Toroidal response in nuclear magnetic resonance

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A review is given of the recently developed theory of magnetic-dipole and toroidal responses of a nuclear spin system to the action of alternating uniform and solenoidal magnetic fields. Using various approximate methods and computer simulation, a detailed study is made of the dynamics of a system of interacting nuclear spins with allowance for a nonuniform distribution of the spin orientations in space. An analysis is made of the conditions for excitation and observation of nuclear resonance in this case for both the stationary and the pulsed regimes. It is shown that the introduction of new response functions makes NMR methods much more informative in the study of molecular structure, especially for molecules with an asymmetric distribution of nuclei, which is a case that is important for biological applications.

INTRODUCTION

Modern methods of nuclear magnetic resonance (NMR) are widely used in physics and chemistry investigations.[1–7] Nuclear spins play the role of "labels," by means of which one can recognize the spatial distribution of nuclei and their interaction with the environment, and this makes it possible to solve problems involving the determination of the internal structure of investigated materials and to study dynamical processes. To this end, the investigated sample is placed in a homogeneous magnetic field, which gives rise to a Zeeman splitting of the energy spectrum, and an alternating homogeneous magnetic field is used to excite transitions in this spectrum. Since the nuclear spins interact with each other, the shifts of the energy levels depend on the positions of the spins, and this makes it possible to obtain information about the positions of the nuclei and the fields that act on them. By means of a specially chosen sequence of pulses of the alternating field it is possible to eliminate the influence of certain interactions, and this raises further the accuracy and information content of the NMR methods. To investigate spatial displacements of nuclei, methods of NMR observation in an inhomogeneous magnetic field (NMR microscopy[8,9]) are also used. These methods are based on the fact that the resonance frequency in an inhomogeneous field depends on the position of the spin even if the spins do not interact with one another. The method of NMR microscopy makes it possible to achieve a spatial resolution of the order of 10^{-2}.

In the qualitative respect, the further development of NMR methods consists in an extension of the set of quantities that are measured. Besides the total dipole magnetic moment of a system of spins, which is usually observed in NMR, it is also possible to measure other multipole moments of a nuclear subsystem, which is regarded as a system of magnetic dipoles with a nonuniform distribution in space. From this point of view, the greatest interest attaches to the toroidal moment of a spin system, which can be excited by a solenoidal magnetic field. A detailed exposition of the electrodynamics of toroidal moments and some of its applications can be found in Refs. 10, 13 (see also the references cited there). In accordance with Maxwell's equations, a solenoidal field can be created by displacement currents: curl $\mathbf{H}=\dot{\mathbf{E}}/c$ (or conduction currents, which are possible only in conducting samples; in what follows, we shall restrict ourselves to the most important case of nonconducting media). Therefore, to excite toroidal transitions it is necessary to replace the coil with a current, in which the investigated sample is placed in the NMR spectrometer, by a parallel-plate capacitor.

The toroidal moment is a quantity that characterizes the solenoidal distribution of the orientation of the nuclear spins in space. The dipole interaction, which makes the main contribution to the interaction of nuclear spins with one another in the compact arrangement of nuclei in a molecule, tends to align their spins precisely in individual vortical structures. Therefore, observation of the toroidal moment makes it possible in principle to obtain more complete information about the structure of the investigated object than ordinary NMR methods. Naturally, the observation of multipoles of order higher than the dipole moment raises the requirements on the accuracy of the measurements. However, it is within the capabilities of modern measuring devices, for example, SQUIDs, as is indicated by the experiments recently undertaken to observe the indirect effect of nuclear quadrupole moments on the electron subsystem by Hahn and collaborators.[14]

It is of great interest to investigate "crossed" effects, i.e., to observe the toroidal response when a system is excited by a homogeneous alternating field and, conversely, to observe the magnetic-dipole response when the system is excited by a solenoidal field. Since the vectors of the magnetic dipole and magnetic toroidal moments have different spatial parities (the magnetic moment is an axial vector, while the toroidal moment is a polar vector), the occurrence of crossed responses is possible only for an asymmetric (for example, chiral) distribution of nuclei. Thus, in this case NMR data can be used to obtain direct information about the degree of asymmetry of molecules, which is of great interest for

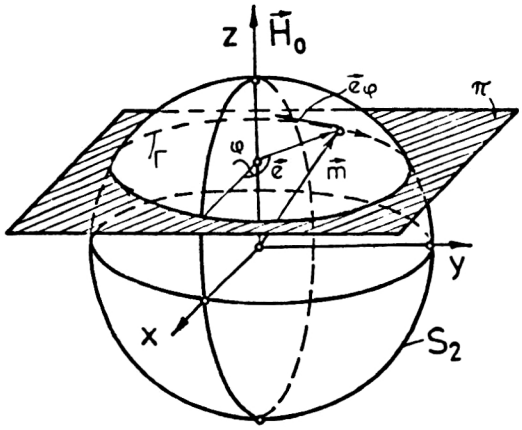


FIG. 1. Phase space of a classical spin.

chemical and biological applications. The introduction of a new quantity—the toroidal moment—into the set of observables requires reconsideration of the theory of magnetic resonance. In this paper, we review the theoretical results (already in part published in our studies of Refs. 15, 18) that have so far been obtained. Using different approximate methods, and also numerical modeling, we investigate in detail the dynamics of a system of nuclear spins with allowance for their nonuniform distribution in space. We analyze the conditions of excitation and observation of resonance by solenoidal and homogeneous fields in both steady-state and pulsed regimes. Our review consists of four sections. In Sec. 1 we consider the dynamics of noninteracting spins. We then analyze the interaction of a system of spins with an alternating field—both homogeneous and solenoidal. In Sec. 2 we solve the problem of the behavior of a system of interacting spins in the absence of alternating fields. We elucidate the conditions for formation of a vortical structure of spins as a function of their initial orientations and the geometry of the system. In Sec. 3 we investigate the response of the system to pulsed homogeneous and solenoidal magnetic fields. Finally, in Sec. 4 we consider the toroidal susceptibility and discuss the conditions for measurement of the toroidal response. At the end, we summarize the main results of the paper.

1. SPIN DYNAMICS IN AN ALTERNATING FIELD

The main object of our study will be a system of interacting spins in a strong homogeneous magnetic field $\mathbf{H}_0$ and subject to the effect of an alternating field $\mathbf{h}(t)$. However, in this section we shall ignore the interaction of the spins with each other, since it can be assumed to be weak compared with their interaction with the field $\mathbf{H}_0$, and therefore at the time of application of the pulses of the alternating field it cannot have a significant effect on the behavior of the spin system. In the theory of nuclear magnetic resonance, it is usually assumed that the alternating field $\mathbf{h}(t)$ is perpendicular to the homogeneous field $\mathbf{H}_0$. However, if an alternating solenoidal magnetic field is applied to the system, this condition cannot be satisfied in the general case for each of the spins simultaneously. Therefore, we shall consider in detail an approximate solution to the problem of the dynamics of a spin in an alternating field for arbitrary mutual orientation of the fields $\mathbf{H}_0$ and $\mathbf{h}(t)$. In NMR theory, one very often uses so-called classical spins, when each spin is associated with a unit "classical" vector. It is usually assumed that in such an approach we obtain an approximate "semiclassical" description of the behavior of the spins that is far from the quantum behavior. In reality, each classical spin can be uniquely associated with a quantum state, which is called a coherent state. The question of the connection between the classical and quantum descriptions of spin systems has not been sufficiently clearly treated in the literature on magnetic resonance, and the recent investigations of quantum coherent states make it possible to trace this connection with the necessary completeness.

1.1. Classical spin in a constant magnetic field

The simplest and most transparent picture of the dynamics of nuclear spins can be obtained by means of a classical picture of the motion of the spins. In this approach, each spin of the system is associated with a certain unit vector $\mathbf{m}$, which moves over the surface of the sphere S^2 (Fig. 1), which plays the role of the phase space of this system. As is well known (see, for example, Ref. 23, Chap. 4), the vector $\mathbf{m}$ can be associated with a quantum coherent state $|\mathbf{m}\rangle$ defined in a $(2S+1)$-dimensional state space of the spin S that is spanned by basis vectors $|S,\mu\rangle$ (here $\mu=-S,\ -S+1,\ldots,S$). Therefore, the solution of the classical problem simultaneously permits a solution of the quantum problem.

Let a classical particle have mechanical angular momentum $\hbar\mathbf{S}$. Here, $\mathbf{S}$ is a dimensionless vector of fixed length (taking into account its spin origin). The spin angular momentum is related to the magnetic moment $\mathbf{m}$ of the particle by the gyromagnetic equation

$$\mathbf{m}=\gamma\hbar\mathbf{S}, \tag{1}$$

where γ is the gyromagnetic ratio, which in the general case can be a tensorial quantity but which for simplicity we shall here assume is a scalar. The equation of motion of the classical mechanical angular momentum has the form

$$\hbar\dot{\mathbf{S}}=\mathbf{K}, \tag{2}$$

where $\mathbf{K}$ is the moment of the force. We shall assume that the particle is in a magnetic field $\mathbf{H}$, and that the energy of the interaction with the field is

$$U=-(\mathbf{mH}). \tag{3}$$

The moment of the force $\mathbf{K}$ can be obtained by differentiating the energy with respect to $\mathbf{m}$ with allowance for the constancy of the length of this vector:

$$\mathbf{K}=-\left[\mathbf{m}\times\frac{\partial}{\partial\mathbf{m}}\right]U=\mathbf{m}\times\mathbf{H}. \tag{4}$$

Substituting this expression in Eq. (2) and using the relation (1) between $\mathbf{S}$ and $\mathbf{m}$, we obtain

$$\dot{\mathbf{m}}=\gamma[\mathbf{mH}]. \tag{5}$$

In what follows, it will be convenient to go over to a system of units of measurement in which the vector $\mathbf{m}$ has unit length and the constant γ is also equal to unity. In these units, Eq. (5) will have the form

$$\dot{\mathbf{m}}=[\mathbf{mH}]. \tag{6}$$

For the transition back to dimensional units in the final expressions, it is necessary to replace $\mathbf{H}$ by $\gamma\mathbf{H}$ and $\mathbf{m}$ by $\gamma\hbar S\mathbf{m}$.

In a static magnetic field $\mathbf{H}_0$, the spin energy U is conserved. The surface of constant energy $U=\text{const}=-(\mathbf{mH}_0)$ in the $\mathbf{m}$ space is a plane π perpendicular to the vector $\mathbf{H}_0$. The intersection of the plane π with the sphere S^2 determines the trajectory of the vector $\mathbf{m}$ in the phase space, which in the present case is a circle (Fig. 1). The nature of the motion of the phase point along the trajectory Γ is readily found by solving the equation of motion (6). We project the vector $\mathbf{m}$ onto the axis of a cylindrical coordinate system:

$$\mathbf{m}=z\mathbf{k}+\rho\mathbf{e}, \tag{7}$$

where $\mathbf{k}$ and $\mathbf{e}$ are unit vectors oriented, respectively, along the z axis and along the direction of the projection of the vector $\mathbf{m}$ onto the plane π (Fig. 1). Differentiating the relation (7) with respect to the time and bearing in mind that $\dot{\mathbf{e}}=\dot{\varphi}\mathbf{e}_\varphi$, where $\mathbf{e}_\varphi$ is the unit vector of the tangent to the circle Γ, we obtain $\dot{\mathbf{m}}=\dot{z}\mathbf{k}+\dot{\rho}\mathbf{e}+\rho\dot{\varphi}\mathbf{e}_\varphi$. Substituting the expression (7) in the right-hand side of Eq. (6), we find

$$[\mathbf{mH}]=[(z\mathbf{k}+\rho\mathbf{e})H_0\mathbf{k}]=-\rho H_0\mathbf{e}_\varphi. \tag{8}$$

Using the expression obtained above for $\dot{\mathbf{m}}$, we find the equations of motion in the form

$$\dot{z}=0; \quad \dot{\rho}=0; \quad \rho\dot{\varphi}=-\rho H_0, \tag{9}$$

which have the solution $z=\text{const}$, $\rho=\text{const}$, $\dot{\varphi}=-H_0$. This means that the phase point rotates uniformly in the clockwise direction (in the opposite direction to which the angle φ is measured) along the trajectory Γ, while the magnetic-moment vector precesses around the direction of the magnetic field. Note that the distance of the plane π from the center of the sphere S^2, which is determined by the coordinate $z=\cos\theta$, and also the radius of the circle Γ, which is equal to the cylindrical coordinate $\rho=\sin\theta$, are uniquely related to the conserved energy U (here, θ is the angle between the direction of the spin and the field H_0):

$$z=\cos\theta=-U/H_0; \quad \rho^2+z^2=1. \tag{10}$$

The energy is a minimum for $z=1$ (when $\theta=0$, $\rho=0$) and a maximum for $z=-1$ (when $\theta=\pi$, $\rho=0$).

The solution of the considered problem can also be obtained directly in the Cartesian coordinates of the vector $\mathbf{m}$. We shall show in what follows that this method is most convenient for investigating the dynamics of interacting spins. As for every linear equation, the solution of Eq. (6) can be sought in the form $\mathbf{a}\exp\{-i\omega t\}$, where $\mathbf{a}$ is some constant vector. Substituting this solution in the equation, we obtain for $\mathbf{a}$ and ω the eigenvalue equation

$$(iH_{jk}-\omega\delta_{jk})a_k=0, \tag{11}$$

where $iH_{jk}=ie_{jkl}H_{0l}$ is a 3×3 Hermitian matrix. After simple calculations, we can find the three eigenvalues of this matrix, $\omega_{1,2}=\pm H_0$, $\omega_3=0$, and the corresponding eigenvectors, $\mathbf{a}_{1,2}=c_{1,2}(\pm i\mathbf{e}_x+\mathbf{e}_y)$, $\mathbf{a}_3=c_3\mathbf{e}_z$, where $c_1=c_2^*$, $c_3=c_3^*$ are constants that must be determined from the initial conditions, and $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are the unit vectors of the Cartesian coordinate system shown in Fig. 1. The general solution can be represented in the form

$$\mathbf{m}=\sum_n \mathbf{a}_n e^{-i\omega_n t}=\sin\theta(\sin(H_0t+\varphi_0)\mathbf{e}_x + \cos(H_0t+\varphi_0)\mathbf{e}_y), \tag{12}$$

where φ_0 is the initial phase, and the angle θ is determined by the initial energy of the spin (10). It is obvious that this solution is identical to the solution of Eqs. (9) given above.

1.2. Coherent states

As we have already noted above, the classical description of spin dynamics by means of the unit vector $\mathbf{m}$ is uniquely related to a quantum coherent state. In the general case, the quantum state of the spin S is defined by a $(2S+1)$-dimensional vector $|\Psi\rangle$ that satisfies the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle=\hat{\mathscr{H}}|\Psi\rangle. \tag{13}$$

The Hamiltonian operator $\hat{\mathscr{H}}$ can be obtained from the classical expression for the energy (3) in the form

$$\hat{\mathscr{H}}=-\gamma\hbar(\hat{\mathscr{S}}\mathscr{H}), \tag{14}$$

where $\hat{\mathbf{S}}$ is the spin operator. Substituting this expression in Eq. (13) and using the same units of measurement as in the classical equation of motion (6), we obtain

$$i\frac{\partial}{\partial t}|\Psi\rangle=-(\hat{\mathscr{S}}\mathscr{H})|\Psi\rangle. \tag{15}$$

In the given basis of spin states $|S,\mu\rangle$, where $\mu=-S, -S+1,\ldots,S$, Eq. (15) corresponds to a system of $2S+1$ linear equations for the complex variables $c_\mu(t)=\langle S,\mu|\Psi\rangle$, which are the coefficients of the expansion of the vector $|\Psi\rangle$ with respect to the basis vectors:

$$|\Psi\rangle=\sum_\mu c_\mu(t)|S,\mu\rangle. \tag{16}$$

However, in this general approach the principal features of the dynamics of the spin system, which are associated with its group structure, are omitted. The spin operators $\hat{\mathscr{S}}$ in the Schrödinger equation (15) are the generators of the Lie algebra of the group $SU(2)$. Therefore, the time evolution of the quantum state of the spin is determined by the time variation of a small number of parameters, which define an element of the group $SU(2)$ and can be regarded as "classical" variables. The group structure of the equations can be taken into account most consistently by means of the basis of coherent states $|\mathbf{m}\rangle$ (Ref. 23). On the one hand, the coherent state $|\mathbf{m}\rangle$

is a $(2S+1)$-dimensional vector of the quantum state of the system, and, like any vector, it can be decomposed with respect to basis vectors $|S,\mu\rangle$ [cf. Eq. (16)]:

$$|\mathbf{m}\rangle=\sum_{\mu} u_{\mu}(\mathbf{m})|S,\mu\rangle. \tag{17}$$

On the other hand, the components u_{μ} of this quantum vector are uniquely related to the components of the unit three-dimensional ("classical") vector $\mathbf{m}$ (Ref. 23):

$$u_{\mu}(\mathbf{m})=\langle S,\mu|\mathbf{m}\rangle=\left(\frac{(2S)!}{(S+\mu)!(S-\mu)!}\right)^{1/2} \times\left(-\sin\frac{\theta}{2}\right)^{S+\mu}\left(\cos\frac{\theta}{2}\right)^{S-\mu}e^{-i(S+\mu)\varphi}, \tag{18}$$

where θ and φ are the spherical angles of the vector $\mathbf{m}$:

$$m_x=\sin\theta\cos\varphi;\quad m_y=\sin\theta\sin\varphi;\quad m_x=\cos\theta. \tag{19}$$

To obtain the coherent state $|\mathbf{m}\rangle$, one specifies in some manner a basis vector $|\Phi_0\rangle$ (usually the vector $|S,-S\rangle$ corresponding to the minimum spin projection $\mu=-S$) and acts on it with the rotation operator $\hat{\mathscr{D}}_{\mathbf{m}}$, which is parametrized by the vector $\mathbf{m}$:

$$|\mathbf{m}\rangle=\hat{\mathscr{D}}_{\mathbf{m}}|\Psi_0\rangle. \tag{20}$$

In explicit form, the operator $\hat{\mathscr{D}}_{\mathbf{m}}$ can be expressed in terms of a different unit vector, $\mathbf{n}$, which has components $n_x=\sin\varphi$, $n_y=-\cos\varphi$, $n_z=0$:

$$\hat{\mathscr{D}}_{\mathbf{m}}=\exp\{i\theta(\mathbf{n}\hat{\mathscr{S}})\}. \tag{21}$$

As a result of rotation through an angle θ around the vector $\mathbf{n}$, the vector $\mathbf{m}_0$ directed along the Z axis is brought into coincidence with the vector $\mathbf{m}$. It can be shown that the expectation value of the spin operator $\hat{\mathscr{S}}$ in the coherent state has the form

$$\langle\mathbf{m}|\hat{\mathscr{S}}|\mathbf{m}\rangle=-S\mathbf{m}. \tag{22}$$

The set of coherent states $\{|\mathbf{m}\rangle\}$, where the end of the unit vector $\mathbf{m}$ ranges over all points of the surface of the unit sphere S^2, satisfies the completeness condition

$$(2S+1)\int|\mathbf{m}\rangle\langle\mathbf{m}|d\mathbf{m}=\hat{I}, \tag{23}$$

where $\hat{I}$ is the unit operator, and $d\mathbf{m}$ is the element of surface of the unit sphere: $d\mathbf{m}=\sin\theta\,d\theta d\varphi/4\pi$. This condition makes it possible to use the coherent states as a basis with respect to which an arbitrary state vector $|\Psi\rangle$ can be decomposed:

$$|\Psi\rangle=(2S+1)\int\Psi(\mathbf{m})|\mathbf{m}\rangle d\mathbf{m}. \tag{24}$$

The coefficients $\Psi(\mathbf{m})$ in this expression can be expressed in terms of the coefficients of the expansions of the states $|\Psi\rangle$ and $|\mathbf{m}\rangle$ with respect to the basis vectors $|S,\mu\rangle$:

$$\Psi(\mathbf{m})=\langle\mathbf{m}|\Psi\rangle=\sum_{\mu}\langle\mathbf{m}|S,\mu\rangle\langle S,\mu|\Psi\rangle=\sum_{\mu}u_{\mu}^{*}(\mathbf{m})c_{\mu}, \tag{25}$$

where c_{μ} and $u_{\mu}(\mathbf{m})$ are determined by the relations (16) and (18), respectively.

