \end{aligned}$$

$$\begin{aligned} S_{2\mathrm{echo}} = {} & -\tfrac{1}{18}\alpha_0\omega_p[(\cos 2\varphi - 1)\sin\Delta(t-2\tau \\ & \times\cos\Omega_p(t-2\tau) - \cos\varphi\sin\Delta(t-2\tau) \\ & \times\sin\Omega_p(t-2\tau)] + (\cos\varphi - 1)\sin(\Delta(t-2\tau)) \\ & \times\cos((\Omega_q-\Omega_r)(t-2\tau))]\sin\varphi_0\cos\theta_L. \end{aligned} \quad (20)$$

It follows from Eq. (20) that the formation of the solid echo signal is connected with two phenomena: refocusing of the offset effects induced by the distribution of the quadrupolar interaction constants, and the refocusing of the dipole interactions.

When $t = 2\tau$, only one component is non-zero.

Averaged for powder magnetization $\langle S\rangle$ equals [10]

$$\langle S\rangle = \frac{1}{2}\int_0^{\pi} S\sin\theta_L\mathrm{d}\theta_L. \quad (21)$$

Induction signal after averaging for powder take the form of [10]

$$\langle S_0\rangle = -\tfrac{1}{3}\alpha_0\omega_p\frac{\varphi_{M0}\cos\varphi_{M0} - \sin\varphi_{M0}}{\varphi_{M0}^2}.$$

Let us assume that $\varphi_M = \varphi_{M0} \simeq 0.66\pi$ ("effective 90° pulse" for powders). Then at $t = 2\tau$

$$\begin{aligned} \frac{\langle S_{\mathrm{echo}}(2\tau)\rangle}{\langle S_0\rangle} = {} & -\frac{\alpha_0\omega_p}{36\langle S_0\rangle}\int_0^{\pi}(\cos(\varphi_M\cos\theta_L) \\ & + \cos(2\varphi_M\cos\theta_L) - 2)\cos\theta_L\sin\theta_L\,\mathrm{d}\theta_L \approx 0.34. \end{aligned}$$

As it is natural to assume that the nature of echo signals, both in the case of multi-pulse sequences (1)–(5) and in the case of the two-pulse sequence considered above, is the same, to carry out an analysis of sequences (4) and (5) one should take into account the dipole interactions of like spins as well as the distribution of resonance frequencies inside the sample.

2.3. Sequence $(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$

Let us consider the effect of quadrupolar nuclei of sequence (4) on the spin system $(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$ under the exact resonance condition.

For sequence (4) the equation of motion in the interaction representation looks as follows:

$$\frac{d\rho}{dt} = -i[H_{rf} + H_T, \rho]. \quad (22)$$

For pulse approximation using δ-functions, the RF Hamiltonian for sequence (4) can be presented as

$$H_{rf} = -\varphi_0\delta(t)[\cos\phi \cdot I_{p,1} + \sin\phi \cdot I_{p,2}] + F(t)\cdot I_{p,1}, \quad (23)$$

pulse function $F(t)$ equals

$$F(t) = \varphi\left[\left(\sum_{k=0}^{n-1}\delta(t-(1+8k)\tau) + \sum_{k=0}^{n-1}\delta(t-(3+8k)\tau)\right) - \left(\sum_{k=0}^{n-1}\delta(t-(5+8k)\tau) + \sum_{k=0}^{n-1}\delta(t-(7+8k)\tau)\right)\right]. \quad (24)$$

The initial equilibrium density matrix equals

$$\rho_{eq} = -\tfrac{1}{9}\alpha_0\omega_p I_{p,3} = -\tfrac{1}{9}\alpha_0\omega_p(2K_1^r + L_3 + M_3). \quad (25)$$

As a result of the preparatory pulse $(\varphi_0)_\phi$ at $\varphi_{M0} = 0.66\pi$ action in correspondence with (12) and (23) the density matrix looks as follows:

$$\begin{aligned}\rho_{0\phi} &= \exp(i\varphi_0(I_{p.1}\cos\phi - I_{p.2}\sin\phi))\rho_{eq} \\ &\quad\times \exp(-i\varphi_0(I_{p.1}\cos\phi - I_{p.2}\sin\phi)) \\ &= -\tfrac{1}{9}\alpha_0\omega_p(I_{p,3}\cos\varphi_0 - I_{p,1}\sin\varphi_0\sin\phi \\ &\quad - I_{p,2}\sin\varphi_0\cos\phi) \\ &= \tfrac{1}{9}\alpha_0\omega_p(-(2K_1^r + L_3 + M_3)\cos\varphi_0 + (2K_1^p + L_1 + M_1) \\ &\quad\times \sin\varphi_0\sin\phi + (2K_1^q + L_2 + M_2)\sin\varphi_0\cos\phi),\end{aligned} \quad (26)$$

For preparatory pulses $(\varphi_0)_x$ and $(\varphi_0)_y$ the initial density matrix equals, respectively,

$$\begin{aligned}\rho_{0x} &= \tfrac{1}{9}\alpha_0\omega_p(-I_{p,3}\cos\varphi_0 + I_{p,2}\sin\varphi_0) \\ &= \tfrac{1}{9}\alpha_0\omega_p(-(2K_1^r + L_3 + M_3)\cos\varphi_0 \\ &\quad + (2K_1^q + L_2 + M_2)\sin\varphi_0);\end{aligned}$$

$$\begin{aligned}\rho_{0y} &= \tfrac{1}{9}\alpha_0\omega_p(-I_{p,3}\cos\varphi_0 + I_{p,1}\sin\varphi_0) \\ &= \tfrac{1}{9}\alpha_0\omega_p(-(2K_1^r + L_3 + M_3)\cos\varphi_0 \\ &\quad + (2K_1^p + L_1 + M_1)\sin\varphi_0).\end{aligned} \quad (27)$$

