Evolution in time of nondiagonal dipole terms of the density matrix of the nuclear spin system in CaF_2

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(Submitted 22 June 1984)
Zh. Eksp. Teor. Fiz. **88**, 569–574 (February 1985)

An experimental study was made of the possibility of time-reversible evolution of nondiagonal dipole elements of the density matrix of spin systems in the specific case of the ^{19}F nuclei in a CaF_2 single crystal. A magic echo of dipole signal was observed at times much longer than the spin-spin relaxation time and this signal was attributed to an operator in the density matrix with just the nondiagonal elements throughout the evolution time of the system.

The action of certain pulse sequences in a multipulse nuclear magnetic resonance gives rise to terms in the density matrix that are not contained in the Hamiltonian and do not commute with it. An example is the density matrix in a rotating coordinate system.

$$\sigma(t)=\exp(-i\mathcal{H}_d't)\sigma_0\exp(i\mathcal{H}_d't),\quad \sigma_0=1-\beta_L\omega_0 I_x,$$

$$\mathcal{H}_d'=\sum_{i<j}a_{ij}[I_{zi}I_{zj}-{}^1/_4(I_{+i}I_{-j}+I_{-i}I_{+j})],\tag{1}$$

describing the state of a spin system after the action of a 90° pulse. The transverse component of the magnetization $I_x(t)$ is well known to give rise to a free-induction signal. The carefully planned and ingenious experiments of Waugh and his colleagues[1,2] demonstrated that the evolution in time of the nondiagonal (in the energy representation) term $I_x(t)$ in the density matrix (1) is reversible, so it is possible to observe a "magic echo" free induction signal at a time t after a 90° pulse several times longer than the spin-spin relaxation time T_2. On the other hand, the very important (in thermodynamics) random-phase hypothesis predicts a disappearance of the nondiagonal terms of the density matrix after times of the order of the relaxation time. The results of Refs. 1 and 2 therefore demonstrate the need for serious restrictions on the use of the random phase hypothesis, at least in the case of spin systems. It is pointed out in Ref. 3 that such restrictions may be related in a natural manner to the general concept of temperature and they apply also to more trivial thermodynamic systems.

We shall study the nature of the restrictions which must be imposed in using the random phase hypothesis by considering the evolution in time of nondiagonal terms of the density matrix of the spin system of the ^{19}F nuclei in a CaF_2 single crystal. The experiments were carried out at $T = 300$ K in a static field of 5618 Oe.

When a system described by the density matrix

$$\sigma=1-\beta\mathcal{H}_d'\tag{2}$$

is subjected to a θ pulse, it transforms the spin system to a state with the density matrix

$$\sigma=1-\beta[{}^1/_2(3\cos^2\theta-1)\mathcal{H}_d'+{}^3/_8P\sin^2\theta-{}^3/_4Q\sin\theta\cos\theta],$$

$$P=\sum_{i<j}a_{ij}(I_{+i}I_{+j}+I_{-i}I_{-j}),\tag{3}$$

$$Q=\sum_{i<j}a_{ij}[I_{zi}(I_{+j}+I_{-j})+I_{zj}(I_{+i}+I_{-i})].$$

The operator Q in the density matrix (3) makes it possible to observe a signal proportional to the reciprocal of the temperature of the dipole system or the dipole signal.[4] This dipole signal reflects a certain stage of the evolution in time of the term Q in the density matrix and is described by the following expression [Eq. (4.31) in Ref. 4]

$$\langle I_y\rangle=\beta\sin\theta\cos\theta\,\mathrm{Sp}(I_y^2)\frac{d}{dt}G(t),$$

where $G(t)$ gives the profile of the free-induction signal.

If $t > T_2$, then $dG/dt \to 0$ and the signal due to the term Q in the density matrix disappears. During the observation of the dipole signal the Hamiltonian of such a system, considered in a rotating coordinate system, becomes $\mathcal{H} = \mathcal{H}'_d$. Therefore, the disappearance of the dipole signal should correspond on the random phase hypothesis to an irreversible disappearance of the nondiagonal term Q in the density matrix.