In the decomposition (24), the integration over the angles can be replaced by a summation over a certain set of $2S+1$ coherent states $|\mathbf{m}_a\rangle$, where the index a ranges over $2S+1$ values. The fact is that the system of coherent states $\{|\mathbf{m}\rangle\}$ is overcomplete. This means that one can select from them $2S+1$ states $|\mathbf{m}_a\rangle$, where the vectors $\mathbf{m}_a$ are not parallel to each other, but can be taken as the basis of the quantum state space. Thus, besides the decompositions (16) and (24) we can also write, for an arbitrary vector $|\Psi\rangle$,

$$|\Psi\rangle=\sum_{a} b_a|\mathbf{m}_a\rangle. \tag{26}$$

The basis states $|\mathbf{m}_a\rangle$ are not mutually orthogonal, and therefore to calculate the coefficients b_a of the decomposition it is necessary to solve a system of linear equations, which we shall not give here in explicit form. The advantage of this basis compared with other bases is that, knowing the dynamics of the classical vectors $\mathbf{m}_a$ and the initial vector of the quantum state (i.e., the coefficients b_a at the initial time), we can uniquely determine the quantum state at all subsequent times for any spin S.

To demonstrate this, we return to consideration of the problem of the dynamics of a quantum spin state in a magnetic field. We shall assume that at the initial time $t=0$ the spin is in some coherent state $|\mathbf{m}(0)\rangle$. Since in accordance with Eq. (15) the Hamiltonian $\hat{\mathscr{H}}$ is linear in the spin operators $\hat{\mathscr{S}}$, which, as we have already noted, are the generators of the Lie algebra of the group $SU(2)$, the operator of the time evolution of the system is identical to a representation $\hat{\mathscr{D}}(g_t)$ of some element g_t of the group $SU(2)$. Thus, the solution of the Schrödinger equation (15) can be written in the form

$$|\Psi(t)\rangle=\hat{\mathscr{D}}(g_t)|\mathbf{m}(0)\rangle. \tag{27}$$

In accordance with the expression (20), the initial state $|\mathbf{m}(0)\rangle$ can be represented in the form

$$|\mathbf{m}(0)\rangle=\hat{\mathscr{D}}(g_0)|\Psi_0\rangle, \tag{28}$$

where g_0 is some element of the group $SU(2)$. Bearing in mind that in accordance with the property of group representations $\hat{\mathscr{D}}(g_t)\hat{\mathscr{D}}(g_0)=\hat{\mathscr{D}}(g_tg_0)$, and also bearing in mind that when applied to a state $|\Psi_0\rangle$ any operator $\hat{\mathscr{D}}$ can be represented in the form $\exp(i\phi)\hat{\mathscr{D}}_{\mathbf{m}}$, where ϕ is some phase and the operator $\hat{\mathscr{D}}_{\mathbf{m}}$ is defined by Eq. (21), we obtain after simple manipulations of the expressions (27) and (28) the equation

$$|\Psi(t)\rangle=\hat{\mathscr{D}}(g_tg_0)|\Psi_0\rangle=e^{i\phi(t)}|\mathbf{m}(t)\rangle. \tag{29}$$

Thus, if at the initial time the state of the system was coherent, then except for the phase ϕ it also remains coherent at any subsequent time.

Substituting the function (29) in the Schrödinger equation, we obtain for the coherent state the equation

$$i|\dot{\mathbf{m}}\rangle=(\hat{\mathscr{H}}-\dot{\phi})|\mathbf{m}\rangle. \tag{30}$$

We differentiate, with respect to the time, the right- and left-hand sides of Eq. (22) and use for the manipulations Eq. (30), the explicit form of the Hamiltonian (14), and the commutation relations for the spin operators. As a result, we obtain for the vector $\mathbf{m}$ an equation of motion that is identical to the classical equation

$$\dot{\mathbf{m}}=[\mathbf{mH}]. \tag{31}$$

With regard to the phase ϕ, it can be shown[23] that it satisfies the equation of motion

$$\dot{\phi}=S(\mathbf{H}(\mathbf{m}+\mathbf{m}_0)), \tag{32}$$

where the unit vector $\mathbf{m}_0$ is directed along the quantization axis used to construct the state $|\Psi_0\rangle$.

We now return to the question of the dynamics of an arbitrary quantum state vector $|\Psi(t)\rangle$ that satisfies the Schrödinger equation (15). Let $|\Psi(0)\rangle$ be the known initial value of this vector, which is decomposed with respect to a certain basis of coherent states $|\mathbf{m}_a(0)\rangle$ in accordance with the expression (26). Applying to the vector $|\Psi(0)\rangle$ the time-evolution operator $\hat{\mathscr{D}}(g_t)$, we can, in accordance with (27)–(29), represent the vector $|\Psi(t)\rangle$ in the form

$$|\Psi(t)\rangle=\sum_a b_a e^{i\phi_a(t)}|\mathbf{m}_a(t)\rangle, \tag{33}$$

where the b_a are the coefficients of the decomposition of the initial state $|\Psi(0)\rangle$ with respect to the basis $|\mathbf{m}_a(0)\rangle$, and the "classical" quantities—the vectors $\mathbf{m}_a$ and the phases ϕ_a—are determined by solving Eqs. (31) and (32) with the initial values $\mathbf{m}=\mathbf{m}_a(0)$ and $\phi=0$, respectively. At the same time, in Eq. (32) it is necessary to replace $\mathbf{m}$ by $\mathbf{m}_a$.

We consider in somewhat more detail the connection between the "classical" vector $\mathbf{m}$ and the coherent quantum state $|\mathbf{m}\rangle$. The simplest case is for spin $S=1/2$. The quantum state is described by a two-component spinor $|\mathbf{m}\rangle=|\Psi\rangle=\binom{\Psi_1}{\Psi_2}$, and in accordance with the general expression (18) these components have the form

$$\psi_1=u_{1/2}=-\sin\frac{\theta}{2}e^{-i\phi};\quad \psi_2=u_{-1/2}=\cos\frac{\theta}{2}. \tag{34}$$

Forming from these components a symmetric spinor tensor, which has the form $\{\psi_\mu\psi_\nu...\psi_\rho\}$, where the curly brackets denote symmetrization with respect to the spin indices μ, ν,...,ρ, we can show that the independent components of this tensor are identical to the components of the coherent state for the spin S. Thus, instead of the classical vector $\mathbf{m}$ we can also use a two-component spinor, which in the mathematical respect is a simpler object.

A physically transparent way of introducing the correspondence between the classical and quantum descriptions of the spin $S=1/2$ is as follows. We associate with the vector $\mathbf{m}$ a spinor tensor of rank 2 (i.e., a density matrix of spin 1/2):

$$\hat{\rho}=\frac{1}{2}(\hat{1}+\mathbf{m}\hat{\sigma}), \tag{35}$$

where $\hat{\boldsymbol{\sigma}}$ are the Pauli matrices, and $\hat{1}$ is the 2×2 unit matrix:

$$\hat{\sigma}_x=\begin{pmatrix}0&1\\1&0\end{pmatrix};\quad \hat{\sigma}_y=\begin{pmatrix}0&-i\\i&0\end{pmatrix};\quad \hat{\sigma}_z=\begin{pmatrix}1&0\\0&-1\end{pmatrix};$$

$$\hat{1}=\begin{pmatrix}1&0\\0&1\end{pmatrix}. \tag{36}$$

Since in the general case $\mathbf{m}$ is a unit vector, it is readily verified that the operator $\hat{\rho}$ is idempotent, i.e., $\hat{\rho}\hat{\rho}=\hat{\rho}$. Therefore, the 2×2 matrix $\hat{\rho}$ can be represented as the direct product of two-dimensional normalized vectors $|\psi\rangle=\binom{\psi_1}{\psi_2}$ and $\langle\Psi|=(\psi_1^*\psi_2^*)$:

$$\hat{\rho}=|\psi\rangle\langle\psi|;\quad \langle\psi|\psi\rangle=1, \tag{37}$$

since in this case the condition of idempotency is satisfied automatically: $\hat{\rho}\hat{\rho}=|\psi\rangle\langle\psi||\psi\rangle\langle\psi|=|\psi\rangle\langle\psi|=\hat{\rho}$. The connection between the components of the spinor $|\psi\rangle$ and the vector $\mathbf{m}$ is given by a relation that follows from (35) and (37):

$$\mathbf{m}=\mathrm{Tr}\{\hat{\rho}\hat{\boldsymbol{\sigma}}\}=\langle\psi|\hat{\boldsymbol{\sigma}}|\psi\rangle. \tag{38}$$

We obtain an identity if as the components of the 2-spinor $|\psi\rangle$ we use here the components of the coherent state that are given by the expressions (34). It is also easy to see that the relation (38) corresponds to the general expression (22) if $|\psi\rangle$ is understood as a coherent spin state.

1.3. Spin in an alternating field

The investigation of spin dynamics in an alternating magnetic field $\mathbf{h}(t)$ is very important for magnetic resonance, since information about the internal structure of a system can be deduced from its response to an alternating field. It is usual in NMR to employ a combination of two fields: a strong static field $\mathbf{H}_0$ and a rotating field perpendicular to it:

$$\mathbf{h}(t)=h(\mathbf{e}_x\cos\omega t+\mathbf{e}_y\sin\omega t). \tag{39}$$

In a coordinate system K_{rot} rotating with the alternating field $\mathbf{h}$, the spin will be subject to a constant effective field $\mathbf{H}_{\mathrm{eff}}=\mathbf{H}_0+h\mathbf{e}_x$. Therefore, in this system the spin will precess around $\mathbf{H}_{\mathrm{eff}}$, as described in the previous section. In the laboratory coordinate system K_{lab}, the spin will execute a complicated motion of precession and rotation, since in K_{lab} the precession axis itself rotates around the static field $\mathbf{H}_0$.

In a weak field $\mathbf{h}(t)$, the influence of the field on the motion of the system will in general be slight. It reduces to certain small distortions of the trajectory of the motion, which ceases to be planar (cf. Fig. 1), while the motion itself in the trajectory becomes nonuniform. The effect of even a weak alternating field will become appreciable in the case of resonance, when the rotation frequency ω of the field and the frequency $\omega_0=-H_0$ of Larmor precession of the spin in the field H_0 are equal. In this case, the trajectory of the spin on the sphere S^2 will be a helical (spiral) line, which "winds" around the sphere from top to bottom, then in the opposite direction, and so forth. The amplitude of the field h determines the pitch of this spiral.

The actual solution of the equations of spin dynamics in the rotating magnetic field $\mathbf{h}(t)$ is most readily obtained in the 2-spinor representation (cf. Ref. 21, p. 547 of the Russian

original). Substituting in the Hamiltonian $\hat{\mathscr{H}}$ the field $\mathbf{H}$ in the form of the sum $\mathbf{H}_0+\mathbf{h}(t)$, we obtain the Schrödinger equation in the original laboratory coordinate system K_{lab} in the form

$$i|\dot{\psi}\rangle=\hat{\mathscr{H}}|\psi\rangle; \quad \hat{\mathscr{H}}=-H_0\hat{\mathscr{S}}_z-h(\hat{\mathscr{S}}_x\cos\omega t-\hat{\mathscr{S}}_y\sin\omega t). \tag{40}$$

We go over to the rotating coordinate system K_{rot}. The state vector $|\psi_{\text{rot}}\rangle$ in this system is related to the vector $|\psi\rangle$ by a unitary transformation of rotation around the z axis: $\hat{\mathscr{U}}_z(\omega t)=\exp(i\omega\hat{\mathscr{S}}_z t)$, $|\psi_{\text{rot}}\rangle=\hat{\mathscr{U}}_z(\omega t)|\psi\rangle$.

Differentiating this relation with respect to the time and noting that $\hat{U}_z=i\omega\hat{\mathscr{S}}_z\hat{\mathscr{U}}_z$, we find that the vector $|\psi_{\text{rot}}\rangle$ also satisfies a Schrödinger equation but with effective Hamiltonian $\hat{\mathscr{H}}_{\text{rot}}$ equal to

$$\hat{\mathscr{H}}_{\text{rot}}=\omega\hat{\mathscr{S}}_z+\hat{\mathscr{U}}_z\hat{\mathscr{H}}\hat{\mathscr{U}}_z^+=-(H_0+\omega)\hat{\mathscr{S}}_z-h\hat{\mathscr{S}}_x. \tag{41}$$

In the derivation of this expression, we took into account the fact that the action of any rotation operator $\hat{\mathscr{U}}$ on the spin operators reduces to a linear transformation

$$\hat{\mathscr{U}}\hat{\mathscr{S}}_i\hat{\mathscr{U}}^+=U_{ik}\hat{\mathscr{S}}_k, \tag{42}$$

where

$$\hat{\mathscr{U}}_z(\omega t)=\begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2}\end{pmatrix};$$

$$U_{zik}=\begin{pmatrix} \cos\omega t & \sin\omega t & 0 \\ -\sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 1\end{pmatrix}. \tag{43}$$

As can be concluded by analyzing the expression (41) for the Hamiltonian $\hat{\mathscr{H}}_{\text{rot}}$, in the system K_{rot} the effective field is static and has components $\mathbf{H}_{\text{eff}}=(h,0,H_0+\omega)$. We go over to a new coordinate system K'_{rot}, in which the Z axis is directed along the effective field. This transition reduces to a rotation of the system K_{rot} around the Y axis through an angle α, where $\tan\alpha=h/(H_0+\omega)$, i.e., α is defined as the angle between the fields $\mathbf{H}_0$ and $\mathbf{H}_{\text{eff}}$. The rotation operator $\hat{\mathscr{U}}_y(\alpha)=\exp(-i\hat{\mathscr{S}}_y\alpha)$ can be expressed in explicit form as

$$\hat{\mathscr{U}}_y(\alpha)=\begin{pmatrix} \cos\dfrac{\alpha}{2} & -\sin\dfrac{\alpha}{2} \\ \sin\dfrac{\alpha}{2} & \cos\dfrac{\alpha}{2}\end{pmatrix}. \tag{44}$$

The Hamiltonian in the system K'_{rot} is

$$\hat{\mathscr{H}}'_{\text{rot}}=\hat{\mathscr{U}}_y(\alpha)\hat{\mathscr{H}}_{\text{rot}}\hat{\mathscr{U}}_y^+(\alpha)=-\Omega\hat{\mathscr{S}}_z;$$

$$\Omega=H_{\text{eff}}=\sqrt{h^2+(H_0+\omega)^2}. \tag{45}$$

The Hamiltonian $\hat{\mathscr{H}}'_{\text{rot}}$ controls the dynamics of the vector $|\psi'_{\text{rot}}\rangle=\hat{\mathscr{U}}_y(\alpha)|\psi_{\text{rot}}\rangle$, namely, $i|\dot{\psi}'_{\text{rot}}\rangle=\hat{\mathscr{H}}'_{\text{rot}}|\psi'_{\text{rot}}\rangle$. The solution of this equation can be expressed in the form $|\psi'_{\text{rot}}(t)\rangle=\hat{\mathscr{U}}_z(\Omega t)|\psi'_{\text{rot}}(0)\rangle$, where the operator $\hat{\mathscr{U}}_z(\Omega t)$ is defined by the relations (43), and $|\psi'_{\text{rot}}(0)\rangle$ is the initial value of the state vector in the system K'_{rot}.

Taking into account all the relations obtained above, we can write the solution of the Schrödinger equation in the original system K_{lab} in the form

$$|\psi(t)\rangle=\hat{\mathscr{U}}_z^+(\omega t)\hat{\mathscr{U}}_y^+(\alpha)\hat{\mathscr{U}}_z(\Omega t)\hat{\mathscr{U}}_y(\alpha)|\psi(0)\rangle, \tag{46}$$

where $|\psi(0)\rangle$ is the initial spin state in the system K_{lab}. Multiplying the matrices in the expression (46), we finally obtain for the components of the spinor $|\psi\rangle$ the expressions

$$\begin{aligned}\psi_1(t)&=e^{-i\omega t/2}\left[\left(\cos\frac{\Omega}{2}t+i\cos\alpha\sin\frac{\Omega}{2}t\right)\psi_1(0)\right.\\&\left.-i\sin\alpha\sin\frac{\Omega}{2}t\psi_2(0)\right];\\ \psi_2(t)&=e^{i\omega t/2}\left[-i\sin\alpha\sin\frac{\Omega}{2}t\psi_1(0)+\left(\cos\frac{\Omega}{2}t\right.\right.\\&\left.\left.-i\cos\alpha\sin\frac{\Omega}{2}t\right)\psi_2(0)\right].\end{aligned} \tag{47}$$

We consider an initial state $|\psi(0)\rangle$ in which the spin is oriented along the field H_0, i.e., we assume that $\psi_1(0)=1$, $\psi_2(0)=0$. Bearing in mind that

$$\sin\alpha=\frac{h}{\sqrt{h^2+(H_0+\omega)^2}}, \tag{48}$$

we can see that far from resonance, when $H_0+\omega\sim H_0\gg h$, we have $\sin\alpha\sim h/H_0$, and therefore $\alpha\to 0$. In this case, for the chosen initial conditions we have $\psi_2(t)\to 0$, and the trajectory will be concentrated mainly near the north pole of the sphere S^2 in Fig. 1 [We recall that to obtain the dependence $\mathbf{m}(t)$ it is necessary to use the relation (38)]. Near resonance, we have $\omega\approx\omega_0=-H_0$, and therefore $\sin\alpha\to 1$, i.e., $\alpha\to\pi/2$, and in accordance with the expression (45) the frequency will have the value $\Omega\approx h$, so that in this case we obtain from the expressions (47) the components

$$\psi_1(t)=e^{-i\omega t/2}\cos\frac{h}{2}t; \quad \psi_2(t)=-ie^{i\omega t/2}\sin\frac{h}{2}t. \tag{49}$$

Calculating the mean value of the spin in accordance with the expressions (38), we can show that in the case of resonance the dependence of the vector $\mathbf{m}$ on the time can be expressed in terms of the spherical angles θ and φ in the form (19), and $\theta=ht$, $\varphi=\omega_0 t-\pi/2$. Under conditions of magnetic resonance, we usually have $h\ll H_0$; it follows from this that the mean magnetic moment will rotate around the Z axis, and simultaneously the angle θ will slowly increase. The phase trajectory will then be a spiral with pitch (with respect to the angle θ) equal to the amplitude h of the rotating field.

1.4. Excitation of resonance by a solenoidal field

We now discuss the conditions of excitation of magnetic resonance by a solenoidal field, ignoring as before the interaction between the spins. We consider a system of N nuclear spins that have coordinates $\mathbf{r}_1$, $\mathbf{r}_2$,...,$\mathbf{r}_N$. In what follows, we shall assume that the coordinate origin is at the geometrical center of the system, i.e., that we have fulfillment of the condition

$$\sum_a \mathbf{r}_a = 0. \tag{50}$$

We assume that the spins interact with an inhomogeneous magnetic field $\mathbf{H}(\mathbf{r})$. The interaction energy can be expressed in the form

$$U = -\sum_a (\mathbf{m}_a \cdot \mathbf{H}(\mathbf{r}_a)). \tag{51}$$

We shall assume that the inhomogeneity of the field is weak, i.e., the scale of variation of the field is assumed to be large compared with the dimensions of the spin system (multipole approximation). In this case, the field $\mathbf{H}(\mathbf{r})$ can be expanded in a power series with respect to the coordinates in the neighborhood of the center of the system of spins ($\mathbf{r}=0$), and a restriction can be made to the first approximation in $\mathbf{r}$:

$$\mathbf{H}(\mathbf{r}_a) \approx \mathbf{H}(0) + (\mathbf{r}_a \nabla)\mathbf{H}|_{\mathbf{r}=0}. \tag{52}$$

We decompose the tensor of the magnetic field gradient $\nabla_i H_k$ into irreducible parts in accordance with the general expression of such a decomposition for a product of two vectors a_i and b_k:

$$a_i b_k = \tfrac{1}{3}(\mathbf{ab})\,\delta_{ik} + \tfrac{1}{2}\,e_{ikj}[\mathbf{ab}]_j + \{\mathbf{ab}\}_{ik}, \tag{53}$$

where the round and square brackets denote as usual the scalar and vector products of vectors, and the curly brackets are used to denote the tensor product, i.e., the irreducible second-rank tensor formed from the components a_i and b_k:

$$\{\mathbf{ab}\}_{ik} = \frac{1}{2}\left(a_i b_k + b_k a_i - \frac{2}{3}(\mathbf{ab})\,\delta_{ik}\right). \tag{54}$$

Applying these expressions to the tensor $\nabla_i H_k$ and making use of Maxwell's equation $\operatorname{div}\mathbf{H}=0$, we can write the decomposition (54) in the form

$$\mathbf{H}(\mathbf{r}_a) = \mathbf{H} + \tfrac{1}{2}[\mathbf{G}\mathbf{r}_a] + \mathbf{r}_a \cdot \{\nabla \mathbf{H}\}|_{\mathbf{r}=0}, \tag{55}$$

where $\mathbf{H}=\mathbf{H}(0)$, $\mathbf{G}=\operatorname{curl}\mathbf{H}|_{\mathbf{r}=0}$.