The effect of each pulse of sequence (4) is described by the rotation operator in the form of

$$\begin{aligned}P_j &= \exp(-(-1)^j i\varphi I_{p,1}) \\ &= \exp(-(-1)^j i\varphi(2K_1^p + M_1 + L_1)),\end{aligned} \quad (28)$$

where j is the number of the pulse in a cycle. It is obvious that $P_1 = P_2 = P_3^{-1} = P_4^{-1}$. As the pulses of the cycle of sequence (4) fulfil the condition

$$\prod_{j=1}^{4} P_j = 1, \quad (29)$$

we can use the average Hamiltonian theory to analyse sequence (4).According to [20] average zero-order Hamiltonian can be written down as follows:

$$\begin{aligned}\bar{H}_0 &= \frac{1}{t_c}\sum_{k=0}^{4}\bar{H}_{Tk}\tau_k \\ &= \tfrac{1}{4}[H_T + 2P_1H_TP_1^{-1} + (P_1)^2H_T(P_1^{-1})^2] \\ &= \Omega_p(K_E + K_e^p - \tfrac{1}{4}((1 + 2\cos 2\varphi + \cos 4\varphi)K_3^p \\ &\quad + 2\sin 2\varphi(1 + \cos 2\varphi)K_2^p)) + \Delta\tfrac{1}{2}((1 + 2 \\ &\quad \times \cos\varphi + \cos 2\varphi)K_1^r + 2\sin\varphi(1 \\ &\quad + \cos\varphi)K_1^q) + \tfrac{1}{4}[\Delta + (\Omega_q - \Omega_r)][(1 + 2\cos\varphi \\ &\quad + \cos 2\varphi)M_3 + 2\sin\varphi(1 + \cos\varphi)M_2] + \tfrac{1}{4}[\Delta \\ &\quad - (\Omega_q - \Omega_r)][(1 + 2\cos\varphi + \cos 2\varphi)L_3 + 2 \\ &\quad \times \sin\varphi(1 + \cos\varphi)L_2].\end{aligned} \quad (30)$$

In equation (30) we used notations

$$\bar{H}_{Tk} = \left(\prod_{j=0}^{k}P_j\right)^{-1} H_T\left(\prod_{j=0}^{k}P_j\right); \quad (31)$$

$P_0 = 1;\ \ \tau_0 = \tau_4 = \tau;\ \ \tau_1 = \tau_2 = \tau_3 = 2\tau;\ \ t_c = 8\tau.$

Let us consider two probable extreme cases: $\Delta \ll \Omega_i$ and $\Delta \gg \Omega_i$ $(i = p, q, r)$.

The first case occurs rather rarely and conforms to the condition $T_2 \approx T_2^*$, the second one is the most frequent and complies with the in equation $T_2 \gg T_2^*$.

First let us consider the case of $\Delta \ll \Omega_i$.

Omitting all terms proportional to Δ in expression (30), we obtain:

$$\begin{aligned}\bar{H}_0 &= \Omega_p(K_E + K_e^p - \tfrac{1}{4}((1 + 2\cos 2\varphi + \cos 4\varphi)K_3^p \\ &\quad + 2\sin 2\varphi(1 + \cos 2\varphi)K_2^p)) + \tfrac{1}{4}(\Omega_q - \Omega_r) \\ &\quad \times [(1 + 2\cos\varphi + \cos 2\varphi)(M_3 - L_3) \\ &\quad \times +2\sin\varphi(1 + \cos\varphi)(M_2 - L_2)].\end{aligned} \quad (32)$$

Hamiltonian (32) does not contain a single K-operator that would make an input into the observed signal. Therefore, K-operators in expression (32) can be excluded from consideration. The truncated version of Hamiltonian $\bar{H}_0$ looks as follows:

$$\begin{aligned}\bar{H}_0 &= \tfrac{1}{4}(\Omega_q - \Omega_r)[(1 + 2\cos\varphi + \cos 2\varphi)(M_3 - L_3) \\ &\quad + 2\sin\varphi(1 + \cos\varphi)(M_2 - L_2)].\end{aligned} \quad (33)$$

It takes $2 \div 3T_2$ (T_2 is the time of spin–spin relaxation) for the quasi-stationary state to be established in the spin system, the quasi-stationary state is described by the density matrix as ρ_{qst}. When $\rho_0 = \rho_{0x}$ operator ρ_{qst}

can be calculated as a total of projections of the density matrix ρ_{0x} on Hamiltonians $\bar{H}_0$ [21]:

$$\bar{H}_0 = \bar{H}_{01} + \bar{H}_{02};$$

$$\bar{H}_{01} = \tfrac{1}{4}(\Omega_q - \Omega_r)[(1 + 2\cos\varphi + \cos 2\varphi)M_3 + 2\sin\varphi(1+\cos\varphi)M_2];$$

$$\bar{H}_{02} = -\tfrac{1}{4}(\Omega_q - \Omega_r)[(1 + 2\cos\varphi + \cos 2\varphi)L_3 + 2\sin\varphi(1+\cos\varphi)L_2];$$

$$(\bar{H}_{01}|\bar{H}_{02}) = 0.$$

$$\begin{aligned}\rho_{qst} &= \sum_{i=1}^{2}\frac{\mathrm{Tr}(\rho_{0x}\cdot\bar{H}_{0i})}{\mathrm{Tr}(\bar{H}_{0i})^2}\bar{H}_{0i} = \sum_{i=1}^{2}\alpha_{xi}\bar{H}_{0i}\\ &= -\tfrac{1}{9}\alpha_0\omega_p(1+2\cos\varphi+\cos 2\varphi)^2\cos\varphi_0(M_3+L_3)\\ &\quad - 4\sin^2\varphi\cdot(1+\cos\varphi)^2\sin\varphi_0(M_2+L_2)/\\ &\quad ((1+2\cos\varphi+\cos 2\varphi)^2 + 4\sin^2\varphi\cdot(1+\cos\varphi)^2.)\end{aligned} \tag{34}$$

It is obvious that coefficients $\alpha_{xi} = \frac{\mathrm{Tr}(\rho_{0x}\cdot\bar{H}_{0i})}{\mathrm{Tr}(\bar{H}_{0i})^2}$ coincide with the values of reverse spin temperatures of thermodynamic reservoirs determined by $\bar{H}_{0i}$ interactions [21].