We investigated evolution of the term Q in the density matrix at times much longer than T_2 and this was done using a pulse sequence 1 shown in Fig. 1. Before the θ pulse the density matrix is described by Eq. (2) with a high value of the reciprocal dipole temperature β. After the θ pulse in the $\theta = 54°$ case, we have

$$\sigma=1-\beta(0.245P-0.357Q).\tag{4}$$

In agreement with Ref. 4, after the θ pulse the dipole signal is due to the term Q in Eq. (4). In the presence of an rf field the Hamiltonian of the spin system considered in an inclined rotating system of coordinates, the conversion to which is achieved by the operator $\exp(\frac{1}{2}i\pi I_y)$, is

$$\mathcal{H}=\omega_1 I_z-\frac{1}{2}\mathcal{H}_d'+\frac{3}{8}P,\qquad \omega_1=\gamma H_x.\tag{5}$$

If on application of an rf field we go over to an inclined rotating coordinate system and after the end of the rf field pulse we return to a rotating coordinate system, then the evolution of the term Q in the density matrix (4) after the θ pulse can be described by

$$Q(t_1+t_2+t_3)=A^{-1}QA,$$

$$A=\exp(i\mathcal{H}_d't_1)\exp[i(\omega_1I_z-{}^1/_2\mathcal{H}_d'+{}^3/_8P)t_2]\exp(i\mathcal{H}_d't_3).\tag{6}$$

In our experiments the amplitude of the rf field was 50 Oe. Neglecting in Eq. (6) the operator $(3/8)P$ against the background of $\omega_1 I_z$, we obtain

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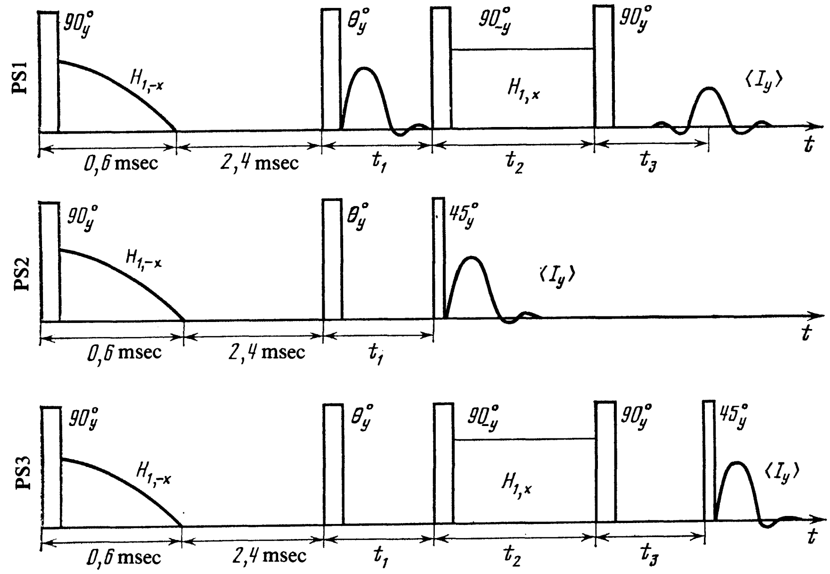

FIG. 1. Pulse sequences (PS) used in the present study.

$$Q(t_1+t_2+t_3)=A_1^{-1}QA_1,$$
$$A_1=\exp(i\omega_1 I_z t_2)\exp[i\mathcal{H}_d'(t_1-t_2/2+t_3)]. \tag{7}$$

If the random-phase hypothesis is invalid in the description of the time evolution of the term Q in a density matrix, as it is invalid in the case of the operator of the simpler structure $I_x=\Sigma_i I_{xi}$, it follows from Eq. (7) that we can observe a new physical effect which is a magic echo of the dipole signal or a dipole magic echo when the condition $t_1+t_3=t_2/2$ is satisfied. Variation of the values t_1 and t_2 allows us to observe always a dipole magic echo at $t_1+t_3=t_2/2$ (Fig. 2). The amplitude $\langle I_y\rangle_{\max}$ of the observed dipole magic echo signal is 50% of the signal after the θ pulse. The reduction in the dipole magic echo signal compared with the initial signal can be explained by the influence of nonsecular interactions in A, and also by the inhomogeneity of the rf field. It should be stressed that in our experiments we have $t_1+t_2+t_3=360$ μsec, which is much longer than T_2 for CaF_2 deduced from the decay of the free-induction signal and amounts to ~20 μsec for the [111] orientation. The invalidity of the random phase hypothesis in the description of the time evolution of the nondiagonal operator Q in the density matrix (4) thus becomes self-evident.