Thus, in this approximation each spin is subject to: 1) the homogeneous field $\mathbf{H}$; 2) an inhomogeneous field that, in its turn, consists of two parts—the solenoidal field $\frac{1}{2}[\mathbf{G}\mathbf{r}_a]$ and the symmetric gradient field $\mathbf{r}_a \cdot \{\nabla \mathbf{H}\}$. Each of these fields is produced by its "own" source: the homogeneous field by a cylindrical coil with a current, the solenoidal field by the displacement currents in the capacitor, and the gradient field by a system of coils. Therefore, we can consider each term in the expression (55) independently. In what follows, we shall be interested in only the homogeneous and solenoidal fields, i.e., we assume that $\{\nabla \mathbf{H}\}=0$.

Substituting the field $\mathbf{H}(\mathbf{r}_a)$ in the form (55) in the expression (51) for the energy, we obtain

$$U = -\sum_a (\mathbf{m}_a \mathbf{H}) - \frac{1}{2}\sum_a (\mathbf{m}_a[\mathbf{G}\mathbf{r}_a]). \tag{56}$$

This expression can also be represented in the form

$$U = -(\mathbf{MH}) - (\mathbf{TG}), \tag{57}$$

where we have introduced the magnetic and toroidal moments of the spin system:

$$\mathbf{M} = \sum_a \mathbf{m}_a; \quad \mathbf{T} = \tfrac{1}{2}\sum_a [\mathbf{r}_a \mathbf{m}_a]. \tag{58}$$

The moments $\mathbf{M}$ and $\mathbf{T}$ have the following geometrical meaning. The total magnetic moment $\mathbf{M}$ describes a homogeneous distribution of the spin orientations in space—it has its maximum value when all the spins are parallel. The toroidal moment is maximal when the spin distribution has a vortical configuration.[25]

Returning to the expression (56), we can see that in the solenoidal field each particle is acted on by its "own" field, which depends not only on the amplitude of the curl of the field $\mathbf{G}$ but also on the spatial positions of the nuclei. In the previous subsection, we considered excitation of magnetic resonance by a homogeneous alternating field $\mathbf{H}=\mathbf{H}_0+\mathbf{h}(t)$, and it was assumed that $\mathbf{h}(t)\perp\mathbf{H}_0$. Here, we consider the conditions of excitation of resonance by an alternating solenoidal field. In accordance with the expression (55), we now assume that each spin is acted on by a field $\mathbf{H}_a=\mathbf{H}_0+\mathbf{h}_a(t)$, with

$$\mathbf{h}_a(t) = \tfrac{1}{2}[\mathbf{g}(t)\mathbf{r}_a], \tag{59}$$

where $\mathbf{g}(t)$ is the alternating curl of a magnetic field that varies periodically in time:

$$\mathbf{g}(t) = \mathbf{g}\cos(\omega t + \delta). \tag{60}$$

This situation will arise, for example, in a parallel-plate capacitor, in which $\mathbf{g}(t) = (1/c)\dot{\mathbf{E}}(t)$. Returning to the problem of magnetic resonance of the complete system of N spins, we see that under these conditions the alternating field $\mathbf{h}_a(t)$ at the ath spin is, first, not perpendicular to $\mathbf{H}_0$ (i.e., there is a component parallel to $\mathbf{H}_0$) and, second, has different magnitude at different points of space. In a weak field ($h_a \ll H_0$) and near resonance we can, to a good approximation, take into account only one component of the alternating field, namely, the component that is perpendicular to $\mathbf{H}_0$ and rotates together with the spin. This result was obtained in Ref. 1 on the basis of perturbation theory for classical spins. Since in a solenoidal field the conditions of resonance in the usual formulation ($\mathbf{H}_0 \perp \mathbf{h}$) cannot in principle be satisfied for all spins at once, we shall show the validity of the result of Ref. 1 by a different method, Kapitsa's approximate method,[16,22] by solving the Schrödinger equation for a particle with spin 1/2. In what follows, these results can be applied to particles with arbitrary spin, as was shown in Sec. 1.2.

In the original laboratory coordinate system K_{lab}, the Hamiltonian of the ath spin (for simplicity, we shall henceforth omit the index a) has the form

$$\hat{\mathscr{H}} = -H_0 \hat{\mathscr{S}}_z - (\mathscr{h}\hat{\mathscr{S}})\cos(\omega t + \delta), \tag{61}$$

where we have written $\mathbf{h}=(1/2)[\mathbf{g}\mathbf{r}_a]$. Going over to the rotating coordinate system K_{rot} as described in the previous section, we obtain in this case the effective Hamiltonian in the form

$$\hat{\mathscr{H}}_{\text{rot}} = -(H_0+\omega)\hat{\mathscr{S}}_z - h_i U_{zik}(\omega t)\hat{\mathscr{S}}_k \cos(\omega t + \delta), \tag{62}$$

where $U_z(\omega t)$ is the 3×3 matrix determined by the expression (43); in the derivation of the expression (62), we have used the relation (42). Thus, in contrast to the expression

(41), in this case the Hamiltonian in the rotating coordinate system depends on the time. We shall assume that the frequency ω of the field oscillations is fairly high, i.e., ω is of the order of, or greater than, H_0. Using the explicit form of the transformation matrix (43), we represent the Hamiltonian (62) as a sum that consists of a constant and an oscillating part:

$$\hat{\mathscr{H}}_{\text{rot}} = -(\mathbf{H}_{\text{eff}} \cdot \hat{\mathscr{S}}) - \sum_n (\mathbf{h}_n(t) \cdot \hat{\mathscr{S}}), \tag{63}$$

where the index n takes two values, $n=1, 2$, and the fields $\mathbf{H}_{\text{eff}}$ and $\mathbf{h}_n(t)$ have the form

$$\begin{aligned} \mathbf{H}_{\text{eff}} &= (H_0+\omega)\mathbf{e}_z + (h_x \cos\delta + h_y \sin\delta)\mathbf{e}_x + (h_y \cos\delta \\ &\quad - h_x \sin\delta)\mathbf{e}_y; \\ \mathbf{h}_n(t) &= \mathbf{h}_n^{(c)} \cos(n\omega t) + \mathbf{h}_n^{(s)} \sin(n\omega t), \end{aligned} \tag{64}$$

in which we have introduced the amplitudes $\mathbf{h}_n^{(c)}$ and $\mathbf{h}_n^{(s)}$:

$$\begin{aligned} &\mathbf{h}_1^{(c)} = h_z \cos\delta \mathbf{e}_z; \mathbf{h}_1^{(s)} = -h_z \sin\delta \mathbf{e}_z; \\ &\mathbf{h}_2^{(c)} = \tfrac{1}{2}[(h_x \cos\delta - h_y \sin\delta)\mathbf{e}_x + (h_y \cos\delta + h_x \sin\delta)\mathbf{e}_y]; \\ &\mathbf{h}_2^{(s)} = \tfrac{1}{2}[-(h_x \sin\delta + h_y \cos\delta)\mathbf{e}_x + (h_x \cos\delta \\ &\quad - h_y \sin\delta)\mathbf{e}_y], \end{aligned} \tag{65}$$

where h_x, h_y, and h_z are the projections of the field $\mathbf{h}$ onto the axes of the system K_{lab}, and $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are unit vectors directed along the axes of the coordinate system K_{rot}. It can be seen from these expressions that the field $\mathbf{h}_1$ is directed along the Z axis and oscillates with frequency ω; the field $\mathbf{h}_2$ is perpendicular to $\mathbf{H}_0$ and varies with the doubled frequency 2ω.

We represent the solution of the Schrödinger equation $i|\dot{\psi}_{\text{rot}}\rangle = \hat{\mathscr{H}}_{\text{rot}}|\psi_{\text{rot}}\rangle$ as the sum of a constant part $|\psi_0\rangle$ and oscillating parts $|\psi_n\rangle$ in the form

$$|\psi_{\text{rot}}\rangle = |\psi_0\rangle + |\psi_1\rangle + |\psi_2\rangle \tag{66}$$

and, substituting it in the Schrödinger equation, we obtain

$$\begin{aligned} i|\dot{\psi}_0\rangle + i\sum_n |\dot{\psi}_n\rangle &= -(\mathbf{H}_{\text{eff}} \cdot \hat{\mathscr{S}})|\psi_0\rangle - \sum_n (\mathbf{h}_n \cdot \hat{\mathscr{S}})|\psi_0\rangle \\ &\quad - \sum_n (\mathbf{H}_{\text{eff}} \cdot \hat{\mathscr{S}})|\psi_n\rangle - \sum_{nn'} (\mathbf{h}_n \cdot \hat{\mathscr{S}})|\psi_{n'}\rangle. \end{aligned} \tag{67}$$

For the rapidly oscillating parts, we obtain in the first approximation (cf. Ref. 22, Sec. 30)

$$i|\dot{\psi}_n\rangle = -\sum_n (\mathbf{h}_n \cdot \hat{\mathscr{S}})|\psi_0\rangle; \quad n=1,2. \tag{68}$$

Assuming in the same approximation that in these equations $|\psi_0\rangle$ does not depend on the time, i.e., that $|\psi_0\rangle = \text{const}$, we find after integration that

$$|\psi_n\rangle = \frac{i}{n\omega}((\sin(n\omega t)\mathbf{h}_n^{(c)} - \cos(n\omega t)\mathbf{h}_n^{(s)}).\hat{\mathscr{S}})|\psi_0\rangle. \tag{69}$$

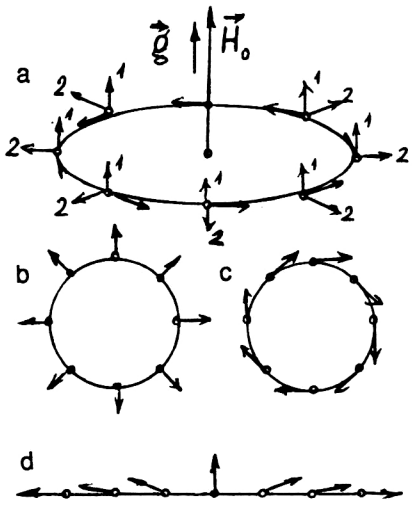


FIG. 2. System of spins in a solenoidal magnetic field. The curl of the field $\mathbf{g}$ is parallel to the homogeneous field $\mathbf{H}_0$.

Substituting the last expression in the equation and averaging over the time, we obtain

$$i|\dot{\psi}_0\rangle = -\left(\left(\mathbf{H}_{\text{eff}} + \sum_n [\mathbf{h}_n^{(c)}\mathbf{h}_n^{(s)}]\frac{1}{n\omega}\right)\hat{\mathscr{S}}\right)|\psi_0\rangle. \tag{70}$$

In the derivation of this relation we have used a well-known property of the Pauli matrices:

$$(\hat{\boldsymbol{\sigma}}\mathbf{a})(\hat{\boldsymbol{\sigma}}\mathbf{b}) = (\mathbf{ab}) + i(\hat{\boldsymbol{\sigma}}[\mathbf{ab}]). \tag{71}$$

Using the expressions (64), we can readily show that $[\mathbf{h}_1^{(c)}\mathbf{h}_1^{(s)}]=0$, and the vector product $[\mathbf{h}_2^{(c)}\mathbf{h}_2^{(s)}]$ is directed along the Z axis. Thus, we can say that under the influence of the alternating solenoidal field each spin moves on the average as if in the system K_{rot} an effective static field acted along the direction of the Z axis with strength $\mathbf{H}_0 + [\mathbf{h}_2^{(c)}\mathbf{h}_2^{(s)}]$, together with an effective rotating field perpendicular to it with amplitude equal to the projection of the vector $\mathbf{h} = (1/2)[\mathbf{g}\mathbf{r}_a]$ onto the XY plane of the laboratory coordinate system. The change of the longitudinal field changes the resonance frequency slightly, and for a weak solenoidal field it can be ignored. With regard to the amplitude and direction of the effective rotating field, as can be seen from the treatment in the previous subsection, they determine, respectively, the rate of spin reorientation in the vertical direction (i.e., the pitch of the spiral trajectory of the phase point) and the phase of the rotation around the static field $\mathbf{H}_0$.

We consider two examples of the behavior of a spin system in a pulsed solenoidal magnetic field of resonance frequency $\omega = -H_0$. We assume first that the curl of the field $\mathbf{g}$ is oriented along the Z axis parallel to $\mathbf{H}_0$ (Fig. 2). It follows from the expressions (59) and (60) that the lines of force of the solenoidal field are circles whose centers lie on the Z axis, which passes through the origin (the point $\mathbf{r}=0$). Suppose that before application of the field the spins were oriented along the direction of the field $\mathbf{H}_0$ (along the Z axis). Their initial positions are shown in the figure by the numbers 1. When the field is switched on, each spin in the rotating coordinate system K_{rot} will rotate around the local effective

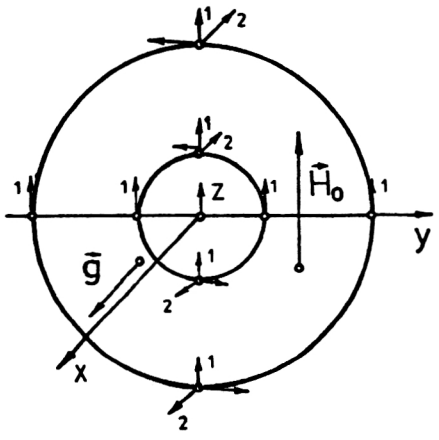


FIG. 3. The same as in Fig. 2. The curl of the field **g** is perpendicular to the homogeneous field $\mathbf{H}_0$.

field, which in the considered case is directed along the tangent to the circle. After a certain time, the spins lying on a given line of force will take the positions indicated in Fig. 2 by the numbers 2, i.e., the spin configuration will have a "fan" (or "petal") structure. With respect to the laboratory coordinate system, each spin is not only reoriented in the vertical direction but also rotates around the field $\mathbf{H}_0$. Therefore, in the system K_{lab} the fan structure of the spins will be periodically replaced by a vortical structure (Figs. 2b and 2c). At the same time, spins that are at different distances from the center of system (i.e., on circles of different radii) will be turned in the same time through different angles—the further from the center, the greater the solenoidal field, and the larger the rotation angle (Fig. 2d).

We now assume that the curl of **g** is oriented along the X axis, i.e., is perpendicular to the homogeneous field $\mathbf{H}_0$ (Fig. 3) and that the spins at the initial time are, as before, oriented along the Z axis, as is shown in the figure by the numbers 1. The circles lying in the YZ plane represent the lines of force of the solenoidal field. As can be seen from the figure, for spins that lie in the XY plane, the solenoidal field does not have components perpendicular to $\mathbf{H}_0$, and therefore the spins of the nuclei in this plane will not change their orientation under the action of the alternating field. At the same time, the spins lying above the XY plane (with positive Z coordinate) will rotate in the direction opposite to the rotation of the spins that lie below the XY plane (with negative Z coordinate). Therefore, the system of spins as a whole will be described by magnetic and toroidal moments, and with respect to the laboratory coordinate system the toroidal moment rotates in the XY plane with frequency ω_0.

1.5. Spin relaxation

For a complete description of the NMR phenomenon, it is necessary to take into account the magnetic relaxation of the nuclear spins. Indeed, in the absence of relaxation, the spin system initially absorbs energy of the alternating magnetic field but then returns it. The reason for this is the compactness of the phase space in which the spins move. This makes them very different from linear operators, for which the amplitude of the oscillations can increase unboundedly in resonance. By virtue of relaxation, a spin system loses part of its energy to "friction," and as a result a certain balance is established between the absorbed and the dissipated energy. The appearance of relaxation mechanisms gives valuable information about the internal processes taking place in a system.[1–6]

In this review, it is not our aim to consider relaxation processes in their entirety, and we restrict ourselves merely to a brief description of new approaches to the investigation of spin kinetics based on the concept of a coherent state. The problem of introducing dissipation into quantum equations is here solved especially transparently, since the parameters that describe the quantum states satisfy classical equations of motion. In addition, these methods make it possible to include readily new variables, which may include the toroidal moment in which we are interested.

We consider a quantum system that interacts with a "lattice" (as it is usual to call all nonspin degrees of freedom) that has only classical degrees of freedom. The states of the system as a whole are described by the set of variables $|\Psi\rangle$, $\langle\Psi|$, and X, where $|\Psi\rangle$ is the quantum state and the X are the classical variables. We note that the conjugate state $\langle\Psi|$ is also included in the set of variables, since in the general case the vector $|\Psi\rangle$ has complex components. We introduce the classical Hamiltonian, which depends on all these variables:

$$\mathscr{H}(|\Psi\rangle,\langle\Psi|,X)=\langle\Psi|\hat{\mathscr{H}}(X)|\Psi\rangle+V(X), \tag{72}$$

where $\hat{\mathscr{H}}(X)$ is the quantum Hamiltonian operator and $V(X)$ is the energy of the classical degrees of freedom. In principle, in this expression we could take into account in addition to the coordinates X their conjugate momenta, but for simplicity we assume that the classical motion is strongly damped, the friction is large, and inertial effects can be ignored. In addition, we assume that random forces (thermal fluctuations) act on the classical system. As a result, the equation of motion for the classical variables can be written in the form

$$\dot{X}=-\frac{1}{\tau}\frac{\partial}{\partial X}\beta\mathscr{H}+K(t), \tag{73}$$

where $\beta=1/kT$, and the product τkT is the coefficient of friction, in which we have separated for convenience the relaxation time τ. The random forces are assumed to be δ-correlated in time (white noise). In principle, by adding new variables to the set of state parameters we could take into account not only white noise but also "colored" noise.

We can arrive at the quantum Schrödinger equation by means of the Hamiltonian (72). It is obtained as a "classical" Hamiltonian equation by differentiating the function (72) with respect to the conjugate variables:

$$|\dot{\Psi}\rangle=\frac{1}{i\hbar}\frac{\partial\mathscr{H}}{\partial\langle\Psi|};\quad \langle\dot{\Psi}|=-\frac{1}{i\hbar}\frac{\partial\mathscr{S}}{\partial|\Psi\rangle}. \tag{74}$$

Since random forces are present in (73), all the state variables will be random functions of the time. Therefore, to obtain a probabilistic description of the system (spins plus lattice), we introduce a distribution function

$$W=W(|\Psi\rangle,\langle\Psi|,X,t). \tag{75}$$

By means of the general methods of the theory of random processes,[30] we can obtain from Eqs. (73) and (74) a kinetic Fokker–Planck equation for the distribution function W (Refs. 27–29):

$$\frac{\partial W}{\partial t}+\frac{\partial|\dot{\Psi}\rangle W}{\partial|\Psi\rangle}+\frac{\partial\langle\dot{\Psi}|W}{\partial\langle\Psi|}+\frac{\partial}{\partial X}\dot{X}W=0, \tag{76}$$

which has the form of the ordinary continuity equation $\partial W/\partial t+(\partial/\partial y)\dot{y}W=0$. To obtain a closed equation, we must substitute in this expression the derivatives (73) and (74) and, in addition, make the formal substitution

$$K(t)=-\frac{1}{\tau}\frac{\partial}{\partial X}\ln W. \tag{77}$$

Knowing the distribution function W, we can average any function of the variables $|\Psi\rangle$, $\langle\Psi|$, and X. For example, by averaging the density matrix of the pure state $|\Psi\rangle\langle\Psi|$, we obtain the operator

$$\hat{\rho}(X,t)=\int|\Psi\rangle\langle\Psi|W(|\Psi\rangle,\langle X,t)d|\Psi\rangle d\langle\Psi|, \tag{78}$$

which is called the "not completely averaged density matrix" and for which by means of the kinetic equation (76) we can obtain the so-called stochastic Liouville equation

$$\frac{\partial}{\partial t}\hat{\rho}(X,t)=-i\omega[\hat{\mathscr{H}}(X),\hat{\rho}(X,t)]+\frac{1}{\tau}\hat{\mathscr{L}}_X\hat{\rho}(X,t). \tag{79}$$

This equation was first obtained in Ref. 31 by a different method—by reduction of the dynamical equations in the consideration of slow motions of the classical system (in the limit $\omega\tau\gg1$). In the presented derivation, we do not take into account only the back reaction of the spin system on the lattice (this is justified in the high-temperature approximation), and no restrictions on the time intervals are assumed. It can be shown[27] that in the limit of fast motions, $\omega\tau\ll1$, the well-known Bloch–Redfield equation[1–6] can be obtained from Eq. (79).