Magnetisation in this case has only one component

$$\begin{aligned}S &= \mathrm{Tr}(\rho_{qst}I_{p,2}\cos\theta_L)\\ &= \mathrm{Tr}(\rho_{qst}(2K_1^q + M_2 + L_2))\cos\theta_L\\ &= \tfrac{1}{9}\alpha_0\omega_p\cos\theta_L\\ &\quad\times\frac{4\sin^2\varphi\cdot(1+\cos\varphi)^2\sin\varphi_0}{(1+2\cos\varphi+\cos 2\varphi)^2+4\sin^2\varphi\cdot(1+\cos\varphi)^2}\\ &= \tfrac{1}{9}\alpha_0\omega_p\cos\theta_L\times 4\sin^2(\varphi_M\cos\theta_L)\\ &\quad\cdot(1+\cos(\varphi_M\cos\theta_L))^2\sin(\varphi_{M0}\cos\theta_L)\\ &\quad/(1+2\cos(\varphi_M\cos\theta_L)+\cos(2\varphi_M\cos\theta_L))^2\\ &\quad+4\sin^2(\varphi_M\cos\theta_L)\cdot(1+\cos(\varphi_M\cos\theta_L))^2.\end{aligned} \tag{35}$$

In accordance with expression (21) averaged for powder magnetisation $\langle S\rangle$ at $\varphi_{M0} \simeq 0.66\pi$ equals

$$\langle S\rangle = \tfrac{1}{9}\alpha_0\omega_p I(\varphi_M), \tag{36}$$

where

$$\begin{aligned}I(\varphi_M) = \int_0^{\pi} &\{(\sin^2(\varphi_M\cos\theta_L)\cdot(1+\cos(\varphi_M\cos\theta_L))^2\\ &\times\sin(0.66\pi\cos\theta_L))/((1+2\cos(\varphi_M\cos\theta_L)\\ &+\cos(2\varphi_M\cos\theta_L))^2+4\sin^2(\varphi_M\cos\theta_L)\\ &\cdot(1+\cos(\varphi_M\cos\theta_L))^2)\}\times\sin 2\theta_L \mathrm{d}\theta_L.\end{aligned}$$

Numerical integration shows that function $I(\varphi_M)$ reached its maximum value at $\varphi_M \approx 0.65\pi$. At $\varphi_M = 0.66\pi$ the value of function $I(\varphi_M)$ differs from the maximum by less than 0.1% and equals $I(0.66\pi) \approx 0.37$. Thus, magnetisation averaged for powder equals

$$\langle S\rangle \approx \frac{0.37}{9}\alpha_0\omega_p. \tag{37}$$

The amplitude of magnetisation in powder, created by preparatory pulse $\varphi_{M0} = 0.66\pi$, equals

$$\begin{aligned}\langle S_0(0.66\pi)\rangle &= \tfrac{1}{3}\alpha_0\omega_p\frac{0.66\pi\cdot\cos 0.66\pi - \sin 0.66\pi}{(0.66\pi)^2}\\ &\approx \frac{0.44}{3}\alpha_0\omega_p.\end{aligned} \tag{38}$$

From (37) and (38) we obtain the maximum ratio of the echo signal amplitude to the induction signal in powder

$$\frac{\langle S\rangle}{\langle S_0\rangle} \approx 0.28. \tag{39}$$

Expressions (35)–(38) were obtained for the case $\Delta \ll \Omega_i$, corresponding to similar relaxation times T_2 and T_2^*.

Now let us find expressions for a much more frequent case of magnetization $\Delta \gg \Omega_i$, when $T_2 \gg T_2^*$.

If in expression (30) we neglect all members $\sim\Omega_i$, we obtain

$$\begin{aligned}\bar{H}_0 &= \frac{\Delta}{2}((1+2\cos\varphi+\cos 2\varphi)K_1^r + 2\sin\varphi(1+\cos\varphi)K_1^q)\\ &\quad+\frac{\Delta}{4}[(1+2\cos\varphi+\cos 2\varphi)(M_3+L_3)\\ &\quad+2\sin\varphi(1+\cos\varphi)(M_2+L_2)].\end{aligned} \tag{40}$$

Average Hamiltonian $\bar{H}_0$ can be presented as a total of three mutually commuting operators $\bar{H}_{0i}$, which also satisfy the requirement of being mutually orthogonal:

$$\begin{aligned}\bar{H}_0 &= \sum_{i=1}^{3}\bar{H}_{0i};\bar{H}_{01}\\ &= \Delta\tfrac{1}{2}((1+2\cos\varphi+\cos 2\varphi)K_1^r + 2\sin\varphi(1+\cos\varphi)K_1^q);\end{aligned}$$

$$\bar{H}_{02} = \tfrac{1}{4}\Delta[(1+2\cos\varphi+\cos 2\varphi)M_3 + 2\sin\varphi(1+\cos\varphi)M_2];$$

$$\bar{H}_{03} = \tfrac{1}{4}\Delta[(1+2\cos\varphi+\cos 2\varphi)L_3 + 2\sin\varphi(1+\cos\varphi)L_2];$$