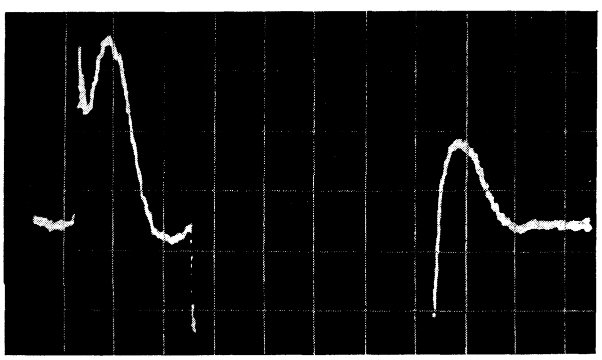

FIG. 2. Oscillogram of the dipole magic echo signal. Horizontal scale 50 μsec/div.

The signal corresponding to the nondiagonal operator P in the density matrix (4) cannot be observed directly. However, the action of a θ_1 pulse on the system transforms the operator P as follows:

$$\exp(i\theta_1 I_y)P\exp(-i\theta_1 I_y)=2\mathcal{H}_d'\sin^2\theta_1+Q\sin\theta_1\cos\theta_1 +(1-{}^1/_2\sin^2\theta_1)P. \tag{8}$$

Since the right-hand side of Eq. (8) contains the operator Q, it is obvious that after the θ_1 pulse it is possible to observe a signal due to the operator P in the density matrix (4).

The signal due to the operator P can be investigated by subjecting a spin system to pulse sequences 2 and 3. Ahead of a 45° pulse in the sequence 2 the density matrix of the system is ($\theta=90°$)

$$\sigma=1-\beta\exp(-i\mathcal{H}_d't_1)({}^3/_8P-{}^1/_2\mathcal{H}_d')\exp(i\mathcal{H}_d't_1). \tag{9}$$

After the 45° pulse the density matrix can be written in the form

$$\sigma=1-\beta\exp\left(i\frac{\pi}{4}I_y\right)\exp(-i\mathcal{H}_d't_1)\left(\frac{3}{8}P-\frac{1}{2}\mathcal{H}_d'\right)\times\exp(i\mathcal{H}_d't_1)\exp\left(-i\frac{\pi}{4}I_y\right). \tag{10}$$

In accordance with Eqs. (10) and (8), the signal observed after the 45° pulse includes a contribution independent of t_1 and originating from the operator $\mathcal{H}_d'$ in the density matrix (9), as well as a contribution due to the operator P in Eq. (9), which decreases to zero on increase in t_1. Figure 3 shows the dependence of the amplitude of the signal due to the operator P on the time t_1. In all the orientations the signal described by the operator P disappears much faster than the free-induction signal, which is accounted for by the structure of P.

When the pulse sequence 3 is applied to a spin system, the density matrix after a θ pulse ($\theta=90°$) becomes

