ON THE EFFECT OF ACOUSTIC RESONANCE PULSES ON A NUCLEAR SPIN SYSTEM

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Submitted to JETP editor May 3, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 872-877 (September, 1960)

The effect of acoustic pulses of a resonance frequency ω and duration $t_\omega \ll T_2$ on a system of nuclear spins ($I > 1/2$) is examined theoretically. It is shown that in contrast to the effect of an electromagnetic field on the spin system, a single acoustic pulse does not induce a free procession signal to the first approximation in $\hbar\omega/kT$. Two acoustic pulses produce a spin-echo signal which is equal in magnitude to that produced by electromagnetic pulses.

1. In recent years a number of experiments[1-6] has been performed which confirm the effect predicted by Al'tshuler[7] of ultrasonic resonance absorption in paramagnetic substances. This phenomenon differs from ordinary paramagnetic resonance absorption by the fact that here ultrasonic phonons are absorbed instead of photons. Experiments[1-6] have made it possible to measure the probabilities of transition between sublevels of paramagnetic particles under the influence of acoustic oscillations. In carrying this out the ultrasonic pulses were of such duration that a stationary mode had time to be established in the substance.

In order to study magnetic properties of matter in addition to resonance absorption the phenomena of spin echo and of nuclear induction have been successfully utilized in which electromagnetic pulses rotate the nuclear spins into a plane perpendicular to the constant magnetic field in which they then precess with the Larmor frequency. For example, two pulses each of duration t_ω spaced by a time interval τ produce a spin-echo signal, with the induced emf due to the rotation of the total magnetic moment of the sample M_0 being equal to[8]

$$\mathscr{E} = -nS\frac{\partial}{\partial t}\sum \hbar\gamma I_x(t) = -nSM_0\omega\sin(\gamma H_1 t_\omega)$$
$$\times \sin^2(\gamma H t_\omega/2)\cos\omega(t-2\tau)\exp\left[-\frac{(t-2\tau)^2}{2T_2^2}\right], \qquad (1)$$

where $t > t_\omega + \tau$, $2H_1$ is the amplitude of the pulse, γ is the gyromagnetic ratio, nS is the number of turns and the cross section of the receiver coil.

It appears to be of interest to carry out an investigation of similar phenomena stimulated by ultrasonic methods. In order to rotate a magnetic moment in a constant magnetic field a certain amount of energy has to be expended. As Al'tshuler has shown[7] the coefficient of sound absorption is usually larger than the coefficient of absorption for the electromagnetic field; moreover, modern sound emitters can produce energy fluxes equal in magnitude to the electromagnetic energy introduced into the sample in spin echo experiments. All this suggests that ultrasonic pulses can rotate magnetic moments no less effectively than the electromagnetic field.

The action of sound on spins may be explained by the following model. Suppose that an acoustic pulse of the Larmor frequency and of duration t_ω is introduced in the direction of the x axis into a substance containing nuclei possessing magnetic and quadrupole moments and situated in a constant magnetic field $\mathbf{H}_0(0, 0, H_0)$. Longitudinal acoustic oscillations will produce a time-dependent electric field gradient $\nabla E = (\nabla E)_0 \sin(\omega t - kx)$, which can be resolved into two components rotating in opposite directions.

We now go over into a system of coordinates rotating with the Larmor frequency,[8] in which the magnetic moment and one of the components of the gradient are stationary, while $\mathbf{H}_0$ and the second component rotating with double the Larmor frequency are not effective. In this coordinate system the quadrupole moment of the particle will begin to precess about the stationary gradient[9] with a certain frequency ω_Q and will be rotated through the angle $\varphi = \omega_Q t_\omega$. The magnetic moment rigidly coupled to the quadrupole moment will rotate simultaneously. The problem consists of selecting the conditions and the combinations of pulses which will rotate the magnetic moment in such a way that in the laboratory coordinate system it will precess in a plane perpendicular to H_0 and will induce a measurable induced emf in the receiver coil.