$$(\bar{H}_{0i}|\bar{H}_{0j}) = 0,\quad i \neq j.$$

The density matrix assumes the form

$$\begin{aligned}\rho_{qst} &= \sum_{i=1}^{3}\frac{\mathrm{Tr}(\rho_{0x}\cdot\bar{H}_{0i})}{\mathrm{Tr}(\bar{H}_{0i})^2}\bar{H}_{0i} = \sum_{i=1}^{3}\alpha_{xi}\bar{H}_{0i}\\ &= -\tfrac{1}{9}\alpha_0\omega_p\frac{(1+2\cos\varphi+\cos 2\varphi)^2(K_1^r+M_3+L_3)}{(1+2\cos\varphi+\cos 2\varphi)^2+4\sin^2\varphi\cdot(1+\cos\varphi)^2}\\ &\quad\times\cos\varphi_0 + \tfrac{1}{9}\alpha_0\omega_p\\ &\quad\times\frac{4\sin^2\varphi\cdot(1+\cos\varphi)^2(K_1^q+M_2+L_2)}{(1+2\cos\varphi+\cos 2\varphi)^2+4\sin^2\varphi\cdot(1+\cos\varphi)^2}\\ &\quad\times\sin\varphi_0.\end{aligned} \tag{41}$$

Magnetization has one component and equals

$$S = \mathrm{Tr}(\rho_{qst} I_{p,2}) = \mathrm{Tr}(\rho_{qst}(2K_1^q + M_2 + L_2)) = \tfrac{2}{9}\alpha_0\omega_p \times \frac{4\sin^2\varphi \cdot (1+\cos\varphi)^2 \sin\varphi_0}{(1+2\cos\varphi+\cos 2\varphi)^2 + 4\sin^2\varphi\cdot(1+\cos\varphi)^2}. \quad (42)$$

Averaging for powder at $\varphi_{M0} = 0.66\pi$ gives

$$\langle S\rangle = \tfrac{2}{9}\alpha_0\omega_p I(\varphi_M). \quad (43)$$

At $\varphi_M = 0.66\pi$ we obtain the value of $\langle M\rangle$ close to maximum

$$\langle S\rangle = \frac{0.74}{9}\alpha_0\omega_p. \quad (44)$$

The ratio of the echo signal amplitude to the induction signal observed after the preparatory signal, does not exceed the value

$$\frac{\langle S\rangle}{\langle S_0\rangle} \approx 0.56. \quad (45)$$

If $\rho_0 = \rho_{0y}$, then

$$\rho_{qst} = \sum_{i=1}^{2} \frac{\mathrm{Tr}(\rho_{0y}\cdot \bar{H}_{0i})}{\mathrm{Tr}(\bar{H}_{0i})^2}\bar{H}_{0i} = \sum_{i=1}^{2}\alpha_{yi}\bar{H}_{0i} = 0, \quad (46)$$

where

$$\alpha_{yi} = \frac{\mathrm{Tr}(\rho_{0y}\cdot\bar{H}_{0i})}{\mathrm{Tr}(\bar{H}_{0i})^2}. \quad (47)$$

It follows from expression (46) that the choice of a preparatory pulse $(\varphi_0)_\phi$ with phase $\phi = y$ leads to a complete absence of observed NQR signal at times $\geqslant T_2$.

Expressions (41), (46) describe the density matrix of the spin system corresponding to the stroboscopic observation of the NQR signals in the middle of each last interval of a cycle of sequence (4). Let us obtain the expressions for the density matrix for the other intervals of the sequence. We transform the equation of pulse sequence (4) as

$$[(\varphi_0)_\phi - \tau - \varphi_x - \tau] - (\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - 2\tau - \varphi_x - \tau)_n, \quad (48a)$$

$$[(\varphi_0)_\phi - \tau - \varphi_x - 2\tau - \varphi_x - \tau] - (\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - 2\tau - \varphi_x - 2\tau - \varphi_x - \tau)_n, \quad (48b)$$

$$[(\varphi_0)_\phi - \tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - \tau] - (\tau - \varphi_{-x} - 2\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - \tau)_n. \quad (48c)$$

In this form, the pulses in square brackets play the preparatory role and their effect corresponds to the initial matrix of the sequence ρ_0. For all pulse groups in the round brackets the requirement of cyclic recurrence holds (29), therefore, these pulse groups can be regarded as cycles. Formulating the sequences as in ((48a)–(48c)) reflects the method of signal detection corresponding in each case with the end of the cycle.

Let us determine propagators expressed as

$$U_{\pm x} = \exp(-\mathrm{i}H_d\tau)\exp(\pm\mathrm{i}\varphi I_{p,1})\exp(-\mathrm{i}H_d\tau) = \exp(-\mathrm{i}H_d\tau)\exp(\pm\mathrm{i}\varphi(2K_1^p + L_1 + M_1))\exp(-\mathrm{i}H_d\tau). \quad (49)$$

The initial density matrixes after the impact of sequences (48a)–(48c) equal, respectively,

$$\rho_{0\phi}^A = U_x\rho_{0\phi}U_x^{-1}; \quad \rho_{0\phi}^B = U_xU_x\rho_{0\phi}U_x^{-1}U_x^{-1}; \quad \rho_{0\phi}^C = U_{-x}U_xU_x\rho_{0\phi}U_x^{-1}U_x^{-1}U_{-x}^{-1}. \quad (50)$$

In expressions (40) the upper indices A, B, and C correspond to sequences (48a), (48b), and (48c).

One can see that the full propagator of the cycle of sequence (48a) can be expressed through the average Hamiltonian of sequence (4):

$$U_A = U_xU_{-x}U_{-x}U_x = U_x^{-1}(U_xU_xU_{-x}U_{-x})U_x = U_x^{-1}\exp(-\mathrm{i}t_c\bar{H}_0)U_x = \exp(-\mathrm{i}t_c(U_x^{-1}\bar{H}_0U_x)). \quad (51)$$

On the other hand, propagator U_A can be presented as

$$U_A = \exp(-\mathrm{i}t_c\bar{H}_0^A), \quad (52)$$

where $\bar{H}_0^A$ is the average Hamiltonian of sequence (48a).

