Spin echo in magnetics with a quadrupole-split NMR spectrum

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A study is made of the characteristics of the formation of a nuclear spin echo in magnetics, with allowance for an inhomogeneity of the Zeeman and quadrupole splittings. The dependence of the echo amplitude on the carrier frequency of the exciting pulses is investigated for the spin $I = 3/2$. It is shown that the amplitude of the first echo has the maximum order of magnitude when the frequencies of the pulses are identical and coincide with the frequencies of one-photon transitions. The order of magnitude of the secondary echo is maximal if the frequency of the first pulse is the same as that of one of the resonance frequencies of the system, whereas the frequency of the second pulse coincides with the central line of an NMR spectrum.

The spin echo is the best known example of time reversal processes, which include also the phonon and photon echoes and the closely related phase conjugation (wavefront reversal). In particular, the nuclear spin echo has become one of the main methods for the investigation of NMR in magnetically ordered media. Magnetics are characterized by an unavoidable inhomogeneity of the internal magnetic field at the nuclei and the nuclear spin echo makes it possible to determine the longitudinal and transverse relaxation times, which are usually much longer than the characteristic time of dephasing of nuclear spins because of the inhomogeneity. Moreover, the spin echo is used widely in studies of NMR spectra involving determination of the dependence of the echo amplitude A on the carrier frequency ω of the exciting pulses. The quadrupole splitting of NMR in magnetics is usually also investigated by the spin echo methods. The theory of the quadrupole spin echo[1,2] starts with the assumption that the magnetic field is inhomogeneous, but the quadrupole constant Q is inhomogeneous. A theory of the spin echo in magnetics with the quadrupole interaction[3] is based on the opposite approach: the Zeeman splitting Ω is assumed to be inhomogeneous, whereas the value of Q is postulated to be homogeneous. Both theories deal with the simplest situation when the carrier frequencies of the exciting pulses ω coincide with the Zeeman frequency Ω.

In the case of real magnetics it is frequently found that both Ω and Q are strongly inhomogeneous so that in addition to the usual spin echo there are also secondary spin-echo signals as a result of an inhomogeneous quadrupole interaction.[4–6] In experiments on ferromagnetic films containing ^{59}Co nuclei,[4,5] the smallness of Q prevents observation of the quadrupole splitting of NMR, and the spectra of the primary and secondary echo are approximately identical. On the other hand, in experiments on $CdCr_2Se_4$ involving observation of the quadrupole splitting of the NMR spectrum of ^{53}Cr the dependences $A_1(\omega)$ and $A_2(\omega)$ are found to be quite different for the primary and secondary echoes.[6] This provides an opportunity for utilizing the secondary echo in order to obtain new spectroscopic information. In view of this, we shall study theoretically the dependence of the echo signal amplitude on the carrier frequency of the exciting pulses in the specific case when the nuclear spin is $I = 3/2$. Moreover, we shall find the conditions for the formation of a spin echo for any value of I and we shall do this allowing for the inhomogeneity of Ω and Q.

We shall write down the Hamiltonian of such a system in the form[2]

$$H=-\left\{\Omega I_z+QI_z^2+\frac{1}{2}\sum_{p=1}^{2}q_p(t)\left[I_+\exp(i\omega_p t)+\text{c.c.}\right]\right\}, \quad (1)$$

where $q_p(t)$ is the envelope of the pth pulse in units of the frequency and $\hbar = 1$. The evolution of nuclear spins is described by the equation of motion for the density matrix ρ:

$$i\dot{\rho}=[H, \rho]. \quad (2)$$

An analysis of the solution of this equation can be carried out conveniently using symbolic formulas: a similar method has been applied earlier to calculate the spin echo of two-level systems.[7] After the action of exciting pulses the matrix element ρ_{ik} represents a sum of terms of the type $\tilde{A}\exp(-i\Phi)$, where $\tilde{A}$ is the amplitude which depends on the parameters of the pulses and Φ is the time phase which grows in the intervals between the pulses and after their ends. Each of these terms is represented by a separate spin echo demonstrating which pulses and which transformations of the initial matrix elements ρ_{jj}^0 are responsible for the given term. For example, a two-pulse spin echo is described by a symbolic formula of the type