$$\sigma=1-\beta({}^3/_8P-{}^1/_2\mathcal{H}_d'). \tag{11}$$

By analogy with Eq. (6), we find that the operator P is described by

$$P(t_1+t_2+t_3)=A^{-1}PA. \tag{12}$$

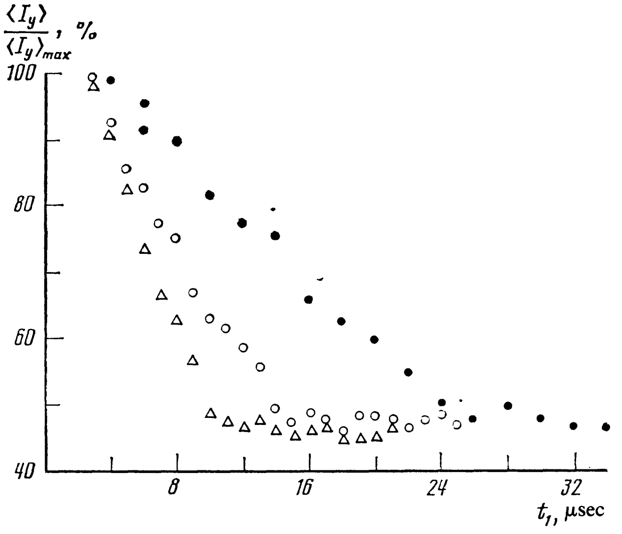

FIG. 3. Dependence of the amplitude of the signal due to the operator P on the time t_1: ●) [111] orientation; ○) [110] orientation; △) [100] orientation.

On the basis of Eq. (12) it would seem that it should be possible to observe a dipole magic echo due to the operator P if $t_1 + t_3 = t_2/2$. We varied the value of t_1 between 40 and 120 μsec and t_2 from 150 to 300 μsec (maintaining the condition $t_1 + t_3 = t_2/2$). If $t_3 < 28$ μsec (28 μsec is the time of disappearance of the signal due to P in the [111] orientation), it follows from the law of conservation of energy that the formation of a dipole magic echo due to the operator P should be accompanied by a change in the coefficient in front of $\mathscr{H}'_d$ in the density matrix or by the appearance of the operator $\omega_1 I_z$ with a certain coefficient. This fairly complex process can be considered in principle by assuming that our measurements demonstrate both the absence of a dipole magic echo and the absence of a Zeeman signal at $t_3 < 28$ μsec. However, if t_1 and t_3 are both greater than 28 μsec, the dipole magic echo due to the operator P should not be accompanied by a change in the coefficients in front of $\mathscr{H}'_d$ and $\omega_1 I_z$ in the density matrix. However, in this case as well we found no dipole magic echo.

It should be mentioned particularly that after a pulse sequence 3 the operator P in the density matrix corresponds, during the action of the rf field, to the operator $(3/8)P$ in the Hamiltonian of the system. Consequently,the operator P is not purely nondiagonal. This is sufficient for violation of the reversibility of the time evolution of the operator P, i.e., for the use of the thermodynamic approach to the description of the evolution of this operator. Since the Hamiltonian of the system during the action of an rf field is given by Eq. (5), the density matrix at times $t_2 > T_2$ should assume the following form in an inclined rotating system of coordinates:

$$\sigma = 1 - \beta_1(\omega_1 I_z - {}^1/_2 \mathscr{H}_d' + {}^3/_8 P). \qquad (13)$$

In our experiments the quantity β_1 was very small and the likely signal due to the operator P in the density matrix (13) was not observed.

The fact that thermodynamic systems are irreversible in time is closely related to the circumstance that systems of this kind are miscible.[5] Miscibility means that points in a small initial region of the phase space tend to establish a uniform distribution on the surfaces of single-valued integrals of motion during the relaxation time. Miscibility depends on instabilities of the equations of motion for a large number of particles against a small change in the initial conditions. This small change may be in the form of inaccuracy of the equations of motion which cannot be controlled for systems with small numbers of particles.

Our experiments and the results reported in Refs. 1 and 2 demonstrate that it is incorrect to apply the random-phase hypothesis to the description of the time evolution of purely nondiagonal operators Q and I_x in the density matrix that make no contribution to the energy. In other words, the corresponding multiparticle operators do not represent miscible systems. It should be stressed that the random phase hypothesis does not apply to the postulates of thermodynamics. The limits of validity of this hypothesis may be of different nature in the case of thermodynamic systems and they do not necessarily imply limitation of the validity of the spin temperature concept.

The question whether pure nondiagonality of the operator in the density matrix is sufficient to make the random-phase hypothesis invalid cannot be settled for spin systems or for thermodynamic systems of other types. This question is of general theoretical and practical importance, since in situations in which a magic echo can appear the purely nondiagonal operators either govern the magnitude of the observed signals or may contribute significntly to these signals.

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Translated by A. Tybulewicz