2. We now proceed to a quantum-mechanical investigation of the effect of ultrasonic oscillations on a spin system. We assume that a crystal of cubic symmetry containing nuclei of quadrupole moment Q and spin I is situated in a constant magnetic field H_0. At a time $t = 0$ we apply along the C_4 crystal axis an ultrasonic pulse of Larmor frequency and of duration t_ω. The acoustic pulse traverses the sample during the time $t = d/v$ where d is the sample size and v is the velocity of sound. This leads to a retardation in the rotation between the nuclei in the ends of the sample by the angle $\varphi = \omega d/v$. We can show that, on the one hand, the acoustic pulse passing through the sample does not give rise to a total magnetic moment of the sample different from zero $M_x = \Sigma\hbar\gamma I_x(t)$ if the condition $\omega d/v < \pi$ is not satisfied, and, on the other hand, that $\mathscr{E}$ is proportional to $\omega^2 d$ and is greatly reduced when the condition $\omega d/v < \pi$ is satisfied. Therefore, it is more advantageous to utilize both the progressive and the reflected waves simultaneously. If we neglect absorption and reflection losses, then the oscillations of the particles of the substance can be represented in the form

$$u = u_1 + u_2 = A\,[\sin(\omega t - kx - kd) + \sin(\omega t + kx - kd)],$$

and the relative displacement of two neighboring particles is given by

$$\delta = 2Aa\sin kx\sin(\omega t - kd),$$

where A is the oscillation amplitude, a is the lattice constant.

The energy of the nucleus consists of a Zeeman and a quadrupole part:

$$\mathscr{H} = -\gamma H_0\hbar I_z - \sum_{i=-2}^{2} Q_i\nabla E^{-i} \qquad (2)$$

In a perfect cubic crystal $\nabla E^i \equiv 0$, and the nucleus is described by the eigenfunctions Ψ_m of the component of the spin along H_0. During the time $0 \le t \le t_\omega$ the acoustic oscillations distort the cubic symmetry and produce a time-dependent electric field gradient. This leads[6] to nonvanishing terms in the sum (2)

$$Q_{\pm1}\nabla E^{\mp1} = -\hbar\omega_1\sin kx\sin\omega t'\,[\hat{I}_\pm\hat{I}_z + \hat{I}_z\hat{I}_\pm],$$
$$Q_{\pm2}\nabla E^{\mp2} = \hbar\omega_2\sin kx\sin\omega t'\hat{I}_\pm^2, \qquad (3)$$

where

$$\omega_1 = \frac{3e^2Qq_1Ak}{8I(2I-1)\hbar}\sin 2\theta e^{\pm i\varphi}, \qquad \omega_2 = \frac{3e^2Qq_1Ak}{8I(2I-1)\hbar}\sin^2\theta e^{\pm i2\varphi},$$

$q_1 = \partial(\nabla E^0)/\partial(\delta/a)$, $t' = t - (d/v)$, θ is the angle between H_0 and the propagation vector $\mathbf{k}$, φ is the angle between the component of $\mathbf{k}$ in the xy plane and the x axis. In future we shall assume for the sake of simplicity that $\varphi = 0$. We write the nuclear spin wave function in the interval $0 \le t \le t_\omega$ in the following form

$$\Psi(t) = \sum_m C_m(t)\exp\{-iE_m t/\hbar\}\Psi_m, \qquad (4)$$

and after the acoustic pulse $(t > t_\omega)$ it has the form

$$\Psi(t) = \sum_m C_m(t_\omega)\exp\{-iE_m(t - t_\omega)/\hbar\}\Psi_m. \qquad (5)$$

On substituting (2) — (4) into the Schrödinger equation we obtain a system of differential equations for $C_m(t)$. A solution of such a system for spin $I = 1$ and for an acoustic pulse of resonance frequency $\omega = \gamma H_0 = \omega_0$ will be given by

$$C_1(t) = -\frac{1}{\sqrt{2}}C_0(0)\sin\xi + C_1(0)\cos^2\frac{\xi}{2} - C_{-1}(0)\sin^2\frac{\xi}{2},$$
$$C_0(t) = C_0(0)\cos\xi + \frac{1}{\sqrt{2}}[C_1(0) + C_{-1}(0)]\sin\xi,$$
$$C_{-1}(t) = -\frac{1}{\sqrt{2}}C_0(0)\sin\xi + C_{-1}(0)\cos^2\frac{\xi}{2} - C_1(0)\sin^2\frac{\xi}{2}, \qquad (6)$$

where $C_m(0)$ are constants which specify the state before the beginning of the acoustic pulse at $t = 0$, $\xi = |\omega_1\sin kx|t$. If the acoustic frequency is equal to $\omega = 2\omega_0$, i.e., if $\Delta m = 2$ transitions are induced, then

$$C_1(t) = C_1(0)\cos\eta + C_{-1}(0)\sin\eta, \qquad C_0(t) = C_0(0),$$
$$C_{-1}(t) = C_{-1}(0)\cos\eta - C_1(0)\sin\eta, \qquad \eta = |\omega_2\sin kx|t. \qquad (7)$$

Table I gives the results of calculations of the time dependence of the average values of certain components of the spin and of the nuclear quadrupole moment. $\Psi(t)$ is given by (4) and (5) with the coefficients $C_m(t)$ given by (6), if the transitions $\Delta m = 1$ are induced, and given by (7) in the case of the $\Delta m = 2$ transitions. The average value, naturally, depends on the initial conditions at $t = 0$.