$$(1_{jj}^{in}-2_{in}^{k+1,k}), \quad i\neq n. \quad (3)$$

This means that under the action of the first pulse the initial matrix element ρ_{jj}^0 becomes an off-diagonal element ρ_{in} (i.e., a simultaneous transition takes place from a level j to levels i and n). In a time interval τ between the pulses the quantity ρ_{in} "acquires" a time phase $\omega_{in}\tau$, where $\omega_{in} = E_i - E_n$ (E_k is the energy of the k th level). The second pulse transforms ρ_{in} into $\rho_{k+1,k}$. Then, the advance of the time phase continues and we then obtain

$$\Phi=\omega_{in}\tau+\omega_{k+1,k}t, \quad (4)$$

where the time t is measured from the end of the second pulse. In writing down the symbolic formula of Eq. (3) an allowance is made for the fact that, firstly, under equilibrium conditions only the diagonal terms of the density matrix are nonzero and, secondly, experiments on magnetic resonance record the transverse component of the spin $\mathrm{Tr}(I_+\rho)$, which can be expressed in terms of $\rho_{k+1,k}$. If the phase Φ assumes

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at some time $t>0$ the same value for all the spins, the corresponding term obtained after averaging over the inhomogeneity describes a spin echo signal with a carrier frequency $\omega_{k+1,k}$.

Bearing in mind that $I_z = I + 1 - j$ for the jth level, we find that

$$\omega_{in}=(i-n)\,[\Omega+Q(2I+2-i-n)\,],$$
$$\omega_{k+1,k}=\Omega+Q(2I+1-2k). \tag{5}$$

If $Q = \text{const}$ (Ref. 3), by including in Eq. (5) an inhomogeneous correction $\Omega \to \Omega + \delta\Omega$, we obtain the following condition for the formation of a spin echo:

$$t=(n-i)\,\tau, \quad n>i. \tag{6}$$

If both quantities Ω and Q are strongly inhomogeneous, i.e., if the characteristic inhomogeneity parameters Γ and Γ_Q satisfy the inequalities $\Gamma\tau$, $\Gamma_Q\tau \gg 1$, then assuming that $Q \to Q + \delta Q$ and postulating that δQ and $\delta\Omega$ are independent, we obtain an additional condition for the formation of a spin echo which, subject to Eq. (6) is of the form

$$k=(i+n-1)/2. \tag{7}$$

Hence it follows in particular that the difference $n - i$ in Eq. (6) can assume only odd values. We shall consider such a situation in greater detail, because it is easiest to deal with theoretically (since it is characterized by the smallest number of the symbolic formulas). Since $n - i$ is odd, there is no secondary spin echo in the case when the spin is $I = 1$; we shall therefore consider the case when $I = 3/2$. If $I = 3/2$, the condition of Eq. (7) is satisfied by the following symbolic formulas:

$$(1_{jj}{}^{12}-2_{12}{}^{21}), \quad (1_{jj}{}^{23}-2_{23}{}^{32}), \quad (1_{jj}{}^{34}-2_{34}{}^{43}),$$
$$(1_{jj}{}^{14}-2_{14}{}^{32}), \quad 1\leqslant j\leqslant 4. \tag{8}$$

For the sake of simplicity we shall assume that we can ignore inhomogeneous dephasing during a pulse ($\Gamma\tau_p$, $\Gamma_Q\tau_p \ll 1$, where τ_p is the duration of the pth pulse). Then the terms corresponding to the first twelve symbolic formulas describe, after averaging over $\delta\Omega$ and δQ, a spin echo with a maximum at $t = \tau$. The last four symbolic formulas described a secondary spin echo signal with a maximum at $t = 3\tau$.