From expressions (51) and (52) it follows that

$$\bar{H}_0^A = U_x^{-1}\bar{H}_0U_x = \sum_{i=1}^{4}\bar{H}_{0i}^A, \quad (53)$$

where

$$\bar{H}_{0i}^A = U_x^{-1}\bar{H}_{0i}U_x. \quad (54)$$

In a similar way, for average Hamiltonians $\bar{H}_0^B$ and $\bar{H}_0^C$ of sequences (48b) and (48c) we obtain

$$\bar{H}_0^B = U_x^{-1}U_x^{-1}\bar{H}_0U_xU_x = \sum_{i=1}^{4}\bar{H}_{0i}^B, \quad (55)$$

$$\bar{H}_0^C = U_{-x}^{-1}U_x^{-1}U_x^{-1}\bar{H}_0U_xU_xU_{-x} = \sum_{i=1}^{4}\bar{H}_{0i}^C, \quad (56)$$

$$\bar{H}_{0i}^B = U_x^{-1}U_x^{-1}\bar{H}_{0i}U_xU_x, \quad (57)$$

$$\bar{H}_{0i}^C = U_{-x}^{-1}U_x^{-1}U_x^{-1}\bar{H}_{0i}U_xU_xU_{-x}. \quad (58)$$

It is obvious that operators $\bar{H}_{0i}^J$ ($J = A$, B or C) have the same commutative and orthogonal properties as operators $\bar{H}_{0i}$. Therefore, density matrixes of the quasi-stationary state for sequences (48a)–(48c) can be presented in a way similar to that in expressions (34) and (41):

$$\rho^A_{qst} = \sum_{i=1}^{4} \frac{\mathrm{Tr}(\rho^A_{0\phi} \cdot \bar{H}^A_{0i})}{\mathrm{Tr}(\bar{H}^A_{0i})^2} \bar{H}^A_{0i} = \sum_{i=1}^{4} \alpha^A_{\phi i} \bar{H}^A_{0i}, \tag{59a}$$

$$\rho^B_{qst} = \sum_{i=1}^{4} \frac{\mathrm{Tr}(\rho^B_{0\phi} \cdot \bar{H}^B_{0i})}{\mathrm{Tr}(\bar{H}^B_{0i})^2} \bar{H}^B_{0i} = \sum_{i=1}^{4} \alpha^B_{\phi i} \bar{H}^B_{0i}, \tag{59b}$$

$$\rho^C_{qst} = \sum_{i=1}^{4} \frac{\mathrm{Tr}(\rho^C_{0\phi} \cdot \bar{H}^C_{0i})}{\mathrm{Tr}(\bar{H}^C_{0i})^2} \bar{H}^C_{0i} = \sum_{i=1}^{4} \alpha^C_{\phi i} \bar{H}^C_{0i}. \tag{59c}$$

Equations (49) designate:

$$\alpha^J_{\phi i} = \frac{\mathrm{Tr}(\rho^J_{0\phi} \cdot \bar{H}^J_{0i})}{\mathrm{Tr}(\bar{H}^J_{0i})^2}, J = A, B \text{ or } C. \tag{60}$$

Having substituted expressions (50), (54), (57), into (60) we obtain

$$\alpha^A_{\phi i} = \alpha^B_{\phi i} = \alpha^C_{\phi i} = \alpha_{\phi i} = \frac{\mathrm{Tr}(\rho_{0\phi} \cdot \bar{H}_{0i})}{\mathrm{Tr}(\bar{H}_{0i})^2}. \tag{61}$$

The standard procedure of calculating the average zero-order Hamiltonian [20] for each of the three sequences (48a)–(48c) results in:

$$\begin{aligned}\bar{H}^A_{0i} &= \tfrac{1}{4}[2H_T + P_1 H_T P_1^{-1} + P_1^{-1} H_T P_1] \\ &= \Omega_p(K_E + K^p_e - K^p_3 \tfrac{1}{2}(1+\cos 2\varphi)) + \Delta K^r_1(1 \\ &\quad + \cos\varphi) + \tfrac{1}{2}[\varDelta + (\Omega_q - \Omega_r)] M_3 (1+\cos\varphi) \\ &\quad + \tfrac{1}{2}[\Delta - (\Omega_q - \Omega_r)] L_3 (1+\cos\varphi),\end{aligned} \tag{62a}$$

$$\begin{aligned}\bar{H}^B_{0i} &= \tfrac{1}{4}[H_T + 2P_1^{-1} H_T P_1 + (P_1^{-1})^2 H_T (P_1)^2] \\ &= \Omega_p(K_E + K^p_e - \tfrac{1}{4}((1 + 2\cos 2\varphi + \cos 4\varphi) K^p_3 \\ &\quad - 2\sin 2\varphi (1+\cos 2\varphi) K^p_2)) \\ &\quad + \varDelta \tfrac{1}{2}((1 + 2\cos\varphi + \cos 2\varphi) K^r_1 \\ &\quad - 2\sin\varphi(1+\cos\varphi) K^q_1) + \tfrac{1}{4}[\varDelta + (\Omega_q - \Omega_r)] \\ &\quad \times [(1 + 2\cos\varphi + \cos 2\varphi) M_3 - 2\sin\varphi(1+\cos\varphi) M_2] \\ &\quad + \tfrac{1}{4}[\varDelta - (\Omega_q - \Omega_r)][(1 + 2\cos\varphi + \cos 2\varphi) L_3 \\ &\quad - 2\sin\varphi(1+\cos\varphi) L_2],\end{aligned} \tag{62b}$$

$$\bar{H}^C_{0i} = \bar{H}^A_{0i}. \tag{62c}$$

Hamiltonians $\bar{H}^A_{0i}$ and $\bar{H}^C_{0i}$ do not contain the operators that have an input in the observed signal. Therefore, at any preparatory pulses the signals for sequences (48a) and (62) equal zero.