As an example, we consider the application of this general theory to spin relaxation.[28] As was shown above, quantum states can be described by a unit vector $\mathbf{m}$, and the Schrödinger equation is equivalent to the spin-precession equation $\dot{\mathbf{m}}=[\mathbf{m}\times\mathbf{H}]$. We assume that the classical subsystem creates at a nucleus a fluctuating magnetic field

$$\dot{\mathbf{m}}=[\mathbf{m}\times(\mathbf{H}+H_1\mathbf{e})], \tag{80}$$

where $\mathbf{e}$ is a classical unit vector that satisfies the equation of motion

$$\dot{\mathbf{e}}=[\boldsymbol{\Omega}\mathbf{e}];\quad \boldsymbol{\Omega}=-\frac{1}{\tau}\hat{\mathscr{R}}\beta V(\mathbf{e})+\mathbf{K}(t), \tag{81}$$

in which Ω is the angular velocity of the rotation of the unit vector $\mathbf{e}$, $V(\mathbf{e})$ is the classical potential, $\mathbf{K}(t)$ is the random moment of the forces, and $\hat{\mathscr{R}}=[\mathbf{e}(\partial/\partial\mathbf{e})]$ is the operator of an infinitesimal rotation of the vector $\mathbf{e}$.

From Eqs. (80) and (81) we readily obtain the Fokker–Planck equation for the distribution function $W(\mathbf{m},\mathbf{e},t)$:

$$\frac{\partial W}{\partial t}-\frac{1}{\tau}\hat{\mathscr{R}}(W\hat{\mathscr{R}}\beta V+\hat{\mathscr{R}}W)-((\mathbf{H}_0+H_1\mathbf{e})\hat{\mathscr{L}})W=0, \tag{82}$$

where $\hat{\mathscr{L}}=\mathbf{m}(\partial/\partial\mathbf{m})$. Multiplying this equation by $\mathbf{m}$ and integrating with respect to the variables $\mathbf{m}$ and $\mathbf{e}$, we obtain the equation for the moment $\langle\mathbf{m}\rangle=\mathbf{M}$:

$$\dot{\mathbf{M}}=[\mathbf{MH}]+H_1\langle[\mathbf{me}]\rangle, \tag{83}$$

which contains the moment of higher order $\langle[\mathbf{me}]\rangle$. The system of equations for the moments can be decoupled by means of the usual variational procedure of kinetic theory. We shall seek the distribution function in the form

$$W=W_0(1+(\mathbf{p}(t)\mathbf{m})), \tag{84}$$

where $W_0=c\exp(-\beta V)$ is the equilibrium distribution function, and $\mathbf{p}(t)$ is a variational parameter that is related to $\langle\mathbf{m}\rangle$ by means of the equilibrium moments. In the limit of fast relaxation, the equation for $\mathbf{M}$ reduces to the Bloch equation

$$\dot{\mathbf{M}}=[\mathbf{MH}]-\mathbf{k}\frac{M_z-M_{z0}}{T_1}-\frac{1}{T_2}\mathbf{M}_\perp, \tag{85}$$

in which the relaxation times T_1 and T_2 depend on the field and temperature,[29] and this dependence can be expressed explicitly in terms of the equilibrium mean values.

1.6. Threshold of the excitation field

Dissipative processes have an appreciable effect on the dynamics of a spin system and are the reason for broadening of the magnetic-resonance line and shift of the resonance frequencies.[1–8] In addition, it can be shown that in the presence of dissipation excitation of magnetic resonance is possible only when the amplitude of the alternating field h exceeds a certain threshold value h_c. This question has not been sufficiently discussed in the literature. At the same time, the estimate of the threshold field is important for elucidating the general conditions of observation of the toroidal response of a spin system, since in the case of excitation of resonance by a solenoidal magnetic field there exist physical restrictions on the amplitude of the local alternating field h_{loc} at a nucleus. For example, in an insulating sample a solenoidal field can be produced only by displacement currents induced by an alternating electric field $E(t)$ that is bounded in amplitude, in particular by the field of electric breakdown of the insulator. Obviously, if $h_{\text{loc}}\sim\omega E/c$ is less than the threshold field (i.e., $h_{\text{loc}}<h_c$), observation of toroidal response to a solenoidal field is altogether impossible.

For our purposes, it is convenient to take into account the dissipation in the equation of motion of the spin in the form of the well-known relaxation term of Landau and Lifshitz,

$$\dot{\mathbf{m}}=[\mathbf{mH}]-\alpha[\mathbf{m}[\mathbf{mH}]], \tag{86}$$

which describes relaxation of the spin to the equilibrium value determined by the direction of the field $\mathbf{H}$. In the case of weak deviation of the magnetic moment $\mathbf{m}$ from the equilibrium value $\mathbf{H}/H$, Eq. (86) goes over, in the linear approximation in the deviation $\delta\mathbf{m}$ from equilibrium, into the Bloch

equation (85): $\delta\dot{\mathbf{m}} \approx [\delta\mathbf{m}\mathbf{H}] - \alpha H \delta\mathbf{m}_\perp$, from which it can be seen that the parameter α is proportional to the reciprocal of the transverse relaxation time T_2:

$$\alpha = 1/T_2 H. \tag{87}$$

To solve Eq. (86), it is convenient to use stereographic projection of the points of the sphere S^2 (which, we recall, plays the role of the phase space of the classical spin) from its south pole onto the plane of the complex variable ζ, which can be expressed in terms of the spherical angles θ and φ of the vector $\mathbf{m}$ (19) in the form $\zeta = -\tan(\theta/2)e^{-i\varphi}$. Going over to cyclic components of the vectors $\mathbf{m}$ and $\mathbf{H}$,

$$H_0 = H_z; \quad H_\pm = H_x \pm i H_y; \quad z = m_z; \quad x = m_x - i m_y, \tag{88}$$

we first rewrite the equation of motion (86) in these components:

$$\begin{aligned} \dot{x} &= x(i+\alpha z)H_0 + \tfrac{1}{2}(\alpha - 2iz + \alpha z^2)H_- - \tfrac{1}{2}\alpha x^2 H_+; \\ \dot{z} &= \alpha(1-z^2)H_0 + \tfrac{1}{2}x^*(i-\alpha z)H_- - \tfrac{1}{2}x(i+\alpha z)H_+. \end{aligned} \tag{89}$$

Bearing in mind that the complex variable ζ can be expressed in terms of x and z in the form

$$\zeta = -\frac{x}{1+z} = -\frac{1-z}{x^*}, \tag{90}$$

we obtain after simple manipulations the equation of motion of the spin in the form

$$\frac{i}{1+i\alpha}\dot{\zeta} = -\tfrac{1}{2}H_- - \zeta H_0 + \tfrac{1}{2}\zeta^2 H_+. \tag{91}$$

Thus, in these variables the role of the dissipation described by the nonlinear relaxation term of Landau and Lifshitz reduces to a renormalization of the time, $t \to (1+i\alpha)t$, as is discussed in detail in Ref. 33. In a static field H directed along the Z axis (i.e., under the condition $H_+ = H_- = 0$) Eq. (91) becomes linear, and its solution has the form $\zeta = \zeta_0 \exp[(i-\alpha)H_0 t]$. This means that in the plane of the complex variable ζ the phase point moves along a spiral, approaching the origin $\zeta = 0$, which corresponds to the equilibrium position, while the phase point on the sphere S^2 will approach the north pole, which corresponds to its equilibrium position.

In the general case, Eq. (91) is a nonlinear Riccati equation, and its solution cannot be found in quadratures.[34,35] An important exception is the case when the magnetic field is the sum of a static field H_0 and a rotating field $\mathbf{h}$ (39) perpendicular to it, i.e., $H_\pm = h e^{\pm i\omega t}$, $H_0 = \text{const}$. We introduce the new variable v, which is related to ζ by the equation

$$\zeta = \frac{2i}{H_+(1+i\alpha)}\frac{\dot{v}}{v}. \tag{92}$$

For this variable, the Riccati equation is transformed into the linear second-order equation

$$\ddot{v} - (iH_0 + \dot{H}_+/H_+)(1+i\alpha)\dot{v} + \tfrac{1}{4}H_- H_+ (1+i\alpha)^2 v = 0, \tag{93}$$

which for a rotating field becomes an equation with constant coefficients:

$$\ddot{v} - i(H_0(1+i\alpha) + \omega)\dot{v} + \tfrac{1}{4}h^2(1+i\alpha)^2 v = 0. \tag{94}$$

Far from the resonance region, i.e., when ω differs appreciably from H_0, the effect of the weak alternating field $h \ll H_0$ is slight, since it occurs quadratically in the equation. We assume that the frequency of the alternating field is in exact resonance, i.e., $\omega = -H_0$. In this case, the second term in Eq. (94) takes the form $\alpha H_0 \dot{v}$. We seek a solution of the equation in the form $v \sim \exp(i\lambda t)$. For the decay rate λ we obtain the characteristic equation

$$\lambda^2 - i\alpha H_0 \lambda - \tfrac{1}{4}h^2(1+i\alpha)^2 = 0, \tag{95}$$

which has the roots

$$\lambda_{1,2} = \frac{1}{2}H_0\left(i\alpha \pm \sqrt{\frac{h^2}{H_0^2}(1+i\alpha)^2 - \alpha^2}\right). \tag{96}$$

In the absence of friction ($\alpha = 0$), the roots of the characteristic equation are real, $\lambda_{1,2} = \pm h/2$, corresponding to the case of resonant effect of the alternating field on the spin system, as discussed in Sec. 1.3. Taking the parameter α to be small compared with unity ($\alpha \ll 1$), and assuming that α and h/H_0 have the same order of smallness, we can represent the roots of the equation in the form

$$\lambda_{1,2} = \frac{1}{2}H_0\alpha\left(i \pm \sqrt{\frac{h^2}{H_0^2\alpha^2} - 1}\right). \tag{97}$$

Thus, if h is less than $h_c = \alpha H_0$, the decay rates will be purely imaginary. Under the condition $h < h_c$, the solution of the equation of motion will have the nature of pure damping (relaxation), i.e., for arbitrarily small amplitude of the alternating field, excitation of resonance is impossible. Going over to dimensional variables and taking into account the relation (87) between the parameter α and the transverse relaxation time, we finally obtain in this approximation the condition for excitation of resonance in the form

$$h > 1/\gamma T_2. \tag{98}$$

The relations (97) obtained for the decay rates also make it possible to analyze the solutions for other ratios of the parameter α and h/H_0.

Concluding this section, we discuss briefly the important problem of the connection between the dissipative classical equation of motion (86) and the quantum Schrödinger equation. Since Eq. (86) preserves the normalization of the vector $\mathbf{m}$, a dissipative system has the same phase space as the system without dissipation, and we can as before associate the vector $\mathbf{m}$ with the quantum coherent state $|\mathbf{m}\rangle$, as was described above in Sec. 1.2. There is then the question of what quantum Hamiltonian controls the motion of this system. The answer is most readily obtained on the basis of the semiclassical theory of Jaynes.[36] In this theory, friction is taken into account by adding to the Hamiltonian terms that take into account the self-interaction of the system that arises on account of the loss of energy to radiation. Obviously, this approach is in agreement with the phenomenological theory of Landau and Lifshitz. In the considered case, we can associate the quantum system with a classical system with Hamiltonian $\hat{\mathscr{H}}$ equal to

$$\hat{\mathscr{H}} = -(\hat{\mathscr{S}}(\mathbf{H} - \alpha[\mathbf{mH}])), \tag{99}$$

where $\mathbf{m}$ must be interpreted as the mean value of the moment, $\mathbf{m} = \langle\Psi|\hat{\mathscr{S}}|\Psi\rangle$. Thus, the Schrödinger equation is a nonlinear equation for the state vector $|\Psi\rangle$.

2. INTERACTING SPINS

In contemporary methods of observing nuclear magnetic-resonance signals, some sequence of pulses of an alternating magnetic field is used to bring the system of spins into a certain initial state. After this, the motion of the spins in the homogeneous field commences, the observation of which gives the free induction signal. The weak interaction of the spins with each other changes their states relatively slowly, and therefore during the application of the short pulses of the alternating field it can be ignored, as is usually done in a theoretical treatment.[1–5] However, subsequently, in the process of "free" precession of the spins, the interaction can no longer be ignored, since for sufficiently large times it can be manifested significantly.

At the qualitative level, the role of the spin–spin interaction can be understood by considering the behavior of the spin system after application of a so-called 90-degree pulse of the alternating field. Suppose, for example, that before application of the pulse the spin system was in thermal equilibrium, so that all the spins were on the average oriented along the field $\mathbf{H}_0$, i.e. directed toward the north pole of the phase sphere S^2 in Fig. 1. After the superposition of a homogeneous rotating field of resonance frequency $\omega = \gamma H$ the rotation angles θ of the precession cones (Fig. 1) of all the spins will increase linearly with the time, as was shown in Sec. 1.3. We shall assume that the pulse duration is such that the angle θ is changed from 0 to 90°. As a result, after the pulse the spins will precess in the plane perpendicular to the field $\mathbf{H}_0$, and their total magnetic moment $\mathbf{M}$ will also lie in this plane.

With the passage of time, the matched (coherent) precession of the spins is destroyed, since the spin–spin interaction will give rise to dephasing of their rotation. (Here, we ignore dissipative processes, which can also cause dephasing.) If it is borne in mind that the nuclear spins are distributed in some definite manner in space (i.e. speaking simply, they are at different points), we may conclude that because of the spin–spin interaction the initial (produced immediately after the pulse) uniform distribution of their orientations is gradually replaced by some different distributions, which is spatially inhomogeneous. As is well known,[25] a distribution of dipoles is described by multipole moments, one of which, corresponding to a uniform distribution, is the magnetic moment $\mathbf{M}$, while the following ones (with respect to the multipolarity parameter) are the toroidal moment $\mathbf{T}$, the quadrupole moment, etc.

Using the language of multipole moments, we can describe the picture of the behavior of the spins considered above in the following manner. Directly after the pulse, the system has the maximum magnetic moment, which with the passage of time decreases, while the other multipole moments will increase. It is obvious that observation of the higher multipoles will give valuable information about the behavior and structure of the spin system. However, in magnetic resonance they are usually not taken into account. In this section, we consider in detail the role of the interaction between the spins in the formation of the multipole structure. We shall devote our main attention to the conditions of formation of the toroidal moment, which is closest to the magnetic moment as regards the conditions of observations.

As will be shown in what follows, the dynamics of the system of interacting spins is determined by three main factors: 1) the initial states; 2) the symmetry of the disposition of the nuclei; 3) the orientation of the magnetic field relative to the system. Thus, the case considered above of excitation of the system by a 90-degree pulse of a homogeneous field $\mathbf{h}(t)$ leads to an initial state with maximum magnetic moment $\mathbf{M}$. If we act on the system with a pulse of the solenoidal field $\mathbf{g}(t)$, then the spin system will have at the initial time the maximum toroidal moment. However, for a certain geometry of the system there can also be "crossed" effects—an initial toroidal moment can be produced by the action of a homogeneous field, and so can a magnetic moment by the action of a solenoidal field. As we shall see, the very existence of crossed effects makes it possible to draw important conclusions about the symmetry of the system. We also discuss here the connection between the classical and quantum descriptions of a system of interacting spins.

2.1. The approximation of classical spins

We consider a system of N interacting "classical" spins $\mathbf{m}_1, \mathbf{m}_2, \ldots, \mathbf{m}_N$ at the spatial points $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$. In what follows, it is assumed that the origin is chosen at the geometrical center of the system, i.e., the condition (50) is satisfied. We assumed that the spins are in a strong homogeneous magnetic field and interact weakly with each other. The energy of the spin system has the form

$$U = -\left(\mathbf{H}\cdot\sum_a \mathbf{m}_a\right) - \frac{1}{2}\sum_a{\sum_b}' (\mathbf{m}_a \cdot A(\mathbf{r}_{ab}) \cdot \mathbf{m}_b), \tag{100}$$

where $A(\mathbf{r})$ is the second-rank tensor

$$A_{ik}(\mathbf{r}) = \frac{3x_i x_k - r^2\delta_{ik}}{r^5}. \tag{101}$$

The prime on the sum over b means that the term with $b = a$ is excluded from the sum. In the second term in the expression (100) we have used an abbreviated notation for the multiplication of two vectors by a tensor, which we shall also use in what follows:

$$(\mathbf{a}\cdot A\cdot\mathbf{b}) = a_i A_{ik} b_k. \tag{102}$$

The same rule will also be used for an abbreviated notation for the multiplication of a tensor by a vector:

$$(A\cdot\mathbf{b})_i = A_{ik}b_k; \quad (\mathbf{b}\cdot A)_i = b_k A_{ki}. \tag{103}$$

The vector $[(A\cdot\mathbf{b})$ or $(\mathbf{b}\cdot A)]$ obtained as a result of such a multiplication will be regarded in what follows as an ordinary vector, and therefore it can occur in expressions of the form $[\mathbf{a}(A\cdot\mathbf{b})]$ or $[\mathbf{a}(\mathbf{b}\cdot A)]$, where it is multiplied vectorially by a.

Differentiating the energy (100) with respect to $\mathbf{m}_a$ with allowance for the constancy of the length of this vector [cf. Eq. (4)], we obtain the equation of motion of the ath spin in the form

$$\dot{\mathbf{m}}_a=[\mathbf{m}_a\mathbf{H}]+\left[\mathbf{m}_a\sum_b{}'(A(\mathbf{r}_{ab})\cdot\mathbf{m}_b)\right]. \tag{104}$$

It is a nonlinear system of equations. In the zeroth approximation in the interaction, it describes N spins that independently precess around the direction of the magnetic field H with frequency $-\gamma H$. If the interaction is "switched on," the following effects can be expected. First, each spin will produce at the neighboring spins an alternating magnetic field of the resonance frequency, and this will give rise to resonant energy transfer from one spin to another. This effect is similar to the oscillations of coupled oscillators with nearly equal frequencies (cf. the description of the oscillations of sympathetic pendulums in Ref. 32, Sec. 20). Such "internal resonances" can be taken into account already in the linear approximation. Second, because the interaction is nonlinear, there may also be oscillations at multiple frequencies, and also a dependence of the precession frequency on the energy. Since the interaction between the spins is weak, the nonlinear effects will also be small, and in what follows we therefore restrict ourselves mainly to the linear approximation. Third, it should be noted that the potential of the dipole interaction itself has several minima, each of which corresponds to a certain fixed orientation of the spins. In a weak external field H (of the order of, or less than, the interaction energy), one could observe a qualitative rearrangement of the motion of the spin system, depending on the strength and orientation of the external fields. However, since in NMR the external magnetic field is as a rule very strong (usually, the spin interaction energy is 2–3 orders of magnitude smaller than the energy of their interaction with the homogeneous field), all such "remagnetization" effects can certainly be ignored.