The mechanism of formation of this signal is clear directly from the nature of the symbolic formulas. Under the action of the first pulse the diagonal element of the density matrix ρ_{jj}^0 is transformed into ρ_{14}. During the interval τ the off-diagonal element ρ_{14} describes oscillations of frequency $\omega_{14} = -3\Omega$ and acquires an inhomogeneous time phase $\delta\Phi = -3\delta\Omega\tau$. The second pulse transforms ρ_{14} into ρ_{32} and the frequency of oscillations of the latter is $\omega_{32} = \Omega$. The inhomogeneous phase advance Φ continues after the end of the second pulse: $\delta\Phi = \delta\Omega(-3\tau + t)$; consequently, a spin echo appears at $t = 3\tau$. It is well known[1-3] that in the absence of the quadrupole interaction only the matrix elements $\rho_{n,n\pm 1}$, corresponding to one-photon transitions are excited by the first pulse. On the other hand, if Q exists, any off-diagonal elements ρ_{in} can be excited and this gives rise to secondary spin echo signals.

We shall study the dependence of the echo amplitude on the carrier frequencies ω_p of the exciting pulses. We shall do this by going over to a rotating coordinate system in which the y axis is linked to the direction of the field of pth pulse. Then, the Hamiltonian of the system is independent of time and the solution of the equation of motion for the density matrix has the simple form

$$\rho(\tau_p)=U(p)\rho(0)\,U^+(p), \quad U(p)=\exp\,[i(H'+q_pI_y)\,\tau_p],$$
$$H'=(\Omega-\omega_p)I_z+QI_z^2. \tag{9}$$

The amplitude $\tilde{A}$ for the symbolic Eq. (3) can be expressed in terms of matrix elements of a unitary operator U:

$$\tilde{A}=\rho_{jj}{}^0U_{ij}(1)\,U_{nj}{}^*(1)\,U_{k+1,\,i}(2)\,U_{kn}{}^*(2). \tag{10}$$

For the sake of simplicity, we shall assume that the deviation of the nuclear spins from the equilibrium position is small ($\theta_p = q_p\tau_p \ll 1$) and we shall expand U in powers of a small parameter θ_p (Ref. 3):

$$U^{(0)}(p)=\exp(iH'\tau_p);$$

$$U^{(n+1)}(p)=-q\exp(iH'\tau_p)\int_0^{\tau_p}\exp(-iH't)\,I_yU_t^{(n)}(p)\,dt, \tag{11}$$

where $U_t^{(n)}$ differs from $U^{(n)}$ by the substitution $\tau_p \to t$. We shall assume that $Q\tau_p \gg 1$, i.e., that the spectrum of the pulse is narrow compared with the quadrupole splitting of the NMR signal. Then, the problem has one additional small parameter $\alpha_p = q_p/Q$, where $\alpha_p \ll \theta_p$.

We can readily calculate the matrix elements U in the first nonvanishing approximation with respect to θ_p and α_p. The diagonal elements are described by the simple expression $U_{kk} = \exp(iH_{kk}\cdot\tau_p)$. We then find that

$$U_{12}=i\frac{\sqrt{3}}{2}U_{11}\frac{q_p}{\omega_p-\omega_{21}}\{\exp[i(\omega_p-\omega_{21})\,\tau_p]-1\}. \tag{12}$$

The dependence of $|U_{12}|$ on ω_p is in the form of a resonance with a maximum at a point $\omega_p = \omega_{21} = \Omega + 2Q$ (for convenience, we included the energy level scheme in Fig. 1). This result is to be expected because the matrix element U_{12} describes one-photon transitions between the levels 1 and 2. Similarly $|U_{23}|$ and $|U_{34}|$ each have a maximum at frequencies $\omega_{32} = \Omega$ and $\omega_{43} = \Omega - 2Q$. The resonance values of all three quantities are proportional to θ_p.