In order to evaluate the effect produced on the nucleus by two acoustic pulses we have to use the systems (5) or (6) twice, with the role of $C_m(0)$ being played the second time by $C_m(\tau)$ — the coefficients that specify the state of the nucleus immediately before the beginning of the second pulse at the instant $t = \tau$.

The result of such a calculation is given in Table II, where the first pulse induces the $\Delta m = 1$ transitions, and the second one induces the $\Delta m = 2$ transitions.

3. Until now we have considered individual nuclei. But in experiments the total effect of all the

TABLE I

	$C_m(0)=\delta_{1,m}$		$C_m(0)=\delta_{0,m}$		$C_m(0)=\delta_{-1,m}$	
	$\Delta m=1$	$\Delta m=2$	$\Delta m=1$	$\Delta m=2$	$\Delta m=1$	$\Delta m=2$
$\widetilde{T}_x$	$-\frac{1}{2}\sin 2\xi \times \sin \omega t'$	0	$\sin 2\xi \times \sin \omega t'$	0	$-\frac{1}{2}\sin 2\xi \times \sin \omega t'$	0
$\widetilde{Q}_1+\widetilde{Q}_{-1}$	$-2\sin\xi \times \cos \omega t'$	0	0	0	$2\sin\xi \times \cos \omega t'$	0
$\widetilde{Q}_2+\widetilde{Q}_{-2}$	$-\sin^2\xi \times \cos 2\omega t'$	$-\sin 2\eta \times \cos \omega t'$	$2\sin^2\xi \times \cos 2\omega t'$	0	$-\sin^2\xi \times \cos 2\omega t'$	$\sin^2\eta \times \cos 2\omega t'$

TABLE II

	$\widetilde{T}_y$
$C_m(0)=\delta_{1,m}$	$-\frac{1}{2}\sin 2\xi \cos\eta \sin \omega t' + \sin\xi \sin\eta \sin \omega(t'-2\tau)$
$C_m(0)=\delta_{0,m}$	$\sin 2\xi \cos\eta \sin \omega t'$
$C_m(0)=\delta_{-1,m}$	$-\frac{1}{2}\sin 2\xi \cos\eta \sin \omega t' - \sin\eta \sin\xi \sin \omega(t'-2\tau)$

nuclei in the sample is observed. Prior to the application of the acoustic pulse the population of the Zeeman levels was determined by the Boltzmann distribution

$$N_m = \frac{N}{2I+1} e^{-E_m/kT} = \frac{N}{2I+1}\left(1 + m\frac{\hbar\omega}{kT} + \ldots\right) \quad (8)$$

(at room temperature $\hbar\omega/kT \sim 10^{-6}$). By utilizing the tables and the first two terms of the expansion of the exponential (8) we obtain the following expressions for the $\Delta m = 1$ transitions:

$$\Sigma \widetilde{T}_x = \Sigma\{\widetilde{Q}_2 + \widetilde{Q}_{-2}\} = 0,$$

$$\Sigma\{\widetilde{Q}_1 + \widetilde{Q}_{-1}\} = 4\frac{N}{2I+1}\frac{\hbar\omega}{kT}\overline{\sin\xi}\cos\omega t' \exp\left[-\frac{t'^2}{2T_2^2}\right], \quad (9)$$

and for the $\Delta m = 2$ transitions we obtain:

$$\Sigma \widetilde{T}_x = \Sigma\{\widetilde{Q}_1 + \widetilde{Q}_{-1}\} = 0,$$

$$\Sigma\{\widetilde{Q}_2 + \widetilde{Q}_{-2}\} = -2\frac{N}{2I+1}\frac{\hbar\omega}{kT}\overline{\sin 2\eta}\cos 2\omega t' \exp\left[-\frac{2t'^2}{T_2^2}\right]. \quad (10)$$

If the first transition is of $\Delta m = 1$ type, and the second transition is of $\Delta m = 2$ type, then

$$\Sigma \widetilde{T}_y = 2\frac{N}{2I+1}\frac{\hbar\omega}{kT}\overline{\sin\xi \sin\eta}\sin\omega(t'-2\tau)\exp\left[-\frac{(t'-2\tau)^2}{2T_2^2}\right]. \quad (11)$$