To linearize the equations of motion, we must first find the equilibrium orientations of the spins $\mathbf{m}_{10}, \mathbf{m}_{20},...,\mathbf{m}_{N0}$ for which the potential U has a minimum. We rewrite the equations of motion (104) in the form

$$\dot{\mathbf{m}}_a=[\mathbf{m}_a\mathbf{H}_a]+\left[\mathbf{m}_a\sum_b{}'(A(\mathbf{r}_{ab})\cdot(\mathbf{m}_b-\mathbf{m}_{b0}))\right], \tag{105}$$

where we have introduced

$$\mathbf{H}_a=\mathbf{H}+\sum_b{}'(A(\mathbf{r}_{ab})\cdot\mathbf{m}_{b0}), \tag{106}$$

which is the equilibrium field that acts on the ath spin. In accordance with the choice of the equilibrium values $\mathbf{m}_{a0}$, they must make the right-hand side of Eq. (105) vanish; this will be possible if the vectors $\mathbf{m}_{a0}$ and $\mathbf{H}_a$ are parallel. Remembering that the vector $\mathbf{m}_{a0}$ has unit length, we can write the equation for it in the form $\mathbf{m}_{a0}=\mathbf{H}_a/H_a$. This equation can be readily solved by iteration. In the first approximation $\mathbf{m}_{a0}=\mathbf{H}/H$, and in the approximation linear in the interaction we obtain

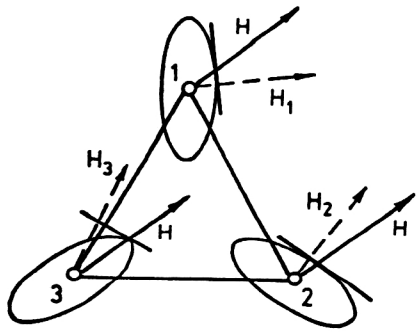


FIG. 4. Scheme of determination of effective magnetic fields at nuclei by means of Poinsot's construction.

$$\mathbf{m}_{a0}\approx\mathbf{H}_1-[\mathbf{H}_1[\mathbf{H}_1\mathbf{A}_a]];\quad \mathbf{H}_1=\mathbf{H}/H;$$

$$\mathbf{A}_a=\sum_b{}'(A(\mathbf{r}_{ab})\cdot\mathbf{H}_1). \tag{107}$$

Using Eqs. (106) and (107), we represent the relation between the fields $\mathbf{H}$ and $\mathbf{H}_a$ in the same approximation in the form

$$\mathbf{H}_a=(\beta^{(a)}\cdot\mathbf{H});\quad \beta_{ik}^{(a)}=\delta_{ik}+\frac{1}{H}\sum_b{}'A_{ik}(\mathbf{r}_{ab}), \tag{108}$$

where we have introduced the "polarizability tensor" $\beta^{(a)}$, which is entirely determined by the geometrical arrangement of the spins. This expression makes it possible to find the orientation of the vectors $\mathbf{H}_a$ from the given orientation of the external field by means of the well-known construction of Poinsot (see, for example, Ref. 32, Sec. 24). Around each nucleus, as around a center, we construct the Poinsot ellipsoid determined by the equation $(\mathbf{r}\cdot\beta^{(a)}\cdot\mathbf{r})=1$ (Fig. 4). If from the center of the nucleus we now describe the vector $\mathbf{H}$ and at the point of its intersection with the ellipsoid construct the plane tangent to the surface of the ellipsoid, then, as follows from Eq. (108), the vector $\mathbf{H}_a$ will be directed along the normal to this plane. A change in the spatial arrangement of the nuclei gives rise to changes of the "polarization tensors" $\beta^{(a)}$, and this is reflected in the orientation and shape of the Poinsot ellipsoids.

It follows from the equations of motion (105) that the influence of the interaction reduces, first, to a renormalization of the magnetic field that acts on each particle ($\mathbf{H}\to\mathbf{H}_a$) and, second, to a "mixing" of the states of the particles, for which the second term in Eq. (105) is responsible. In the case of a small deviation of $\mathbf{m}_a$ from $\mathbf{m}_{a0}$, Eq. (105) can be linearized with respect to the small differences $\mathbf{n}_a=\mathbf{m}_a-\mathbf{m}_{a0}$, for which, using (105), we obtain linear equations of the form

$$\dot{\mathbf{n}}_a=[\mathbf{n}_a\mathbf{H}_a]+\left[\mathbf{m}_{a0}\sum_b{}'(A(\mathbf{r}_{ab})\cdot\mathbf{n}_b)\right]. \tag{109}$$

Multiplying this equation scalarly by $\mathbf{m}_{a0}$, we can readily show that the components of the vectors $\mathbf{n}_a$ longitudinal with respect to the field $\mathbf{H}_a$ do not vary in time, and, taking into

account the normalization condition $|\mathbf{m}_a|=1$, we can assume in accordance with the adopted linear approximation that these components are simply equal to zero. Thus, each vector $\mathbf{n}_a$ varies, though remaining in the plane perpendicular to "its" field $\mathbf{H}_a$.

To solve the system of equations (109), we introduce at each (ath) nucleus its own coordinate system K_a, for which the Z_a axis is directed along the field $\mathbf{H}_a$. We decompose the vector $\mathbf{n}_a$ with respect to the basis vectors $\mathbf{e}_{ax}$ and $\mathbf{e}_{ay}$, which are directed along the axes of the system K_a: $\mathbf{n}_a=x_a\mathbf{e}_{ax}+y_a\mathbf{e}_{ay}$. For the components x_a and y_a, we obtain by means of (109) the system of equations

$$\begin{cases} \dot{x}_a=y_aH_a-\sum_b{}'(A_{yx}(\mathbf{r}_{ab})x_b+A_{yy}(\mathbf{r}_{ab})y_b); \\ \dot{y}_a=-x_aH_a+\sum_b{}'(A_{xx}(\mathbf{r}_{ab})x_b+A_{xy}(\mathbf{r}_{ab})y_b). \end{cases} \tag{110}$$

In the calculation of the components of the tensor $A(\mathbf{r}_{ab})$ of the form $(\mathbf{e}_{ai}\cdot A(\mathbf{r}_{ab})\cdot\mathbf{e}_{bk})$, we have replaced approximately the basis vectors $\mathbf{e}_{ai}$ and $\mathbf{e}_{bk}$ of the systems K_a and K_b by the basis vectors $\mathbf{e}_i$ of the laboratory coordinate system K_{lab}, for which the Z axis is directed along the external field $\mathbf{H}$. Eliminating the variable y_a from the system of equations (110), we obtain for the variable x_a an equation of the form

$$\ddot{x}_a+H_a^2x_a+H\sum_b{}'A_{zz}(\mathbf{r}_{ab})x_b=0, \tag{111}$$

and the coordinates y_a can be found from the known x_a and $\dot{x}_a$ by means of the relation

$$y_a=\frac{1}{H}\left\{\left(2-\frac{H_a}{H}\right)\dot{x}_a+\sum_b{}'\left[A_{yx}(\mathbf{r}_{ab})\frac{\dot{x}_b}{H}+A_{xx}(\mathbf{r}_{ab})x_b\right]\right\}. \tag{112}$$

Thus, as can be seen from Eq. (111), in the linear approximation the system of N spins can be regarded as an oscillatory system with N degrees of freedom. Since the fields H_a differ little from H, we are dealing here with the case of N weakly coupled one-dimensional oscillators with nearly equal frequencies (cf. Ref. 32, Sec. 20). As usual, the solution of the system of equations (111) (see, for example, Ref. 22, Sec. 23) can be expressed in the form of expansions with respect to the normal coordinates. Taking into account the relation (112), we finally obtain

$$x_a=\sum_\gamma u_{a\gamma}Q_\gamma;\quad y_a=\sum_\gamma v_{a\gamma}Q_\gamma;\quad Q_\gamma=c_\gamma e^{i\omega_\gamma t};$$

$$\gamma=1,2,\ldots,N, \tag{113}$$

where the Q_γ are the so-called normal coordinates, and the complex coefficients c_γ must be determined from the initial conditions. With regard to the eigenfrequencies ω_γ of the normal oscillations and the matrix elements $u_{a\gamma}$, they can be expressed in terms of the coefficients in Eq. (111).

By means of simple manipulations, we can also represent our solution (113) of Eq. (109) in the form

$$\mathbf{n}_a=\sum_\gamma[\mathbf{u}_{a\gamma}\cos(\omega_\gamma t+\beta_\gamma)+\mathbf{v}_{a\gamma}\sin(\omega_\gamma t+\beta_\gamma)], \tag{114}$$

where $\mathbf{u}_{a\gamma}$ and $\mathbf{v}_{a\gamma}$ are mutually perpendicular real vectors, and the β_γ are the initial phases. Thus, if only one normal oscillation is excited [one term in the sum over γ in Eq. (114)], then the phase trajectories of the vectors $\mathbf{n}_a$ are ellipses lying in the planes perpendicular to the vectors $\mathbf{H}_a$. At the same time, all the spins rotate coherently with a fixed relative phase shift. If, however, at least two normal modes are simultaneously excited, then the rotations of the spins will have the nature of beats, for which the energy is periodically transferred from one spin to another and back, and this leads to dephasing of the precession of the spins.

We consider as an example a system of two spins. In accordance with the general expression (100), the interaction energy of the spins has the form

$$U=-(\mathbf{m}_1\mathbf{H})-(\mathbf{m}_2\mathbf{H})-(\mathbf{m}_1\cdot A\cdot\mathbf{m}_2), \tag{115}$$

from which we obtain the system of equations for the spin vectors $\mathbf{m}_1$ and $\mathbf{m}_2$:

$$\begin{cases} \dot{\mathbf{m}}_1=[\mathbf{m}_1\mathbf{H}]+[\mathbf{m}_1(A\cdot\mathbf{m}_2)]; \\ \dot{\mathbf{m}}_2=[\mathbf{m}_2\mathbf{H}]+[\mathbf{m}_2(A\cdot\mathbf{m}_1)]. \end{cases} \tag{116}$$

In accordance with (107), in equilibrium the spins are parallel,

$$\mathbf{m}_0=\mathbf{m}_{10}=\mathbf{m}_{20}\approx\mathbf{H}_1-[\mathbf{H}_1[\mathbf{H}_1(A\cdot\mathbf{H}_1)]], \tag{117}$$

and the effective fields that act on them are also parallel and equal: $\mathbf{H}_a=\mathbf{H}+(A\cdot\mathbf{H}_1)\equiv\mathbf{H}_e$, where $a=1, 2$.

In the linear approximation in the deviation from the equilibrium values, the system of equations (116) can be represented in the form

$$\begin{cases} \dot{\mathbf{n}}_1=[\mathbf{n}_1\mathbf{H}_e]+[\mathbf{m}_0(A\cdot\mathbf{n}_2)]; \\ \dot{\mathbf{n}}_2=[\mathbf{n}_2\mathbf{H}_e]+[\mathbf{m}_0(A\cdot\mathbf{n}_1)]. \end{cases} \tag{118}$$

Expressing these equations in the variables x_a and y_a, as described above, we can represent the solution of these equations in the form (113), the frequencies of the normal oscillations and the normal coordinates being determined by the expressions

$$\omega_{1,2}=H+A_{zz}\pm\tfrac{1}{2}A_{zz};\quad Q_{1,2}=x_1\pm x_2. \tag{119}$$

A more transparent picture of the motion of two spins can be obtained directly from Eqs. (118). Adding and subtracting these equations from each other, we can obtain two uncoupled equations for the variables $\mathbf{n}_\pm=\mathbf{n}_1\pm\mathbf{n}_2$:

$$\dot{\mathbf{n}}_\pm=[\mathbf{n}\pm\mathbf{H}_e]\pm[\mathbf{m}_0(A\cdot\mathbf{n}_\pm)]. \tag{120}$$

It follows from this that if at the initial time the spins were parallel [i.e., $\mathbf{n}_-(0)=0$], then they will also remain parallel at all subsequent times. Similarly, the relative phase remains fixed if only one harmonic $\mathbf{n}_-$ is excited and at the same time $\mathbf{n}_+(0)=0$. In both of these cases, the phase trajectories of the vectors $\mathbf{n}_a$ will be ellipses. However, if at the initial time both normal oscillations $\mathbf{n}_\pm$ are excited, then "beats" will be observed in the system. The phase trajectories of the spins are spirals, which periodically unwind and wind "down to

zero." When one spin "is at zero," the other is then at the maximum distance from the origin, and vice versa. A qualitatively similar picture is also obtained by numerical solution of the nonlinear equations (116). The only difference is that in this case the trajectories lie not in a plane but on the surface of the phase sphere.

2.2. Multipole approximation

In the previous section, we have clarified the main features of the motion of interacting spins in an external magnetic field in the framework of the linear approximation in the interaction and in the deviation from equilibrium. We now consider in the same approximation the behavior of the multipole moments of the spin system. As was shown above [see (113)], the components of the vectors $\mathbf{n}_a$ can be expressed as linear combinations of the normal coordinates Q_γ, i.e., $\mathbf{n}_a=\Sigma_\gamma \mathbf{v}_{a\gamma}Q_\gamma$. With allowance for this relation, the magnetic moments of the nuclei can be represented in the form

$$\mathbf{m}_a=\mathbf{m}_{a0}+\sum_\gamma \mathbf{v}_{a\gamma}Q_\gamma. \tag{121}$$

Using these expressions to calculate the magnetic and toroidal moments of the spin system (58), we obtain

$$\mathbf{M}=\mathbf{M}_0+\sum_\gamma \mathbf{M}_\gamma Q_\gamma; \quad \mathbf{T}=\mathbf{T}_0+\sum_\gamma \mathbf{T}_\gamma Q_\gamma, \tag{122}$$

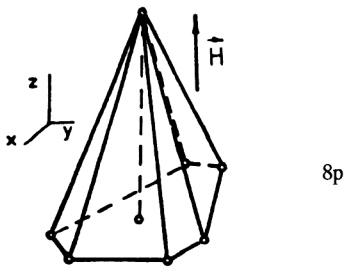
where we have introduced the notation

$$\mathbf{M}_0=\sum_a \mathbf{m}_{a0}; \quad \mathbf{M}_\gamma=\sum_a \boldsymbol{\nu}_{a\gamma},$$

$$\mathbf{T}_0=\tfrac{1}{2}\sum_a [\mathbf{r}_a\mathbf{m}_{a0}], \quad \mathbf{T}_\gamma=\tfrac{1}{2}\sum_a [\mathbf{r}_a\mathbf{v}_{a\gamma}]. \tag{123}$$

The coefficients $\mathbf{M}_\gamma$ and $\mathbf{T}_\gamma$ determine the contributions of the particular normal mode Q_γ to the multipole moments. We shall call the modes for which these coefficients are nonzero and which, therefore, contribute to $\mathbf{M}$ and $\mathbf{T}$ "magnetic" and "toroidal" modes, respectively. Since the magnetic and toroidal moments have different spatial parities, the sets of "magnetic" and "toroidal" modes are not in general the same. If for a given system of spins these sets do not intersect, then when only "magnetic" moments are excited a toroidal moment will not arise in the system, and vice versa. For example, for the system of two spins considered above we find $\mathbf{M}=2\mathbf{m}_0+\mathbf{n}_+$, $\mathbf{T}=[\mathbf{r}_{12}\mathbf{n}_-]$. Thus, for this system the magnetic and toroidal moments depend on different normal coordinates ($\mathbf{n}_+$ and $\mathbf{n}_-$, respectively) and are therefore excited independently.

The presence of particular modes in the sums over γ in the expressions (122) can be established by using the methods of symmetry theory. Suppose that the arrangement of the nuclei in space has a symmetry defined by the group G_0. When the magnetic field H is applied, the symmetry of the system is changed and will be described by a certain subgroup G_H of G_0. In the determination of the group G_H, it must be borne in mind that the magnetic field $\mathbf{H}$ occurs in Eq. (111) quadratically, and therefore the directions of $\mathbf{H}$ and $-\mathbf{H}$ are equivalent. The symmetry G_H will have a figure formed by: 1) the points at which the nuclei are situated; 2) a straight line parallel to the magnetic field. For example, a system of four spins placed at the vertices of a square has symmetry D_{4h}. When a magnetic field is applied in the direction perpendicular to the plane of the square, the symmetry remains the same, i.e., $G_H=D_{4h}$. If the field is directed along a diagonal of the square, then the symmetry of the system is described by the group $G_H=D_{2h}$. For arbitrary orientation of the field relative to the square, we have $G_H=C_i$.



8p

FIG. 5. Example of a distribution of nuclei with symmetry C_{3v}.

Under the action of transformations of the group G_H, each normal oscillation Q_γ transforms in accordance with some irreducible representation of the group. Thus, the index γ corresponds to the number of some irreducible representation, which we shall denote by the same symbol. The classification of the normal oscillations (i.e., the determination of the list of possible values of γ on the set of irreducible representations of the group G_H) can be done as follows. We shall assume that the points $\mathbf{r}_a$ at which the nuclei are situated are the vertices of a graph that represents the matrix of "rigidity coefficients" K_{lab} in Eq. (111) if it is expressed in the form $\ddot{x}_a=-\Sigma_b K_{ab}x_b$. In other words, with each vertex $\mathbf{r}_a$ we associate the number $K_{aa}=H_a^2$, and with each link $a-b$ the number $K_{ab}=HA_{zz}(\mathbf{r}_{ab})$. We note that this graph will have precisely the symmetry G_H. The symmetry operations of the group G_H permute certain vertices of the graph among themselves, and these vertices are regarded as equivalent (they belong to one orbit). We consider a set of scalar functions $\{\phi_a\}$ defined at the nuclei, equivalent nuclei having identical functions ϕ_a. We shall assume that these functions form the basis of a representation and that the oscillation coordinates x_a are the coefficients in the expansion of the state vector ψ with respect to the basis. The set of basis functions realizes a certain, in general reducible, representation Γ of the group G_H. The characters of the elements of the group in the representation Γ are equal to the numbers of vertices of the graph that remain fixed under the action of these elements. It is the irreducible representations that occur in the decomposition of Γ into irreducible parts that will correspond to the required values of γ.

As an example, let us consider the system consisting of seven nuclear spins situated at the vertices of the six-faced pyramid shown in Fig. 5. We assume that the magnetic field is perpendicular to the plane of the base. This system has the symmetry $G_H=C_{3v}$. The characters of the representation Γ

for the elements of the group belonging to the classes E, $2C_3$, and $3\sigma_v$ are, respectively, 7, 1, and 1. Decomposing this representation into irreducible parts, we obtain $\Gamma = 2A_1 + A_2 + 2E$. In other words, in the given case two of the seven normal coordinates Q_γ transform in accordance with the completely symmetric representation A_1, one in accordance with the antisymmetric representation A_2, and four in accordance with the two-dimensional representation E.

A representation γ can contribute to the decomposition of a vector (pseudovector) quantity only if it occurs in a vector (pseudovector) representation of the group. This condition makes it possible to determine the normal modes that contribute to the sums (122). In particular, a given mode Q_γ can contribute to the magnetic and toroidal moments only if there exists in the group G_H an irreducible representation γ, which corresponds to it, with respect to which both a vector and a pseudovector transform. In the symmetry groups G_H for which the inversion transformation $\hat{I}$ is contained as one of the symmetry elements, a vector and a pseudovector transform in accordance with different irreducible representations. Therefore, for all systems with such symmetry (examples are the groups C_i, C_{nh}, D_{nh}, T_d, T_h, and O_h) we certainly cannot observe a crossed response for any orientation of the magnetic field, since the sets of "magnetic" and "toroidal" modes do not intersect for them.

Using the same arguments, we can show that systems with symmetry G_H of the types C_n, C_{nv}, S_4, D_n, D_2, T, O admit the existence of a crossed response. Thus, in the example considered above of the spin system with symmetry C_{3v} (Fig. 5), the two normal modes A_1 occur in the decomposition of the z component of the magnetic moment, and the mode A_2 occurs in the decomposition of the z component of the toroidal moment. At the same time, the modes that transform in accordance with the representation E occur in the decomposition of the x and y components of both the magnetic and the toroidal moment. Therefore, an initial state in which the magnetic moment had x and y components will also give rise to the appearance of x and y components of the toroidal moment, and vice versa.

2.3. Connection between the classical and quantum descriptions of interacting spins

Hitherto, in investigating the dynamics of the spin system, we have used the model of interacting classical spins. From the quantum point of view, the energy (100) must be replaced by the Hamiltonian operator

$$\hat{\mathscr{H}}(1,2,\ldots,N) = -\left(\mathbf{H}\cdot\sum_a \hat{\mathscr{S}}_a\right) - \tfrac{1}{2}\sum_a \sum_b{}' (\hat{\mathscr{S}}_a \cdot A(\mathbf{r}_{ab}) \cdot \hat{\mathscr{S}}_b), \quad (124)$$

where $\hat{\mathscr{S}}_a$ is the spin operator of the ath nucleus. The vector of the quantum state $|\psi(1,2,\ldots,N,t)\rangle$ of this system satisfies the Schrödinger equation

$$i|\dot{\psi}(1,2,\ldots,N,t)\rangle = \hat{\mathscr{H}}(1,2,\ldots,N)|\psi(1,2,\ldots,N,t)\rangle. \quad (125)$$

For further consideration, it is convenient to introduce the density matrix (operator) $\hat{\rho}(t)$, which has the form

$$\hat{\rho}(1,2,\ldots,N,t) = |\psi(1,2,\ldots,N,t)\rangle\langle\psi(1,2,\ldots,N,t)|. \quad (126)$$

Differentiating this operator with respect to the time and using the Schrödinger equation, we obtain for it the equation of motion

$$i\frac{\partial}{\partial t}\hat{\rho}(1,2,\ldots,N,t) = [\hat{\mathscr{H}}(1,2,\ldots,N), \hat{\rho}(1,2,\ldots,N,t)]. \quad (127)$$

We now show that the representation of classical spins used above corresponds to an approximate single-particle description of the quantum system in the framework of the method of the self-consistent Hartree field. We represent the density operator approximately as the product of single-particle operators,

$$\hat{\rho}(1,2,\ldots,N) = \hat{\rho}_1(1)\hat{\rho}_2(2)\ldots\hat{\rho}_N(N), \quad (128)$$

where the single-particle density matrices are related to certain single-particle states by

$$\hat{\rho}_a(a) = |\psi_a(a)\rangle\langle\psi_a(a)|. \quad (129)$$

For the single-particle states, we choose the coherent states $|\mathbf{m}_a\rangle$ of the individual spins whose properties were discussed earlier in Sec. 1.2. We showed that, by restricting ourselves to the case in which the nuclei have spins 1/2, we can then construct coherent states for arbitrary spin. To a coherent state of spin $S = 1/2$ there corresponds a density matrix of the form [cf. (35)]

$$\hat{\rho}_a(a) = \tfrac{1}{2}(\hat{1} + (\mathbf{m}_a\hat{\boldsymbol{\sigma}}_a)), \quad (130)$$

where $\mathbf{m}_a$ is a unit vector ($|\mathbf{m}_a| = 1$).