Expressions for signals observed in the field of sequence (48b), can be obtained by a trivial substitution $\varphi \to -\varphi$ (or $\varphi_M \to -\varphi_M$) in expressions (35), (36) ($\varDelta \ll \Omega_i$) and (42), (43) ($\varDelta \gg \Omega_i$), obtained for sequence (4). As the above expressions are invariant to substitution $\varphi \to -\varphi$, they are also suitable for describing signals in the field of sequence (48b).

It also follows from expressions (30) and (62) that in case of preparatory pulse $(\varphi_0)_y$ no signal is observed in the field of any of the sequences.

Here is a short conclusion from the above theoretical consideration of sequence (4). When the preparatory pulse is chosen with the phase $\phi = x$, the NQR signal at times $> T_2$ should only be observed in the even pulse intervals of the sequence. When the preparatory pulse is chosen with the phase $\phi = y$, the signal equals zero in all intervals.

2.4. Sequence $(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_{2n}$

Let us consider the case when the carrier frequency of the pulses of sequence (5) ω differs from the resonance frequency of the sample ω_p by the value of $\varDelta_0 = \omega_p - \omega$. The RF Hamiltonian for sequence (5) in the laboratory coordinate system in this case looks as follows:

$$\begin{aligned}H_{\mathrm{rf}}(t) = &-2I_{p,1}\{\varphi_0 \delta(t) \cdot \cos(\omega t + \phi) + G_1(t)\cos\omega t \\ &+ G_2(t)\sin\omega t\}.\end{aligned} \tag{63}$$

$$\begin{aligned}G_1(t) &= \varphi \sum_{k=0}^{2n-1} \delta(t - (1+4k)\tau), \\ G_2(t) &= \varphi \sum_{k=0}^{2n-1} \delta(t - (3+4k)\tau).\end{aligned} \tag{64}$$

In the representation of Hamiltonian

$$H = \omega I_{p,3} \tag{65}$$

the density matrix equation equals

$$\mathrm{i}\frac{\mathrm{d}\rho}{\mathrm{d}t} = [\varDelta_0 I_{p,3} + H_{\mathrm{rf}} + H_d + H_\varDelta, \rho],$$

where

$$\begin{aligned}H_{\mathrm{rf}} = &-\varphi_0 \delta(t)[\cos\phi \cdot I_{p,1} + \sin\phi \cdot I_{p,2}] \\ &- G_1(t) \cdot I_{p,1} + G_2(t) \cdot I_{p,2}.\end{aligned} \tag{66}$$

Operators $I_{p,i}$, H_d, and $H_\varDelta$ are determined by expressions (6), (10) and (14). After a canonical transformation of equation (66)

$$\rho(t) = \exp\left(-\mathrm{i}\left[\frac{\pi}{4} \cdot \frac{t}{\tau} - \frac{\pi}{4}\right] I_{p,3}\right) \rho'' \exp\left(\mathrm{i}\left[\frac{\pi}{4} \cdot \frac{t}{\tau} - \frac{\pi}{4}\right] I_{p,3}\right), \tag{67}$$

we obtain

$$\mathrm{i}\frac{\mathrm{d}\rho''}{\mathrm{d}t} = \left[\left(\varDelta_0 - \frac{\pi}{4\tau}\right) I_{p,3} + H''_{\mathrm{rf}} + H_d + H_\varDelta, \rho''\right], \tag{68}$$

where

$$\begin{aligned}H''_{\mathrm{rf}} = &-\varphi_0 \delta(t)\left[\cos\left(\phi - \frac{\pi}{4}\right) \cdot I_{p,1} + \sin\left(\phi - \frac{\pi}{4}\right) \cdot I_{p,2}\right] \\ &+ F(t) \cdot I_{p,1},\end{aligned} \tag{69}$$

pulse function $F(t)$ is determined from equation (24). Hamiltonians H_d and $H_\varDelta$ after transformation (67) stay unchanged.

From the expression of equations (68) and (69) it follows that with frequency offset $\varDelta_0 = \frac{\pi}{4\tau}$ and the preparatory pulse phase $\phi = \phi'' + \frac{\pi}{4}$ these equations fully coincide in form with equations (22) and (23) and describe the resonance effect of sequence $(\varphi_0)_{\phi''}$—$(\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x})_n$ on the spin system. Thus we can expect that the effect of sequences (4) and (5) is identical on condition of a $\frac{\pi}{4\tau}$ shift in the pulse carrier frequency when going from one sequence to the other.

3. Experimental results

All experiments were carried out at a temperature of 20 °C on the spectrometer including the "Apollo" console manufactured by Tecmag, power amplifier Electronic Navigation Industries A-150 model and pre-amplifier Miteq AU-2A-0150-BNC and a home-made probe in the form of a parallel resonance circuit. The Q-factor of the resonance circuit was ~200.

The powdered compound of $NaNO_2$ was used as a sample. The mass of the sample was ~80 g. The measurements were taken for line $\nu_+ = 4.64$ MHz. Relaxation parameters at 20 °C for this line are as follows: $T_2^* = 2.0$ ms, $T_2 = 5.3$ ms, $T_1 = 90$ ms [22] (T_2^* is the time constant of free induction decay, T_2 is the spin–spin relaxation time, T_1 is the spin-lattice relaxation time).

All multi-pulse sequences used in the experiments, had the following parameters: $\varphi \approx 0.66\pi$ (90° pulse in powder), $\tau = 1228$ µs. The acquisition time was 2048 µs. The duration of the 90° pulse in powder was 80 µs.

Figs. 1 and 2 present data obtained upon the irradiation of powdered sodium nitrite $NaNO_2$ by sequences (4) and (5) at $\phi = x$ (Figs. 1A and 2A) and $\phi = y$ (Figs. 1B and 2B). The number of pulses in each sequence is 40.