In the case of the $3\leftrightarrow 1$ two-photon transition (we recall that the conservation laws permit only one-photon transitions between neighboring levels) there are three resonances: ω_{32}, ω_{21}, and $\omega_{31}/2 = \Omega + Q$. Similarly, in the case of the $4\leftrightarrow 2$ transitions there are resonances ω_{43}, ω_{32}, and $\omega_{42}/2 = \Omega - Q$. The resonance values of U_{12} and U_{24} are proportional to $\alpha_p\theta_p$. Finally, in the case of the $4\leftrightarrow 1$ transition we have all the resonances listed so far (the equality $\omega_p = \omega_{41}/3$ does not give rise to an additional resonance because $\omega_{41}/3 = \Omega$). The corresponding values of U_{14} are proportional to $\alpha_p^2\theta_p$. If the frequency ω_p corresponds to an "alien" resonance, the factor θ_p should be replaced with α_p.

We shall now consider the first four symbolic formulas in Eq. (8). Bearing in mind that $|U_{ik}| = |U_{ki}|$, we obtain

$$|\tilde{A}|=\rho_{11}{}^0|U_{12}(1)\,U_{12}{}^2(2)\,|. \tag{13}$$

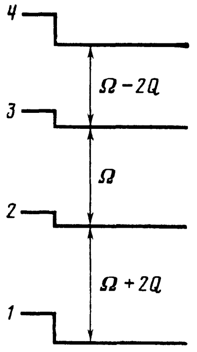

FIG. 1. Energy level scheme for the spin $I = 3/2$ when $Q > 0$.

The modulus $\tilde{A}$ has the maximum order of magnitude of the quantity $\theta_1\theta_2^2$ at $\omega_1 = \omega_2 = \Omega + 2Q$. This is also true for $j = 2$. These two symbolic formulas describe clearly the usual Hahn spin echo for a two-level system 1–2. For $j = 3$ and $j = 4$ the modulus $\tilde{A}$ has a lower order of magnitude (the first pulse excites two- and three-photon transitions) so that these symbolic formulas can be omitted in the first nonvanishing order. Similarly, at $\omega_1 = \omega_2 = \Omega$ the maximum order of magnitude of $\theta_1\theta_2^2$ is exhibited by the amplitudes of the symbolic formulas corresponding to $j = 2,3$ out of the four symbolic formulas of Eq. (8), whereas for $\omega_1 = \omega_2 = \Omega - 2Q$, we have $j = 3,4$ from the third set of four symbolic formulas. Therefore, in the first nonvanishing approximation the resonances of the Hahn spin echo formed at $t = \tau$ correspond to the positions of lines of the quadrupole splitting in an NMR spectrum.

We shall now consider the last four symbolic formulas in Eq. (8), describing the secondary spin echo. The amplitude in these symbolic formulas is given by the expression

$$\rho_{jj}^0 U_{1j}(1) U_{4j}^*(1) U_{31}(2) U_{24}^*(2). \tag{14}$$

The products $|U_{11}U_{41}^*|$ and $|U_{14}U_{44}^*|$ are characterized by the maximum order of magnitude of $\alpha_p^2\theta_p$ for all five resonance values of ω_p, and $|U_{12}U_{42}^*|$ and $|U_{13}U_{43}^*|$ apply to four values of ω_p. The elements U_{31} and U_{24}^* have just one coincident resonance $\omega_p = \Omega$; therefore, the derivative $|U_{31}U_{24}^*|$ reaches its maximum order of magnitude $(\alpha_p\theta_p)^2$ only at this point. It therefore follows that the amplitude A_2 of the secondary spin echo is of the maximum order of magnitude $\theta_1(\alpha_1\alpha_2\theta_2)^2$ in the case when

$$\omega_1=\Omega,\ \Omega\pm Q,\quad \Omega\pm 2Q,\quad \omega_2=\Omega. \tag{15}$$