The choice of the parameters $\mathbf{m}_a$ that best describe the many-particle states is determined by the well-known variational procedure (the method of the self-consistent Hartree field), which reduces to the following operations. Replacing, in Eq. (127), $\hat{\rho}(1,2,\ldots,N)$ by its approximate value (128), for which the single-particle matrices must be chosen in the form (130), and the Hamiltonian in the form (124), and then multiplying the equation by the operator $\hat{\boldsymbol{\sigma}}_a$ and calculating the trace over all the states, we obtain in the given approximation evolution equations for the vectors $\mathbf{m}_a$, which turn out to be identical to the classical equations of motion (104). It follows from this that the model of "classical spins" that was used in the previous subsections corresponds to an approximate single-particle quantum description.

We consider the relationship between the approximate picture and the exact picture for the example of the system of two spins. As is well known, in this case any operator can be decomposed with respect to the complete set of operators $\hat{\boldsymbol{\sigma}}_1$, $\hat{\boldsymbol{\sigma}}_2$, $\hat{\sigma}_{1i}\hat{\sigma}_{2k}$, and $\hat{1}$. Therefore, the *exact* density matrix $\hat{\rho}(1,2)$ can be expressed in the form

$$\hat{\rho}(1,2) = \tfrac{1}{4}(\hat{1} + (\boldsymbol{\mu}_2\hat{\boldsymbol{\sigma}}_1) + (\boldsymbol{\mu}_2\hat{\boldsymbol{\sigma}}_2) + (\hat{\boldsymbol{\sigma}}_1\cdot\nu\cdot\hat{\boldsymbol{\sigma}}_2)), \quad (131)$$

where the vectors $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, and also the second-rank tensor ν_{ik}, are real parameters. Since we assume that in the given

case the density matrix describes a pure state, it must (besides the normalization condition) also satisfy the condition of idempotency, i.e.,

$$\mathrm{Tr}\,\hat{\rho}=1; \quad \hat{\rho}^2=\hat{\rho}. \tag{132}$$

The meaning of the parameters $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$, and ν can be clarified by calculating, by means of the operator (131), the expectation values of the components of the spin operators $\hat{\sigma}_{1i}$ and $\hat{\sigma}_{2k}$ and also their product. It is readily shown that the vectors $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are the expectation values $\langle\hat{\mathscr{S}}_a\rangle$ of the spins (in what follows, in contrast to the vectors $\mathbf{m}_a$, which were called "classical spins," we shall call the vectors $\boldsymbol{\mu}_a$ the quantum spin vectors), and the expectation value of the product $\langle\hat{\mathscr{S}}_{1i}\hat{\mathscr{S}}_{2i}\rangle$ is the tensor ν_{ik}.

We rewrite the exact density matrix (131) in the form closest to the approximate expression (128):

$$\hat{\rho}(1,2)=\hat{\rho}_1(1)\hat{\rho}_2(2)+\tfrac{1}{4}(\nu_{ik}-\mu_{1i}\mu_{2k})\hat{\sigma}_i\hat{\sigma}_k, \tag{133}$$

where we have separated the product of the single-particle density matrices $\hat{\rho}_a(a)=\frac{1}{2}(\hat{1}+\boldsymbol{\mu}_a\hat{\sigma}_a)$. Thus, the difference of the approximate density matrix from the exact one is described by the tensor of the quantum spin correlation:

$$\Delta_{ik}=\nu_{ik}-\mu_{1i}\mu_{2k}=\langle\hat{\mathscr{S}}_{1i}\hat{\mathscr{S}}_{2k}\rangle-\langle\hat{\mathscr{S}}_{1i}\rangle\langle\hat{\mathscr{S}}_{2k}\rangle. \tag{134}$$

We now express the Schrödinger equation in terms of the parameters $\boldsymbol{\mu}_a$ and ν_{ik}. For this, we substitute in the equation $i\dot{\hat{\rho}}=[\hat{\mathscr{H}},\hat{\rho}]$ the density matrix in the form (131) and multiply it successively by the operators $\hat{\sigma}_{1i}$, $\hat{\sigma}_{2i}$, and $\hat{\sigma}_{1i}\hat{\sigma}_{2k}$, and we then calculate the contraction of these products [it is convenient here to use the relation (71)], and as a result we obtain the system of linear equations

$$\begin{aligned}
&\dot{\boldsymbol{\mu}}_1=[\boldsymbol{\mu}_1\mathbf{H}]+[A\cdot\nu];\\
&\dot{\boldsymbol{\mu}}_2=[\boldsymbol{\mu}_2\mathbf{H}]+[\nu\cdot A];\\
&\dot{\nu}=[\nu\times\mathbf{H}]+[\mathbf{H}\times\nu]-[\boldsymbol{\mu}_1\times A]-[A\times\boldsymbol{\mu}_2].
\end{aligned} \tag{135}$$

If in the first two equations we separate the quantum correlation function of the spin operators, making the substitution $\nu_{ik}=\Delta_{ik}+\mu_{1i}\mu_{2k}$, then the first two equations can be rewritten in the form

$$\begin{aligned}
&\dot{\boldsymbol{\mu}}_1=[\boldsymbol{\mu}_1\mathbf{H}]+[\boldsymbol{\mu}_1(A\cdot\boldsymbol{\mu}_2)]+[A\cdot\Delta];\\
&\dot{\boldsymbol{\mu}}_2=[\boldsymbol{\mu}_2\mathbf{H}]+[\boldsymbol{\mu}_2(A\cdot\boldsymbol{\mu}_1)]+[\Delta\cdot A].
\end{aligned} \tag{136}$$

Thus, these equations go over into classical equations if we ignore the correlations between the spins, i.e., if we set $\Delta=0$. As can be seen from these equations, the first important difference of the quantum spin vectors $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ from the classical ones $\mathbf{m}_1$ and $\mathbf{m}_2$ is that the lengths of these vectors are not conserved. This can also be seen from the idempotency condition (132), which imposes on the length of the vectors a constraint of the form $\mu_1^2+\mu_2^2+\nu_{ik}\nu_{ki}=3$. Thus, in the quantum case the phase trajectories of the interacting spins will no longer be lines on the sphere S^2. Nevertheless, in the case of a weak interaction we can, as before, use the classical picture of the motion of the spins, bearing in mind, however, that on account of the interaction the phase sphere has a diffuse surface layer. To avoid misunderstanding, we note that the nonconservation of the length of the spin expectation value $\mu_i^2=\langle\hat{\mathscr{S}}_i\rangle^2$ does not at all mean that the expectation value $\langle\hat{\mathscr{S}}_i^2\rangle$ of the square of the spin is also not conserved. This last quantity has, as it must, a fixed value.

The second (obvious) feature of the quantum equations is that, in contrast to the approximate classical equations, they are linear in the state variables and contain a significantly larger number of unknowns. It is readily verified that this number increases exponentially with increasing number of spins N as $(2S+1)^N$. At the same time, the number of "classical" variables $\mathbf{m}_a$ increases in proportion to N, and in the linear approximation in the interaction it is equal to N itself [cf. Eq. (111)]; this greatly simplifies the investigation of the dynamics of interacting spins and in many cases makes it possible to obtain more transparent results.

2.4. Quantum dynamics of a spin system

The dynamics of a quantum system with Hamiltonian $\hat{\mathscr{H}}$, that does not depend on the time (and it is just such a case that we now consider) is entirely determined by its energy spectrum E_n and stationary states $|\psi_n\rangle$:

$$\hat{\mathscr{H}}|\psi_n\rangle=E_n|\psi_n\rangle. \tag{137}$$

If we know these, any state vector $|\psi(t)\rangle$ can be expressed in the form

$$|\psi(t)\rangle=\sum C_n e^{-iE_nt}|\psi_n\rangle, \tag{138}$$

where the coefficients C_n are determined by the initial state $|\psi(0)\rangle$: $C_n=\langle\psi_n|\psi(0)\rangle$. For this reason, we concentrate our attention here on the analysis of the energy spectrum and eigenstates of the spin system with the Hamiltonian (124).

Since the interaction between the spins is weak, we can use perturbation theory. However, a complication is that the unperturbed Hamiltonian

$$\hat{\mathscr{H}}_0=-\left(\mathbf{H}\sum_a\hat{\mathscr{S}}_a\right) \tag{139}$$

has a degenerate spectrum. Indeed, the sum $\hat{\mathscr{S}}=\Sigma_a\hat{\mathscr{S}}_a$ in the Hamiltonian is the total spin of the system. The operator $\hat{\mathscr{H}}_0$ commutes with the operator of the square of the total spin, $\hat{\mathscr{S}}^2$. Assuming that the field is directed along the Z axis, we find the spectrum of the unperturbed Hamiltonian in the form

$$E_M^{(0)}=-HM; \quad M=S,(S-1),\ldots-(S-1),-S, \tag{140}$$

and the eigenstates are labeled by the numbers K, S, M (here, K stands for all the other quantum numbers apart from those relating to the total spin). Thus, the energy spectrum $E_M^{(0)}$ is degenerate with respect to the numbers K and S.

The values of the total spin S are determined from the given spins $S_1, S_2,\ldots,S_N$ of the nuclei by the rules for adding angular momenta. For example, for three spins $S_1=S_2=S_3=1/2$, the sum S_{12} of the spins of the first and second particle take the two values 0 and 1, and when the spins S_{12} and S_3 are added, the following values of the total spin are obtained: $S=1/2$ twice, for $S_{12}=0$ and $S_{12}=1$, and $S=3/2$. Thus, in this example the energy levels for $M=0$ and $M=\pm1/2$ are triply degenerate (i.e., to each of them there correspond three states), but for $M=\pm3/2$ they are not

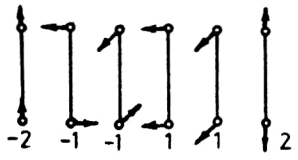


FIG. 6. Vectors of eigenstates of the dipole matrix for a system of two spins. The numbers at the bottom indicate the corresponding values of the energy of the dipole interaction.

degenerate. It follows from this that when a perturbation is introduced it is necessary to use perturbation theory for a degenerate spectrum.

In the solution of magnetic-resonance problems, the dipole–dipole interaction is, as a rule,[1,2] treated in the so-called secular approximation, i.e., the operator $\hat{\mathcal{U}}_{dd}$ of the dipole interaction is projected onto a subspace with given values of S, and all the matrix elements that are not diagonal with respect to S are ignored. In part, this approximation is justified by the fact that in magnetic resonance higher multipoles are usually not observed, and for the description of the magnetic moment this approximation can be sufficient. As numerical calculations show, in this approximation the expectation values of the spins rotate in the static field, remaining parallel or antiparallel to each other. In this case, a toroidal moment can arise only through a change in the projections of the spins onto a common direction. To take into account the dephasing of the rotation of the spins, it is necessary to go beyond the framework of the secular approximation.

We now construct an approximation that makes it possible to separate the main contribution of the dipole interaction to the dynamics of a spin system. For this, we shall regard the tensor $A_{ik}(\mathbf{r}_{ab})$, which determines the strength of the dipole interaction in the Hamiltonian (124), as a $3N\times 3N$ square matrix B given by

$$B_{aibk}=A_{ik}(\mathbf{r}_{ab}), \tag{141}$$

and find the eigenvalues $\mathcal{E}_p$ and eigenvectors $u_{at}^{(p)}$ of this matrix, which satisfy the equation

$$B_{aibk}u_{bk}^{(p)}=\mathcal{E}_p u_{ai}^{(p)}. \tag{142}$$

For given p, we can regard the eigenvectors $u_{ai}^{(p)}$ as a set of three-dimensional vectors $\mathbf{u}_a^{(p)}$ defined at each ath nucleus. Thus, all the eigenstates of the matrix B can be transparently represented as sets of such vectors, which for brevity we shall call dipole configurations, or d configurations. As an example, Fig. 6 shows all d configurations for the two-spin system. The significance of the vectors $\mathbf{u}_a^{(p)}$ is that they determine the points of extremum of the dipole potential for a given spatial distribution of the spins (of the magnetic dipoles). In what follows, we shall call the energetically most advantageous d configuration, with minimum energy $\mathcal{E}_p$, the *ground* configuration and denote it by the vector symbol $\mathbf{u}_a^{(0)}$, and its energy by the symbol $\mathcal{E}_0$. For two spins, the ground configuration is the one in which they have parallel orientation (the extreme left-hand part of Fig. 6).

A qualitative picture of the directions of the vectors $\mathbf{u}_a^{(0)}$ in the ground d configuration can be obtained if it is assumed that at the points at which the nuclei are situated there are point magnetic dipoles ("magnetic arrows") that form a certain oriented structure by virtue of the magnetic attraction. As an example, Fig. 7 shows the ground configurations for three and four dipoles with different spatial distributions of the nuclei.

Knowing the eigenvalues and eigenvectors of the matrix B, we can express it in the form

$$B_{aibk}=\sum_p \mathcal{E}_p u_{ai}^{(p)}u_{bk}^{(p)}, \tag{143}$$

which makes it possible to rewrite the Hamiltonian (124) of the spin system in the form

$$\hat{\mathcal{H}}=-\left(\mathbf{H}\sum_a \hat{\mathbf{S}}\right)-\frac{1}{2}\sum_p \mathcal{E}_p\hat{\mathcal{S}}_p^2, \tag{144}$$

where we have introduced linear combinations of the spin operators at the nuclei corresponding to the d configurations:

$$\hat{\mathcal{S}}_p=\sum_a (\mathbf{u}_a^{(p)}\hat{\mathcal{S}}_a). \tag{145}$$

It is obvious that we can take into account the main contribution of the dipole interaction if we retain in the expression (122) only the one term in the sum over p that corresponds to the ground d configuration $\mathbf{u}_a^{(0)}$. Thus, we obtain the approximate Hamiltonian

$$\hat{\mathcal{H}}\approx-(\mathbf{H}\hat{\mathcal{S}})-\tfrac{1}{2}\mathcal{E}_0\left(\sum_a (\mathbf{u}_a^{(0)}\hat{\mathcal{S}}_a)\right)^2, \tag{146}$$

in which the orientation contribution of the dipole interaction is completely given by the system of vectors $\mathbf{u}_a^{(0)}$.

We assume first that the spin system is a linear chain. In this case, all the vectors $\mathbf{u}_a^{(0)}$ can be assumed to be parallel to each other, $\forall\mathbf{u}_a^{(0)}=\mathbf{u}$, and the Hamiltonian (146) takes the form

$$\hat{\mathcal{H}}=-(\mathbf{H}\hat{\mathcal{S}})-\frac{1}{2}\mathcal{E}_0(\mathbf{u}\hat{\mathcal{S}})^2, \tag{147}$$

where $\hat{\mathcal{S}}$ is the operator of the total spin. Since in this case the Hamiltonian depends only on the total spin, the secular approximation here is completely valid. Formally, the Hamil-

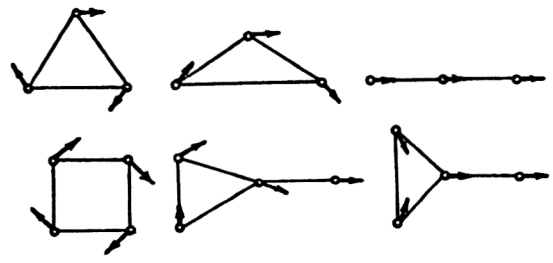


FIG. 7. Examples of ground configurations of the dipole matrix.

tonian (147) describes a quadrupole nucleus (with electric quadrupole moment) in an inhomogeneous electric field and a homogeneous magnetic field.

We now assume that the d configuration of the spins in the ground state has the ring structure that is shown in Fig. 7 for the examples of an equilateral triangle or square. It is obvious that in this case it is no longer possible to take the vectors $\mathbf{u}_a^{(0)}$ in front of the summation sign in the expression (146), and the operator of the dipole–dipole interaction will no longer commute with the operator of the square of the total spin. Thus, in this case the total spin will not be a conserved quantity, and the interaction will certainly "entangle" the degenerate states of the unperturbed Hamiltonian with different values of S. This means that in the given case inhomogeneous spin configurations will arise.

We elucidate this situation in the following simple example. We assume that the spin system can be effectively represented as consisting of two adjacent interacting linear chains with spins $\hat{\mathscr{S}}_1$ and $\hat{\mathscr{S}}_2$ (we assume that $S_1=S_2>1/2$). If the chains are parallel, the effective dipole–dipole interaction has a minimum for antiparallel orientation of the dipoles, i.e., the vectors of the ground d configurations $\mathbf{u}_1^{(0)}$ and $\mathbf{u}_2^{(0)}$ corresponding to the spins S_1 and S_2 are related by an equation of the form $\mathbf{u}_1^{(0)}=-\mathbf{u}_2^{(0)}=\mathbf{u}$. With allowance for the expression (147), the effective Hamiltonian of this system can be represented in the form

$$\hat{\mathscr{H}}_{\text{eff}}=-(\mathbf{H}\hat{\mathscr{S}})-\tfrac{1}{2}\mathscr{E}(\mathbf{u}(\hat{\mathscr{S}}_1-\hat{\mathscr{S}}_2))^2. \tag{148}$$

As a simplification, we assume that $\mathbf{H}\|\mathbf{u}\|OZ$; then the operator (148) gives the following energy spectrum:

$$E_{m_1m_2}=-H(m_1+m_2)-\tfrac{1}{2}\mathscr{E}(m_1-m_2)^2. \tag{149}$$

In the corresponding states of this Hamiltonian, the total spin is not conserved, and, at the same time, as is readily seen, the expectation value of the toroidal moment is nonzero (having components in the XY plane).