Here we have averaged over the frequency distribution which is assumed to be Gaussian.[8] The bar above the expression denotes averaging over the coordinate. If the pulses are so chosen that $\omega_1 t_\omega = \omega_2 t_\omega = \pi/2$, then we have $\overline{\sin\xi \sin\eta} = \frac{1}{2}$. A similar calculation for the case of spin $I = \frac{3}{2}$ gives

$$\Sigma \widetilde{T}_y = \frac{N}{2I+1}\frac{\hbar\omega}{kT}\overline{\sin(2\sqrt{3}\xi)\sin(2\sqrt{3}\eta)}$$

$$\times \sin\omega(t'-2\tau)\exp\left[-\frac{(t'-2\tau)^2}{2T_2^2}\right].$$

It may be seen from formulas (9) and (10) that up to quantities of the first order in $\hbar\omega/kT$ a free precession signal cannot be induced by a single acoustic pulse. However, in this case rotation of the components of the quadrupole moment of the nucleus takes place and, consequently, electric quadrupole radiation must be emitted with the components of the different nuclei rotating in the same phase. The intensity of the electric field of the radiation at small distances from the sample $R \sim k^{-1}$ is equal to[10]

$$E \approx \frac{1}{6}\frac{\partial^3}{\partial R^3}\frac{e}{R}\Sigma\{\widetilde{Q}_{1,2} + \widetilde{Q}_{-1,-2}\} \approx 10^{-60}\frac{\omega^5}{T},$$

where T is the absolute temperature, ω is the ultrasonic frequency, k is the wave number of the radiation. Because of its smallness this effect apparently cannot be observed by direct methods.

Two acoustic pulses produce a spin echo signal already in the first order of expansion (8)

$$\mathscr{E} = -nS\frac{2N}{2I+1}\gamma\frac{(\hbar\omega)^2}{kT}\overline{\sin\xi \sin\eta}\cos\omega(t'-2\tau)$$

$$\times \exp\left[-\frac{(t'-2\tau)^2}{2T_2^2}\right], \quad (12)$$

which for $\omega_1 t_\omega = \omega_2 t_\omega = \pi/2$ is of the same magnitude as the signal (1) produced by two radio-frequency pulses with $\gamma H_1 t_\omega = \pi/2$.

4. In order for the spin-echo effect (1) and (12) to occur it is necessary[8] that the time t_ω during which the pulse acts on the spin system should be much smaller than T_2. On the other hand, the maximum effect will occur when $\omega_1 t_\omega = \omega_2 t_\omega = \pi/2$, so that the optimum condition is $T_2\omega_{1,2} \gg 1$.

It may be seen from this that in order to study dynamic ultrasonic phenomena nuclear spin systems are more convenient since the relaxation times T_2 in electron spin systems are smaller by a factor of $10^3 - 10^6$. In order to estimate $\omega_{1,2}$ we utilize the relation[11] $A = (2J \cdot 10^7/\rho v \omega^2)^{1/2}$ cm, where ρ is the density of the substance, J is the intensity of sound in w/cm^2. According to formulas (3), and according to the data of Bolef and Menes,[6] we shall obtain for KI^{127} and KBr^{79} $\omega_{1,2} \sim 10^3 J^{1/2}$ sec^{-1}. The relaxation time T_2 in these substances is of the order of magnitude of 10^{-4} sec, so that we must use maximum sound intensities. It is known (cf., for example, reference 12), that in the pulsed mode it is possible to obtain from a quartz radiator a sound intensity of the order of 1000 w/cm^2.

Apparently, we must choose substances with large values of T_2, or extend it artifically. This can be done by changing somewhat the method used in the paper by Andrew, Bradbury, and Eades,[13] i.e., by producing a rotating field H_0, which ought to reduce the dipole line width. It is also known[14] that artificial introduction of defects into a sample leads under certain conditions to a narrowing of the nuclear resonance line by a factor of several fold. It should be remembered that T_2, which describes the decay of the spin-echo signal, is determined only by the so-called irreversible contributions to the line width,[15] so that consequently, we took for our estimate too low values of T_2, which were determined from the width of absorption lines produced both by reversible and irreversible contributions.

We can also use shorter pulse lengths such that $\omega_{1,2} t_\omega < \pi/2$. This will lead to a reduction in the signal amplitude which, if necessary, could be compensated by reducing the temperature.

The foregoing enables us to conclude that it is possible to select a substance and experimental conditions in such a way that the inequality $\omega_{1,2} T_2 > 1$ will be satisfied. This will make it possible to observe the effect of spin echos induced by ultrasonic oscillations.

The author is grateful to S. A. Al'tshuler and B. M. Kozyrev for discussion of the results and to R. A. Dautov for useful advice.

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Translated by G. Volkoff
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