The echo signals generated by the preparatory pulses of the sequences (4) and (5) are presented in Figs. 3A and B. To separate echo components of the NQR signals corresponding only to the preparatory pulse, the

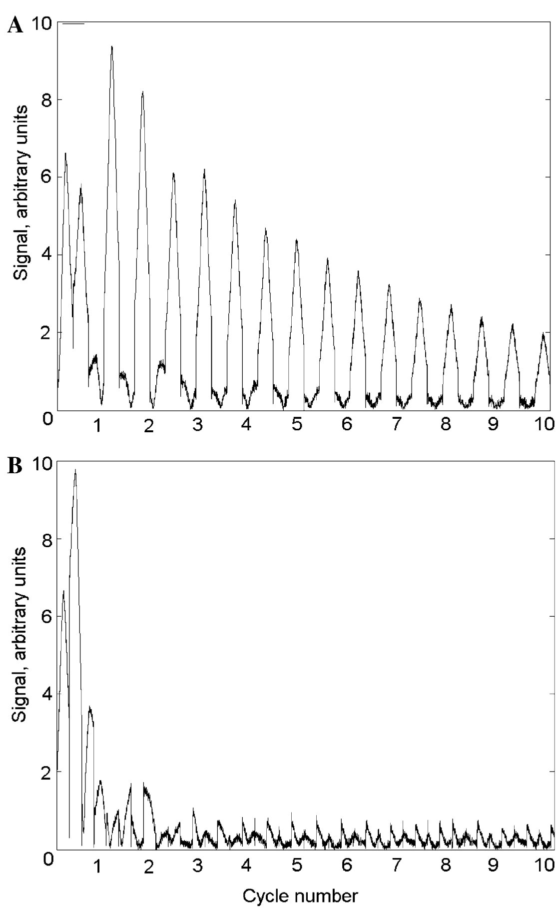

Fig. 1. The NQR signals in $NaNO_2$ (line $\nu_+ = 4.64$ MHz) obtained with sequence $(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$ at (A) $\phi = x$ and (B) $\phi = y$ after 100 averages. Sequence parameters: $\varphi \approx 0.66\pi$, $\tau = 1228$ µs, $n = 10$. The acquisition time is 2048 µs, the duration of the 90° pulse in powder is 80 µs.

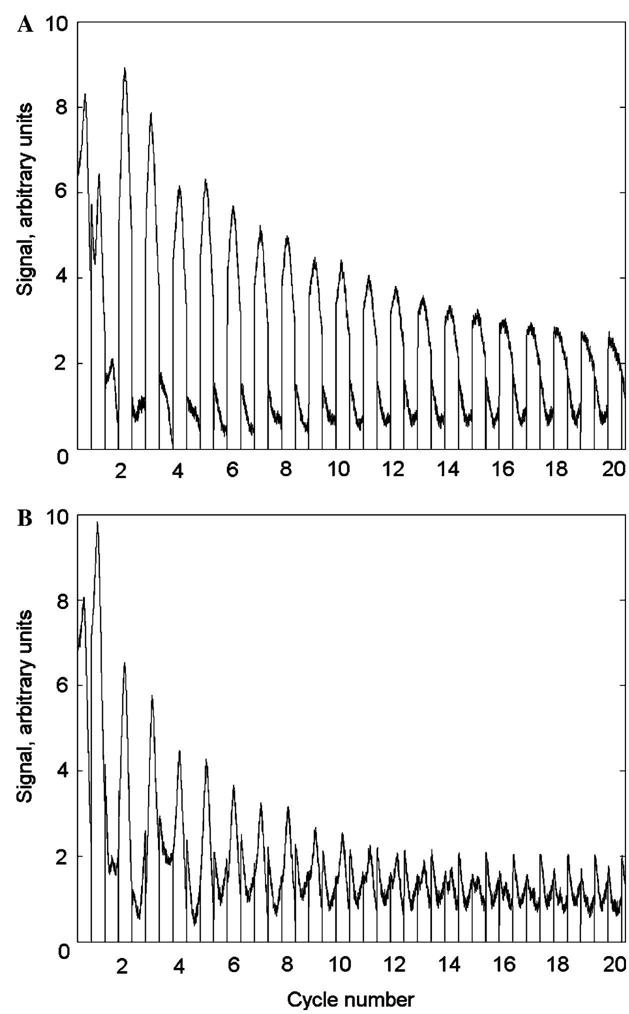

Fig. 2. The signals obtained upon the irradiation of powdered sodium nitrite $NaNO_2$ (resonance line $\nu_+ = 4.64$ MHz) by sequence$(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_n$ with $n = 20$ at $\phi = \pi/4$ and $\phi = 5\pi/4$ correspondingly. The measurements were made under the same conditions and with the same sequence parameters as in Fig. 1.