2.5. Quantum multipoles

For a qualitative understanding of the conditions of occurrence of a toroidal response, it is helpful to introduce at the quantum level an approximate multipole description of the spin system. To this end, we shall expand all functions of the coordinates in power series near the origin $\mathbf{r}=0$ and restrict ourselves to just the homogeneous and solenoidal contributions [we recall that the origin is determined by the relation (50)]. For example, we can regard the eigenvectors of the matrix of the dipole interaction $\mathbf{u}_a^{(p)}$ for given p as the values of a certain function $\mathbf{u}^{(p)}(\mathbf{r})$ at the points $\mathbf{r}_a$, i.e., $\mathbf{u}_a^{(p)}=\mathbf{u}^{(p)}(\mathbf{r}_a)$. Expanding this function in a series, we obtain

$$\mathbf{u}_a^{(p)}\approx\mathbf{u}^{(p)}+\tfrac{1}{2}[\mathbf{g}^{(p)}\mathbf{r}_a], \tag{150}$$

To determine the parameters $\mathbf{u}^{(p)}$ and $\mathbf{g}^{(p)}$ from the given values of $\mathbf{u}_a^{(p)}$, we first find the sum of the right- and left-hand sides of this equation over all the nuclei. Then with allowance for the expression (50) we obtain for the homogeneous part $\mathbf{u}^{(p)}$ the expression

$$\mathbf{u}^{(p)}=\sum_a \mathbf{u}_a^{(p)}/N. \tag{151}$$

We multiply the right- and left-hand sides of Eq. (150) vectorially by $\mathbf{r}_a$ and sum over a. We obtain

$$\mathbf{g}^{(p)}=\left(I^{-1}\cdot\sum_a[\mathbf{r}_a\mathbf{u}_a^{(p)}]\right);\quad I_{ik}=\sum_a(r_a^2\delta_{ik}-x_{ai}x_{ak}), \tag{152}$$

where $(I)_{ik}^{-1}$ is the second-rank tensor that is the inverse of the tensor I_{ik}. Substituting the resulting expressions (150)–(152) in Eq. (145), we can represent it in the form

$$\hat{\mathscr{S}}_p=(\mathbf{u}^{(p)}\cdot\hat{\mathscr{S}})+(\mathbf{g}^{(p)}\cdot\hat{\mathscr{T}}), \tag{153}$$

where we have introduced the operators of the total spin, $\hat{\mathscr{S}}$, and of the toroidal moment, $\hat{\mathscr{T}}$:

$$\hat{\mathscr{S}}=\sum_a\hat{\mathscr{S}}_a;\quad \hat{\mathscr{T}}=\frac{1}{2}\sum_a[\mathbf{r}_a\hat{\mathscr{S}}_a]. \tag{154}$$

By means of this representation of the operators $\hat{\mathscr{S}}_p$, it is easy to transform the Hamiltonian (144) to the form

$$\hat{\mathscr{H}}=-(\mathbf{H}\hat{\mathscr{S}})-k_{ik}\hat{\mathscr{S}}_i\hat{\mathscr{S}}_k-l_{ik}\hat{\mathscr{T}}_i\hat{\mathscr{S}}_k-l_{ki}\hat{\mathscr{S}}_i\hat{\mathscr{T}}_k+\tfrac{1}{2}n_{ik}\hat{\mathscr{T}}_i\hat{\mathscr{T}}_k. \tag{155}$$

Here, the second-rank tensors k_{ik}, l_{ik}, and n_{ik} are composed of the components of the vectors $\mathbf{u}^{(p)}$ and $\mathbf{g}^{(p)}$ as follows:

$$k_{ik}=\tfrac{1}{2}\sum_p\mathscr{E}_pu_i^{(p)}u_k^{(p)};\quad l_{ik}=\tfrac{1}{2}\sum_p\mathscr{E}_pu_k^{(p)}g_i^{(p)};$$

$$n_{ik}=-\sum_p\mathscr{E}_pg_i^{(p)}g_k^{(p)}. \tag{156}$$

Thus, if we take into account the vortical structure of d configurations of the interaction, we obtain the approximate Hamiltonian (155), which is quadratic in the operators $\hat{\mathscr{S}}$ and $\hat{\mathscr{T}}$.

Note that the second of the expressions in (156) indicates that for the existence of a "crossed" tensor l_{ik}, which is responsible in the Hamiltonian (155) for the coupling between the total spin and the toroidal moment, it is necessary that the spatial configuration of the spins admit the simultaneous existence of the pseudovector $\mathbf{g}^{(p)}$ and the vector $\mathbf{u}^{(p)}$. For example, as can be seen from Fig. 6, none of the d configurations of the system of two particles possesses this property. Further, among the ground d configurations of the figures shown in Fig. 7, there is a nonvanishing tensor l_{ik} only for the "irregular" figures—the isosceles triangle and the figure shown below it consisting of four nuclei—an equilateral triangle with a fourth particle at a vertex. These conclusions have an important practical significance: If for a given arrangement of spins the tensor l_{ik} is nonzero, then on excitation of magnetic resonance by means of a pulse of a homogeneous magnetic field, which forms an initial state with homogeneous magnetization, a toroidal response (to a "different" field) will certainly be observed. At the same time, a preliminary estimate of the effect can be made by means of the expressions (156). An analysis of the conditions

of occurrence of the crossed effect on the basis of symmetry arguments was considered earlier in Sec. 2.2 on the basis of the approximation of classical spins.

In the same approximation, which was assumed in the derivation of the Hamiltonian (155), we can find the commutation relations between the operators $\hat{\mathscr{S}}_i$ and $\hat{\mathscr{T}}_i$ defined by the relations (154). Proceeding from the exact commutation relations

$$[\hat{\mathscr{S}}_i\hat{\mathscr{S}}_j]=ie_{ijk}\hat{\mathscr{S}}_k;\quad [\hat{\mathscr{S}}_i\hat{\mathscr{T}}_j]=iK_{il}e_{jlm}I_{mk}^{-1}\hat{\mathscr{T}}_k;$$
$$[\hat{\mathscr{T}}_i\hat{\mathscr{T}}_j]=\tfrac{1}{4}e_{ijk}K_{lk}\hat{\mathscr{S}}_k, \tag{157}$$

where $K_{ik}=\Sigma_a x_{ai}x_{ak}/N$, and restricting ourselves to the linear approximation in $\mathbf{r}_a$, we obtain

$$[\hat{\mathscr{S}}_i,\hat{\mathscr{S}}_k]=ie_{ikj}\hat{\mathscr{S}}_j;\quad [\hat{\mathscr{S}}_i,\hat{\mathscr{T}}_k]=\tfrac{1}{4}ie_{ikl}\hat{\mathscr{T}}_l;\quad [\hat{\mathscr{T}}_i,\hat{\mathscr{T}}_k]=0. \tag{158}$$

These relations correspond to the Lie algebra of the complete group of rotations of three-dimensional space.[27] At the same time, the operator of the toroidal moment corresponds to the translation operator (it is the analog of the momentum operator $\hat{\mathbf{p}}$). Replacing formally $\hat{\mathscr{T}}$ in the Hamiltonian (155) by $\hat{\mathbf{p}}$, one can reduce it to the form of the Hamiltonian of a particle with tensor n_{ik} of the reciprocal mass:

$$\hat{\mathscr{H}}=-(\mathbf{H}\hat{\mathscr{S}})-k_{ik}\hat{\mathscr{S}}_i\hat{\mathscr{S}}_k-l_{ik}\hat{p}_i\hat{\mathscr{S}}_k-l_{ki}\hat{\mathscr{S}}_i\hat{p}_i + \tfrac{1}{2}n_{ik}\hat{p}_i\hat{p}_k\,. \tag{159}$$

The crossed terms (proportional to the axial tensor l_{ik}) describe the coupling of the translational and rotational motion of this "particle" (the analog of the "helical" interaction of a relativistic particle with spin). The nonconservation of the total spin is interpreted in this language as the possibility of polarization of a particle in its translational motion and, conversely, the back reaction of the polarization on the translational motion.

3. TOROIDAL SUSCEPTIBILITY

In the previous sections of the review, we have considered in detail the quantum dynamics of a system of nuclear spins and have shown that when alternating fields—solenoidal or homogeneous—act on it there arises in the general case a spatially nonuniform distribution of the orientations of the spin dipoles. It is obvious that this system must be described not only by the total magnetic moment of the nuclei, which is usually observed in NMR, but also by other multipoles, among which the most important, as regards the conditions of observation and excitation, is the toroidal moment. Ultimately, all details of the behavior of the system can be observed in the values of the corresponding observable quantities—the frequencies and intensities of the spectral lines, the absorbed power of the alternating field, the susceptibilities, and others.

In this section, we develop a theory of absorption with allowance for the reaction of the spin system to a solenoidal magnetic field. Our main aim is to show, first, that if an inhomogeneous alternating field is used directly to excite resonance (and not as an additional factor that influences the NMR parameters), then this also, like the method of NMR microscopy, provides a possibility for investigating the spatial distribution of the spins, but at the same time the arrangement of the experiment is simplified—there is no need for a device to shape the pulses of the alternating homogeneous field. Second, if the solenoidal magnetic field is produced by displacement currents, c curl $\mathbf{H}=\dot{\mathbf{E}}$, then under conditions close to those of the linear Stark effect, the spatial resolution can be improved to 10^{-4} cm. In addition, since the toroidal moment, which describes the polarization of the particles in a solenoidal field, is a polar vector, a solenoidal field excites "forbidden" transitions, and this may provide a source of additional data in the interpretation of complicated NMR spectra.

3.1. Toroidal absorption

To construct a theory of the absorption of the energy of a solenoidal field, we shall use the scheme of calculations that is usually employed for these purposes in the theory of magnetic resonance. We represent the operator of the interaction of the spin system with the external alternating fields—homogeneous and solenoidal—in the form

$$\hat{\mathscr{V}}=-(\hat{\mathscr{S}}\mathscr{h}(t))-(\hat{\mathscr{T}}\mathbf{g}(t)). \tag{160}$$

At the same time, we assume that the time dependence of the fields is periodic:

$$\mathbf{h}(t)=\mathbf{h}e^{-i\omega t}+\mathbf{h}^*e^{i\omega t};\quad \mathbf{g}(t)=\mathbf{g}e^{-i\omega t}+\mathbf{g}^*e^{i\omega t}, \tag{161}$$

where $\mathbf{h}$ and $\mathbf{g}$ are the complex amplitudes of the fields. Substituting (161) in (160), we can represent the interaction energy in the form

$$\hat{\mathscr{V}}=\hat{\mathscr{F}}e^{-i\omega t}+\hat{\mathscr{F}}^*e^{i\omega t};\quad \hat{\mathscr{F}}=-(\hat{\mathscr{S}}\mathbf{h})-(\hat{\mathscr{T}}\mathbf{g}). \tag{162}$$

This energy, regarded as a perturbation, gives rise to transitions in the energy spectrum of the system: $E_n\to E_m$. The transition probability W_{nm} (per unit time) can be calculated by using the theory of time-dependent perturbations:

$$W_{nm}=\frac{\pi}{2\hbar^2}|F_{nm}|^2\{\delta(\omega+\omega_{nm})+\delta(\omega+\omega_{mn})\}, \tag{163}$$

where $\omega_{nm}=(E_n-E_m)/\hbar$. Bearing in mind that in each transition the system absorbs (or gives up) a quantum of energy $\hbar\omega_{nm}$, we can calculate the absorbed power by using the expression

$$Q=\sum_{nm}\rho_n W_{nm}\hbar\omega_{nm}, \tag{164}$$

where ρ_n is the equilibrium distribution function with respect to the states:

$$\rho_n=Ze^{-\beta E_n};\quad Z^{-1}=\sum_n e^{-\beta E_n}, \tag{165}$$

in which Z is the partition function, and β is the reciprocal temperature in energy units.

Noting that the transition probability (163) is symmetric with respect to transposition of the indices n and m, we can represent the absorption (164) in the form

$$Q=\frac{\pi}{2\hbar}\sum_{nm}|F_{nm}|^2\delta(\omega+\omega_{nm})\hbar\omega_{nm}(\rho_n-\rho_m). \quad (166)$$

It is well known that in nuclear magnetic resonance one can, with a good degree of accuracy, use the high-temperature approximation $\beta E_n \ll 1$ (for more details, see Refs. 1 and 2), and this makes it possible to represent the difference $\rho_n-\rho_m$ approximately in the form $Z\beta\hbar\omega_{nm}$. Using this value, we obtain

$$Q=\tfrac{1}{2}\pi\beta\omega^2 Z\sum_{nm}|F_{nm}|^2\delta(\omega+\omega_{nm}). \quad (167)$$

In accordance with this expression, the absorption, as a function of the frequency ω, consists of a set of resonance "lines" at the transition frequencies ω_{nm}, which correspond to the δ functions in the sum (167). The squares of the moduli of the matrix elements, $|F_{nm}|^2$, determine, first, the selection rules for the resonance frequencies—only the frequencies for which the corresponding matrix elements are nonzero can be present in the sum. In magnetic resonance, one usually takes into account only magnetic-dipole selection rules, and the remaining transitions are assumed to be forbidden. The appearance in the interaction energy (160) of a new operator—the toroidal moment—changes the selection rules; i.e., by acting on the system with a solenoidal magnetic field one can excite transitions in the energy spectrum of the spin system that were forbidden in the case of excitation of the system by a homogeneous field. The matrix elements $|F_{nm}|^2$ determine, second, the relative intensities of the spectral lines.

For further analysis of the expression (167) for the absorption, it is convenient to introduce generalized susceptibilities (cf. Ref. 21, Secs. 123–126). We introduce a combined notation for the amplitudes **h** and **g** of the alternating fields and for the operators $\hat{\mathcal{S}}$ and $\hat{\mathcal{T}}$ of the spin and toroidal moments:

$$f_{\mathcal{J}}=(h_1,h_2,h_3,g_1,g_2,g_3);$$
$$\hat{\mathcal{X}}_{\mathcal{K}}=(\hat{\mathcal{S}}_1,\hat{\mathcal{S}}_2,\hat{\mathcal{S}}_3,\hat{\mathcal{T}}_1,\hat{\mathcal{T}}_2,\hat{\mathcal{T}}_3), \quad (168)$$

where the upper-case indices $\mathcal{J}$ and $\mathcal{K}$ take values from 1 to 6. The generalized susceptibilities are defined as the coefficients of the connection between the mean values of the operators $\hat{\mathcal{X}}_{\mathcal{K}}$ and the alternating fields $f_{\mathcal{J}}$. If it is assumed that the field $f_{\mathcal{K}}(t)$ varies periodically with the time, i.e., $f_{\mathcal{K}}(t)=f_{\mathcal{K}\omega}e^{-i\omega t}$, then the *response* of the system $\bar{\mathcal{X}}_{\mathcal{J}}(t)$ will also be periodic, $\bar{\mathcal{X}}_{\mathcal{J}}(t)=\bar{\mathcal{X}}_{\mathcal{J}\omega}e^{-i\omega t}$, and the connection between the field and the response will be determined by generalized susceptibilities:

$$\bar{\mathcal{X}}_{\mathcal{J}\omega}=\alpha_{\mathcal{J}\mathcal{K}}(\omega)f_{\mathcal{K}\omega}. \quad (169)$$

In this expression, as below, a summation from 1 to 6 over repeated upper-case indices J, K,... is understood. If it is assumed that the perturbation varies with the time as in the relation (161), i.e.,

$$f_{\mathcal{J}}(t)=\tfrac{1}{2}(f_{\mathcal{J}}e^{-i\omega t}+f^*_{\mathcal{J}}e^{i\omega t}), \quad (170)$$

then the relationship between $\bar{\mathcal{X}}_{\mathcal{J}}$ and $f_{\mathcal{K}}$ can be expressed in the form

$$\bar{\mathcal{X}}_{\mathcal{J}}(t)=\tfrac{1}{2}[\alpha_{\mathcal{J}\mathcal{K}}(\omega)f_{\mathcal{K}}e^{-i\omega t}+\alpha^*_{\mathcal{J}\mathcal{K}}(\omega)f^*_{\mathcal{K}}e^{i\omega t}]. \quad (171)$$

On the other hand, the absorbed power can be expressed in terms of the external perturbation in accordance with the relation $Q=-\langle\dot{f}_{\mathcal{J}}\bar{\mathcal{X}}_{\mathcal{J}}\rangle$, where the angular brackets denote an average over the time. Using the relations (170) and (171), we finally obtain

$$Q=\frac{i\omega}{4}(\alpha^*_{\mathcal{J}\mathcal{K}}-\alpha_{\mathcal{K}\mathcal{J}})f_{\mathcal{J}}f^*_{\mathcal{K}}. \quad (172)$$

As is well known,[21] the matrix $\alpha_{\mathcal{K}\mathcal{J}}$ possesses a definite symmetry property [analogous to the symmetry of transport coefficients (Onsager's relations)]. This property depends on the manner in which the quantities $\mathcal{X}_{\mathcal{J}}$ and $\mathcal{X}_{\mathcal{K}}$ behave under time reversal—in the same or in the opposite way. In our case, the role of the operators $\hat{\mathcal{X}}_{\mathcal{J}}$ is played by the magnetic and toroidal moments of the spin system, which behave the same way under time reversal, and therefore the symmetry property can be expressed in the form (cf. Ref. 21, Sec. 125)

$$\alpha_{\mathcal{J}\mathcal{K}}(\omega,\mathbf{H})=\alpha_{\mathcal{K}\mathcal{J}}(\omega,-\mathbf{H}), \quad (173)$$

where **H** is a homogeneous magnetic field. We decompose the matrix $\alpha_{\mathcal{J}\mathcal{K}}$ into two parts—the parts that are even and odd with respect to the field **H**:

$$\alpha_{\mathcal{J}\mathcal{K}}(\mathbf{H})=\alpha^{(0)}_{\mathcal{J}\mathcal{K}}(\mathbf{H})+\alpha^{(1)}_{\mathcal{J}\mathcal{K}}(\mathbf{H}) \quad (174)$$

(for brevity, we omit here and below the argument ω), and

$$\alpha^{(0)}_{\mathcal{J}\mathcal{K}}(\mathbf{H})=\alpha^{(0)}_{\mathcal{J}\mathcal{K}}(-\mathbf{H}); \quad \alpha^{(1)}_{\mathcal{J}\mathcal{K}}(\mathbf{H})=-\alpha^{(1)}_{\mathcal{J}\mathcal{K}}(-\mathbf{H}). \quad (175)$$

Then in accordance with the symmetry relations (173) we obtain

$$\alpha^{(0)}_{\mathcal{J}\mathcal{K}}(\mathbf{H})=\alpha^{(0)}_{\mathcal{K}\mathcal{J}}(\mathbf{H}); \quad \alpha^{(1)}_{\mathcal{J}\mathcal{K}}(\mathbf{H})=-\alpha^{(1)}_{\mathcal{K}\mathcal{J}}(\mathbf{H}), \quad (176)$$

i.e., the matrix $\alpha^{(0)}$ that is even in the field is symmetric with respect to the indices $\mathcal{J}$ and $\mathcal{K}$, while the odd part is antisymmetric.

Representing the generalized susceptibility as the sum of real and imaginary parts,

$$\alpha_{\mathcal{J}\mathcal{K}}=\mathrm{Re}\ \alpha_{\mathcal{J}\mathcal{K}}+i\ \mathrm{Im}\ \alpha_{\mathcal{J}\mathcal{K}}, \quad (177)$$

and taking into account the symmetry relations (176), we can represent the absorption (172) in the form

$$Q=\tfrac{1}{2}\omega\beta_{\mathcal{J}\mathcal{K}}f_{\mathcal{J}}f^*_{\mathcal{K}}; \quad \beta_{\mathcal{J}\mathcal{K}}=\mathrm{Im}\ \alpha^{(0)}_{\mathcal{J}\mathcal{K}}+i\ \mathrm{Re}\ \alpha^{(1)}_{\mathcal{J}\mathcal{K}}. \quad (178)$$

Thus, the absorption is determined by the imaginary part of the susceptibility that is even with respect to the field, $\alpha^{(0)}$, and by the real part of the odd part $\alpha^{(1)}$.

We now return to the original notation for the fields $f_{\mathcal{J}}$ in accordance with their definition (168). We first decompose the 6×6 matrix $\beta_{\mathcal{J}\mathcal{K}}$, into four tensor blocks that are each 3×3:

$$\beta=\begin{pmatrix}\chi & \gamma\\ \gamma^+ & \kappa\end{pmatrix}. \quad (179)$$

The tensors χ and κ have the significance of magnetic and toroidal susceptibilities, respectively, and γ is the crossed, magnetic–toroidal, susceptibility. Using this notation, we can represent the absorption (178) in the form

$$Q=\tfrac{1}{2}\omega\{(\mathbf{h}\cdot\chi\cdot\mathbf{h}^*)+(\mathbf{h}\cdot\gamma\cdot\mathbf{g}^*)+(\mathbf{g}\cdot\gamma^+\cdot\mathbf{h}^*)+(\mathbf{g}\cdot\kappa\cdot\mathbf{g}^*)\}. \tag{180}$$

Returning to the above expression (167) for the absorption and the original notation (168) for the operators of the magnetic and toroidal moments, we can express the susceptibilities χ, κ, and γ in terms of the matrix elements of the operators $\hat{\mathscr{S}}$ and $\hat{\mathscr{T}}$:

$$\begin{aligned}\chi_{ik}&=\tfrac{1}{2}\pi\beta\omega Z\sum_{nm}(S_i)_{nm}(S_k)_{mn}\delta(\omega+\omega_{mn});\\ \kappa_{ik}&=\tfrac{1}{2}\pi\beta\omega Z\sum_{nm}(T_i)_{nm}(T_k)_{mn}\delta(\omega+\omega_{mn});\\ \gamma_{ik}&=\tfrac{1}{2}\pi\beta\omega Z\sum_{nm}(S_i)_{nm}(T_k)_{mn}\delta(\omega+\omega_{mn}).\end{aligned} \tag{181}$$

It follows from the symmetry property (173), and also from the general properties of the matrix elements of the operators $\hat{\mathscr{S}}$ and $\hat{\mathscr{T}}$, that the magnetic and toroidal susceptibilities—the tensors χ and κ—are Hermitian matrices. If it is borne in mind that the magnetic and toroidal moments have opposite spatial parities, it can be seen that the tensor γ_{ik} of the crossed susceptibility changes sign under coordinate inversion, i.e., it is an axial tensor (χ and κ are polar tensors).