It therefore follows that the function $A_2(\omega_1,\omega_2)$ obtained in the first nonvanishing approximation has five resonance points, whereas the amplitude of the Hahn spin echo $A_1(\omega_1,\omega_2)$ has only three points. Moreover, in the $\omega_1\omega_2$ plane all the resonance points A_1 lie on a straight line $\omega_2 = \omega_1$; therefore, if $\omega_1 = \omega_2 = \omega$ the function $A_1(\omega)$ still describes three resonances ($\omega = \Omega$, $\Omega \pm 2Q$), whereas $A_2(\omega)$ has only one resonance at the Zeeman frequency of Ω (Fig. 2). It therefore follows that the secondary spin echo has a larger number of resonance points than the Hahn echo, but in the presence of an additional level at $\omega_1 = \omega_2$ we obtain the opposite result: the spectrum of the secondary spin echo becomes simpler than the Hahn spectrum. We can assume that exactly this situation has been responsible for the situation observed experimentally[6] in the case of $CdCr_2Se_4$ ($I = 3/2$) when a sole signal of the secondary echo ($t = 3\tau$) is observed; if $\omega_1 = \omega_2 = \omega$, the dependence $A_2(\omega)$ reflects the NMR spectrum corresponding to the absence of the quadrupole interaction.

The result obtained is valid only if the inequality $\Gamma_Q\tau \gg 1$ is satisfied. If the inhomogeneity of Q is unimportant at times $\sim\tau$, i.e., if $\Gamma_Q\tau \lesssim 1$ (we recall that in this case three spin echo signals appear at $t = \tau, 2\tau, 3\tau$), the spin echo with a maximum at $t = 3\tau$ can be described by allowing additionally for eight symbolic formulas

$$(1_{jj}^{14}-2_{14}^{43}),\quad (1_{jj}^{14}-2_{14}^{21}). \tag{16}$$

We can easily show that in this case the spin echo considered in the first nonvanishing approximation has fifteen resonance points: five of them are already known for ω_1 and three for ω_2: $\omega_2 = \Omega$, $\Omega \pm 2Q$. At $\omega_1 = \omega_2 = \omega$ such a spin echo has three resonance points corresponding to a quadrupole-split NMR spectrum.

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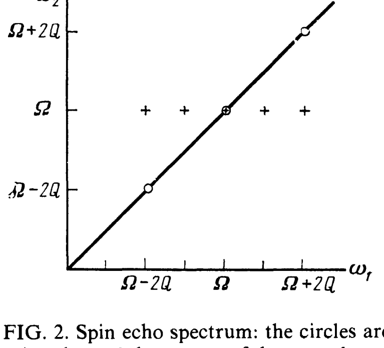

FIG. 2. Spin echo spectrum: the circles are the resonances of the Hahn spin echo and the crosses of the secondary echo.

[1] I. Solomon, Phys. Rev. **110**, 61 (1958).
[2] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961).
[3] H. Abe, H. Yasuoka, and A. Hirai, J. Phys. Soc. Jpn. **21**, 77 (1966).
[4] V. K. Mal'tsev, G. I. Fish, and V. I. Tsifrinovich, Fiz. Tverd. Tela (Leningrad) **23**, 1148 (1981) [Sov. Phys. Solid State **23**, 667 (1981)].
[5] V. K. Mal'tsev, A. E. Reĭngardt, and V. I. Tsifrinovich, Fiz. Tverd. Tela (Leningrad) **24**, 3 (1982) [Sov. Phys. Solid State **24**, 1 (1982)].
[6] G. N. Abelyashev, V. N. Berzhanskiĭ, N. A. Sergeev, and Yu. V. Fedotov, Pis'ma Zh. Eksp. Teor. Fiz. **42**, 453 (1985) [Sov. Phys. Solid State **42**, 561 (1985)].
[7] V. I. Tsifrinovich, Calculation of Echo Signals [in Russian], Nauka, Novosibirsk (1986), Chaps. 2 and 3.

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