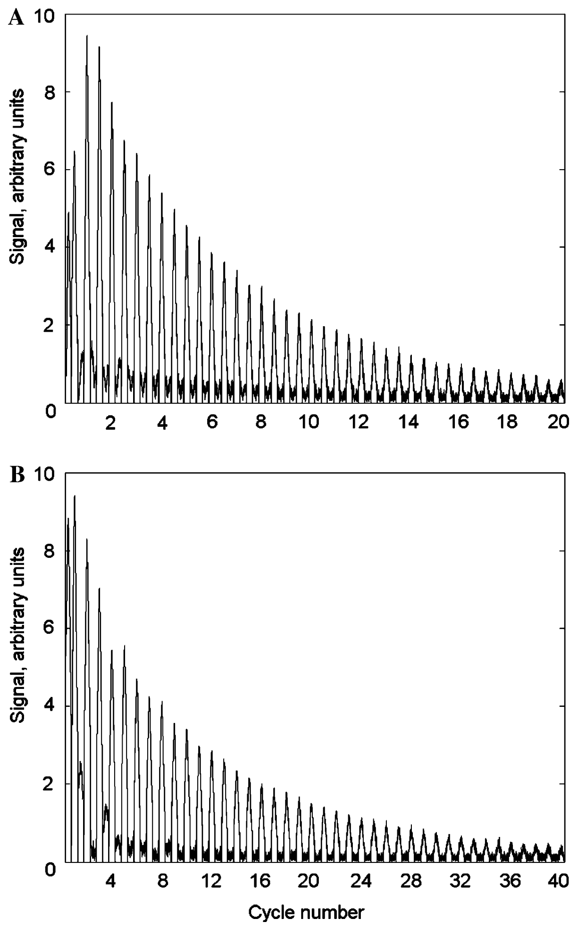

Fig. 3. The echo signals obtained in powdered $NaNO_2$ at line $\nu_+ = 4.64$ MHz with sequences (A) $(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n - 500$ ms $- (\varphi_0)_{-x} - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$, and (B) $(\varphi_0)_{\pi/4} - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_{2n} -$ 500 ms $- (\varphi_0)_{5\pi/4} - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_{2n}$ at $n = 20$ after 100 averages.

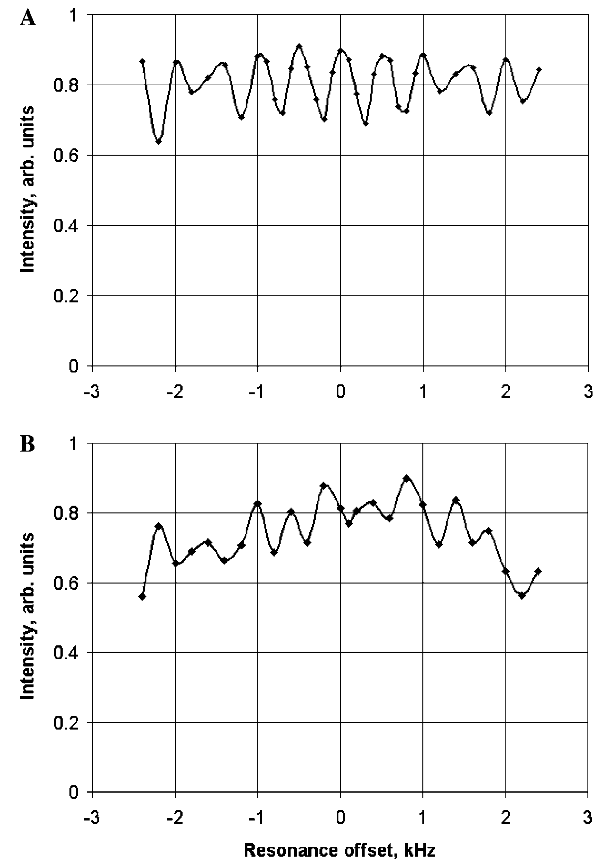

Fig. 4. The results of measuring the dependence of the echo signal intensity variations on the frequency offset for sequences (A) $(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$ and (B) $(\varphi_0)_{\pi/4} - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_n$. The conditions of the measurements and parameters of the sequences are the same as in Fig. 1.

phases of the preparatory pulse and of the detector reference voltage were reversed at each repetition of the multipulse sequence. In this scheme, all free induction and echo signal components generated by sequence pulses other than the preparatory one are subtracted, while the echo signals related to the preparatory pulse are summed. The sequence repetition time was 500 ms, the number of repetitions (averages) was 100.

Figs. 4A and B present the results of measuring the dependence of the echo signal intensity variations on the frequency offset for sequences (4) and (5).

4. Discussion

We would like to forward precede the discussion of the obtained results with a few observations on the physical nature of K, L, and M–operators. According to paper [10], the K—operators correspond to single quantum transitions in two coupled fictitious spins-1/2. In as much as the two coupled fictitious spins-1/2 create a three level equidistant system, the K—operators describing such a system possess all the properties of normal operators of a fictitious spin-1/2 $I_{p,i}$, which also describe a three-level system. In their turn, L and M-operators correspond to double quantum transitions between two levels of energy using the third level as intermediate.

Let us consider average Hamiltonians obtained while using different sequence cycles (4).

One can easily see that the influence of the offset effects and dipole interactions in a double-quantum LM-space are described identically with the same operators. It should be noted that the LM-space input into magnetisation is identical for both $T_2^* \simeq T_2$ ($\Delta \ll \Omega_i$) and $T_2^* \ll T_2$ ($\Delta \gg \Omega_i$) cases.

In a single-quantum K-space the situation is not so simple. The peculiarity here is that the magnetisation corresponding to K-space is ensured not by the dipole Hamiltonian, but by the offset Hamiltonian reflecting the distribution of resonance frequencies in the sample. It should be noted that this result cannot be predicted on the basis of a two-pulse sequence analysis. As follows from expressions (20), the amplitude of the echo signal detected after two pulses does not depend on the relationship between the dipole and the offset Hamiltonians.

Here is one of the conclusions that can be made based on our study. Though when determining the nature of the observed signals it is necessary to take into account dipole interactions, however under condition $T_2 \gg T_2^*$ for the case when flip angles of the pulses are close to 90°, one can get quite a correct phenomenological description of the main peculiarities of the system behaviour while taking into account just the offset Hamiltonian.

5. Conclusion

Experimental study of sequences (4) and (5) presented in this paper deals only with the case of comparatively large pulse intervals 2τ, as compared with the free induction decay time T_2^*. In this case one does not observe the steady-state, its distinguishing feature being the possibility of obtaining a continuous signal chain (when selecting certain flip angles and frequency offset of the pulses) at times $> T_1$. However, when $T_2^* > 2\tau$, the presented above theoretical analysis is also applicable for the description of the behaviour of the spin system in the time interval $T_2 < t < T_1$ (quasistationary state).

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