3.2. Details of toroidal absorption

As we have already noted, the toroidal susceptibility κ depends on the mutual disposition of the spins of the sample. To elucidate the nature of this dependence, we assume first that the spins do not interact with each other. In this case, the sample as a whole can be regarded as a collection of single-spin "systems," and the inhomogeneity of the exciting field can be taken into account by assuming that on each spin there acts its "own" alternating field $\mathbf{h}(\mathbf{r}_a,t)$ with amplitude

$$\mathbf{h}(\mathbf{r}_a)=\mathbf{h}+\tfrac{1}{2}[\mathbf{g}\mathbf{r}_a]. \tag{182}$$

In accordance with the expression (180) obtained above, the absorption at an individual spin has the form $Q_a=\frac{1}{2}\omega(\mathbf{h}_a\chi_1\mathbf{h}_a^*)$, where χ_1 is the magnetic susceptibility of a unit spin. Summing Q_a over all the spins of the sample and replacing $\mathbf{h}_a$ by its value (182), we obtain for the total absorption in the complete sample the expression

$$Q=\sum_a Q_a=\tfrac{1}{2}\omega N(\mathbf{h}\chi_1\mathbf{h}^*)+\tfrac{1}{8}\omega\sum_a([\mathbf{g}\mathbf{r}_a]\cdot\chi_1\cdot[\mathbf{g}^*\mathbf{r}_a]). \tag{183}$$

Comparing this expression with the general expression (180), we can see that in the given case the magnetic and toroidal susceptibilities have the form

$$\chi=N\chi_1;\quad \kappa=-\tfrac{1}{4}\sum_a \mathbf{r}_a\times\chi_1\times\mathbf{r}_a. \tag{184}$$

With regard to the crossed susceptibility γ, for noninteracting spins it vanishes. In this section, we shall not discuss the properties of this quantity, since in stationary experiments (or, as one also says, under conditions of slow passage through the NMR lines) this quantity, which is proportional to the weak interaction between the spins, is difficult to measure on the background of relatively large quantities—the magnetic and toroidal susceptibilities.

The expression (184) shows that the toroidal susceptibility κ depends on the coordinates of the spins, and therefore, by measuring the absorption of energy in a solenoidal magnetic field, we can investigate structural changes in the system. Suppose, for example, that initially all the spin particles are uniformly distributed over the volume of the sample, which itself has a spherical shape. In this case, the tensor $\Sigma_a x_{ai}x_{ak}$ is proportional to the δ symbol:

$$\sum_a x_{ai}x_{ak}=\tfrac{1}{3}N\langle r_a^2\rangle\delta_{ik}, \tag{185}$$

where $\langle r_a^2\rangle$ is the mean-square distance of the spin particles from the origin. As a result, we obtain for the toroidal susceptibility the expression

$$\kappa_{ik}^{(0)}=\tfrac{1}{3}N\langle r_a^2\rangle(\chi_{1ik}-\chi_{1jj}\delta_{ik}). \tag{186}$$

Thus, the principal axes of the tensors χ and κ coincide. If, however, we assume that the distribution of the spins is nonspherical (for example, as a consequence of structural changes), then in place of the expression (185) we shall have some nonisotropic tensor. Separating the isotropic part, we can write it in the form

$$\sum_a x_{ai}x_{ak}=N\langle r_a^2\rangle\left(K_{ik}+\frac{1}{3}\delta_{ik}\right), \tag{187}$$

where K_{ik} is an irreducible second-rank tensor ("second moment" of the distribution of the spins over space). In this case, the toroidal susceptibility can be represented in the form

$$\begin{aligned}\kappa&=\kappa^{(0)}+\kappa^{(1)};\\ \kappa_{ik}^{(1)}&=N\langle r_a^2\rangle[2K_{ij}\chi_{1jk}-\chi_{1jj}K_{ik}-K_{jl}\chi_{1lj}\delta_{ik}].\end{aligned} \tag{188}$$

If (as is usually done in the theory of NMR) we restrict ourselves in the unperturbed Hamiltonian to the secular part of the dipole–dipole interaction, then the stationary states $|\Psi_n\rangle$ (the transitions between which are excited by the alternating fields) can be characterized by the value of the total spin S and its projection M onto the direction of the static magnetic field (the Z axis): $|\Psi_n\rangle\cong|KSM\rangle$, where the symbol K denotes the set of the remaining quantum numbers. In accordance with the Wigner–Eckart theorem (see, for example, Ref. 20) the matrix elements of the operator of the ath spin, $\langle K'S'M'|\hat{\mathscr{S}}_a|KSM\rangle$, as for any vector operator, are proportional to a Clebsch–Gordan coefficient $C^{1q}_{S'M'SM}=\langle S'M'|C^{1q}|SM\rangle$:

$$\langle K'S'M'|\hat{\mathscr{S}}_{aq}|KSM\rangle=C^{1q}_{S'M'SM}\langle K'S'\|\hat{\mathscr{S}}_a\|KS\rangle, \tag{189}$$

where we have introduced the coefficients $\langle K'S'\|\hat{\mathscr{S}}_a\|KS\rangle$, which do not depend on M, M', and q and are called reduced matrix elements of the operator. In what follows, it will be convenient to regard the Clebsch–Gordan coefficient $C^{1q}_{S'M'SM}$ as a Cartesian vector operator $\hat{\mathscr{C}}$ (i.e., in place of spherical components labeled by an index $q=0, \pm 1$, we have introduced the Cartesian components of this vector). In accordance with this, Eq. (189) for the operator $\hat{\mathscr{S}}_a$ can be written in the form

$$\hat{\mathscr{S}}_a=\hat{\mathscr{S}}_a\hat{\mathscr{C}}, \tag{190}$$

where $\hat{\mathscr{S}}_a$ is the scalar operator of the reduced matrix element of the operator of the ath spin. Substituting the last expression in the definition of the operators of the total spin, $\hat{\mathscr{S}}=\Sigma_a\mathscr{S}_a$, and of the toroidal moment, $\mathscr{T}=\frac{1}{2}\Sigma_a[\mathbf{r}_a\hat{\mathscr{S}}_a]$, we obtain

$$\hat{\mathscr{S}}=\hat{\mathscr{S}}\hat{\mathscr{C}}; \quad \hat{\mathscr{T}}=[\hat{\mathscr{R}}\hat{\mathscr{C}}]; \quad \hat{\mathscr{S}}=\sum_a \mathscr{S}_a;$$

$$\hat{\mathscr{R}}=\sum_a \hat{\mathscr{S}}_a\mathbf{r}_a, \tag{191}$$

where the matrix elements of the operators $\hat{\mathscr{S}}$ and $\hat{\mathscr{R}}$ are the reduced matrix elements of the operators of the total spin $\hat{\mathscr{S}}$ and toroidal moment $\hat{\mathscr{T}}$, respectively.

As a specific example, we consider a system of three nuclei possessing spin $S_a=1/2$. The matrix elements of the operators of the total spin and of the toroidal moment can be readily found in the representation of the eigenvectors of the individual spins. Then, using the Clebsch–Gordan coefficients, we can go over to the representation of the basis vectors of the total spin, using the scheme of addition of angular momenta $j=S_1+S_2$; $S=j+S_3$ (for $j=0$, $S=1/2$, and for $j=1$, $S=1/2$, 3/2). After the calculations, we obtain the reduced matrix elements for the operators $\hat{\mathscr{S}}$ and $\hat{\mathscr{T}}$:

$\langle S'j'|\hat{U}|Sj\rangle=$

	S	3/2	1/2	1/2
S	$j'\backslash j$	1	1	0
3/2	1	$2\sqrt{15}$	0	0
1/2	1	0	$\sqrt{6}$	0
1/2	0	0	0	$\sqrt{6}$

(192)

$\langle S'j'|\hat{\mathscr{R}}|Sj\rangle=$

	S	3/2	1/2	1/2
S	$j'\backslash j$	1	1	0
3/2	1	0	$2\sqrt{6}\vec{r}_3$	$2\sqrt{2}\vec{r}_{12}$
1/2	1	$2\sqrt{6}\vec{r}_3$	$\sqrt{6}\vec{r}_3$	$-\sqrt{2}\vec{r}_{12}$
1/2	0	$2\sqrt{2}\vec{r}_{12}$	$-\sqrt{2}\vec{r}_{12}$	$-\sqrt{6}\vec{r}_3$

(193)

In the calculations, it was assumed that the origin is taken at the geometrical center of the system, and the vector $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$ was introduced. Thus, for the operator $\hat{\mathbf{R}}$ we have the following selection rules with respect to the number S: $S'=S$, $S\pm 1$, and it can be expressed linearly in terms of the coordinate vectors $\mathbf{r}_a$ of the spins. The matrix elements of the operators $\hat{\mathscr{S}}$ and $\hat{\mathscr{T}}$ possess different selection rules, and therefore when a solenoidal magnetic field is applied to the system, transitions that are forbidden for ordinary NMR can be excited. Although the polar vector $\hat{\mathscr{T}}$ in general has matrix elements that are diagonal with respect to the number S, this does not signify a violation of the selection rules:[20] They must be satisfied only with respect to the values of the total angular momentum of the system (spin+orbital).

As was shown above, the intensities of the spectral lines I_{nm} are proportional (in what follows, we shall write the equality sign, omitting the coefficient of proportionality) to the squares $|F_{nm}|^2$ of the corresponding matrix elements of the perturbation operator (162), and the total intensity $I=\Sigma_{nm}I_{nm}$ is proportional to the trace of the square of the perturbation operator:

$$I=\mathrm{Tr}_{KSM}\hat{\mathscr{F}}\hat{\mathscr{F}}^+. \tag{194}$$

For the further calculations, we decompose the perturbation operator (162) into dipole and toroidal parts, $\hat{\mathscr{F}}_1$ and $\hat{\mathscr{F}}_2$, and we express them in terms of the vector operator $\hat{\mathscr{C}}$, using the expressions (191) obtained above:

$$\hat{\mathscr{F}}=\hat{\mathscr{F}}_1+\hat{\mathscr{F}}_2; \quad \hat{\mathscr{F}}_1=-\hat{\mathscr{S}}(\mathbf{h}\hat{\mathscr{C}}), \quad \hat{\mathscr{F}}_2=-(\mathbf{g}[\hat{\mathscr{R}}\hat{\mathscr{C}}]). \tag{195}$$

We substitute in the expression (194) the operator $\hat{\mathscr{F}}_1$ and calculate first the total intensity of the lines in ordinary resonance:

$$I_1=h_ih_k\,\mathrm{Tr}_{KSM}\hat{\mathscr{S}}\hat{\mathscr{S}}^+\hat{\mathscr{C}}_i\hat{\mathscr{C}}_k. \tag{196}$$

Taking into account the orthogonality of the Clebsch–Gordan coefficients,[20]

$$\mathrm{Tr}_M\hat{\mathscr{C}}_i\hat{\mathscr{C}}_k=\delta_{ik}, \tag{197}$$

we reduce the expression (196) to the form

$$I_1=h^2\,\mathrm{Tr}_{KS}\hat{\mathscr{S}}\hat{\mathscr{S}}^+. \tag{198}$$

Similar calculations can also be made for the operator $\hat{\mathscr{T}}$ of the toroidal moment. Writing out the vector product $[\hat{\mathscr{R}}\hat{\mathscr{C}}]$ component by component by means of the symbols e_{ijk}, we obtain

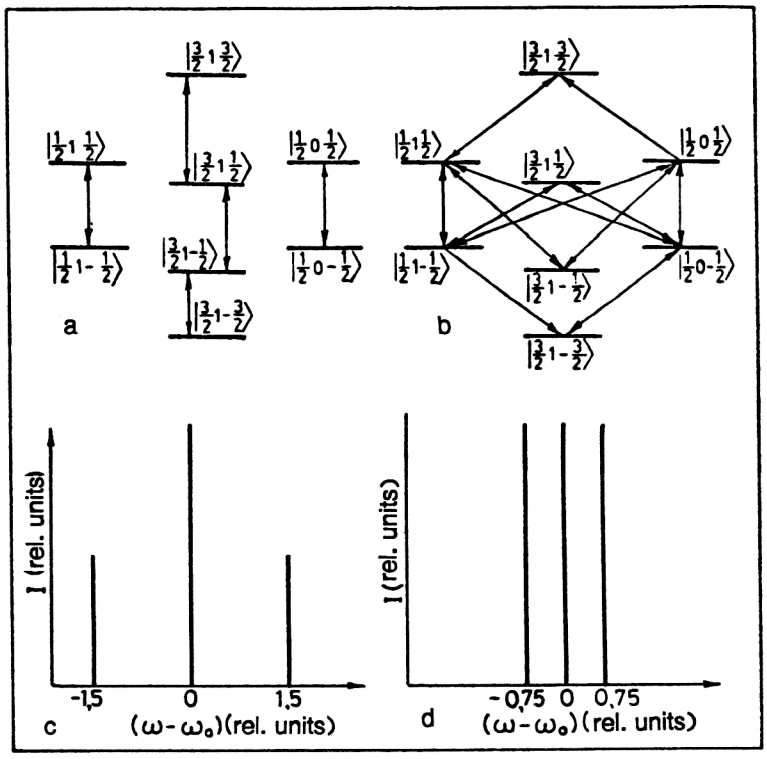


FIG. 8. Scheme of transitions between energy levels of a spin system (shown in the figure by the arrows) excited by homogeneous (a) and solenoidal (b) magnetic fields. The relative intensities of the spectral lines for the same cases are shown in Figs. 8c and 8d, respectively.

$$I_2 = g_i g_k \, \mathrm{Tr}_{KSM}\{e_{ilm}\hat{\mathscr{R}}_l \hat{\mathscr{E}}_m e_{kjn}\hat{\mathscr{R}}_j^+ \hat{\mathscr{E}}_n\} \tag{199}$$

and, using the expression (197), we finally obtain

$$I_2 = g_i g_k \, \mathrm{Tr}_{KS}\{\hat{\mathscr{R}}_j \hat{\mathscr{R}}_j^+ \delta_{ki} - \hat{\mathscr{R}}_k \hat{\mathscr{R}}_i\}. \tag{200}$$

It follows from the last expression that in toroidal resonance the total intensity of the resonance lines is determined by three factors: 1) the intensity of the applied solenoidal magnetic field; 2) the arrangement of the particles; 3) the mutual orientation of the field and the investigated spin system. We note for comparison that in ordinary resonance the considered quantity is determined in accordance with (198) solely by the strength of the perturbing field.

The considered properties of toroidal absorption can be analyzed for the example of a system of three spins at the vertices of an isosceles triangle with angle α at the apex. Substituting in explicit form the components of the vector operator $\hat{\mathscr{R}}$, expressed in terms of the particle coordinates $\mathbf{r}_{12}$ and $\mathbf{r}_3$, we find from the table (193) the expression

$$I_2 = g_i g_k\{(3r_3^2 + r_{12}^2)\delta_{ik} - 3x_{3i}x_{3k} - x_{12i}x_{12k}\}. \tag{201}$$

To study the isosceles triangle, it is convenient to express the coordinates of the particles in terms of the angle α; then in the following calculations we shall have only one variable, which describes well the qualitative changes that occur in the geometry of the system.

We orient the Z axis, as is usually done, along the direction of the static magnetic field and consider the situation in which all the spins lie in the XY plane. Since the vectors $\mathbf{r}_{12}$ and $\mathbf{r}_3$ are mutually perpendicular, it is convenient to direct them along the X and Y axes, respectively; then their coordinates become

$$\mathbf{r}_3 = \left(0; \frac{2}{3}a\cos\frac{\alpha}{2}; 0\right), \quad \mathbf{r}_{12} = \left(2a\sin\frac{\alpha}{2}; 0; 0\right), \tag{202}$$

where a is the length of the lateral side of the triangle. It is convenient to specify the orientation of the solenoidal magnetic field $\mathbf{g}$ in a spherical coordinate system:

$$\mathbf{g} = g(\sin\theta\cos\varphi; \sin\theta\sin\varphi; \cos\theta). \tag{203}$$

Substituting these expressions in (201), we obtain

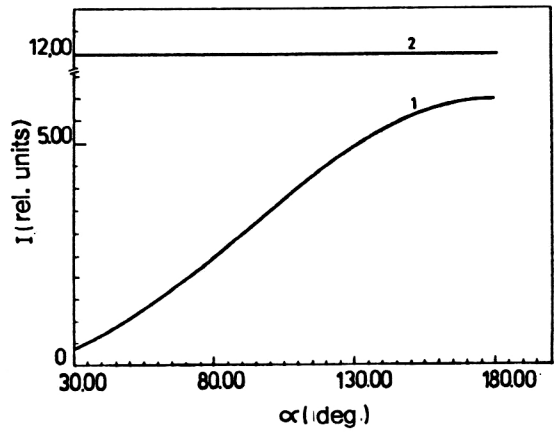


FIG. 9. Dependence of the total intensity of the spectral lines on the spatial distribution of the nuclei in a triatomic molecule (the molecule has the shape of an isosceles triangle with angle α at the apex) for the cases of excitation of resonance by a solenoidal (*1*) and a homogeneous (*2*) magnetic field.

$$I_2=4g^2a^2\left\{\left(1-\tfrac{2}{3}\cos^2\frac{\alpha}{2}\right)-\tfrac{1}{3}\cos^2\frac{\alpha}{2}\sin^2\theta\sin^2\varphi\right.$$
$$\left.-\sin^2\frac{\alpha}{2}\sin^2\theta\cos^2\varphi\right\}. \quad (204)$$

Our analytic expressions agree well with the results of numerical experiments in which resonance excitation was modeled by solenoidal, $\mathbf{g}(t)$, and homogeneous, $\mathbf{h}(t)$, magnetic fields in a system of three spins in the presence of a dipole–dipole interaction. On this basis, the following conclusions were drawn:

1. In the case of toroidal excitations, transitions between levels in the energy spectrum are stimulated that are "forbidden" for ordinary NMR. The reason for this is that, in contrast to the axial vector of the total spin **S**, the toroidal moment **T** is a polar vector, and its matrix elements satisfy different selection rules. As an example, the scheme in Fig. 8 shows transitions excited in a spin system by a homogeneous NMR field (a) and by a solenoidal field (b).

2. The transition frequencies $\omega_{nm}=E_n-E_m$ and the relative intensities I_{nm} of the spectral lines of "dipole" (Fig. 8c) and "toroidal" (Fig. 8d) NMR have been determined. In the calculations it was assumed that $H_0d^3/\hbar\gamma=10^3$; at the same time $\mathbf{g}\|\mathbf{H}_0$, and the magnetic field $\mathbf{H}_0$ was directed at right angles to the plane of the triangle. In ordinary resonance, the energy spectrum of a system of spins situated at the vertices of an equilateral triangle consists of three lines with intensities in the ratios 1:2:1 (Fig. 8c). The spectrum of "toroidal" resonance has three lines, but, in contrast to ordinary NMR, all three lines have the same intensity and are at frequencies differing from those of ordinary NMR.

3. When the angle α is changed, there is a displacement of the lines relative to the ground frequency, and this is accompanied by a change in their relative intensities. Calculations of the total intensity and of the mean frequency made using the expressions

$$I=\sum_{nm} I_{nm}, \quad \bar{\omega}=\frac{\Sigma_{nm}\omega_{nm}I_{nm}}{I}, \quad (205)$$

showed that in ordinary resonance the variation of the angle α leaves the total intensity and the mean frequency unchanged, and independent of α [Fig. 9(*1*)], these quantities being determined solely by the strength of the applied alternating magnetic field $\mathbf{h}(t)$. In "toroidal" resonance, there are smooth variations of the total intensity [see Fig. 9(*2*)], and the nature of the curves $I(\alpha)$ depends on the mutual orientations of the static magnetic field and the alternating solenoidal magnetic field, and also on the arrangement of the spins in space. At the same time, the shape of the curves agrees well with the results of calculations by means of the expression (204).

3.3. Conditions of toroidal excitation of resonance

If an alternating solenoidal magnetic field $\mathbf{g}(t)$ is applied to a system, it is natural to say that there is toroidal excitation of magnetic resonance. If magnetic polarization of the medium as a factor that changes the strength of the magnetic field at the nuclei is ignored (i.e., putting it simply, we assume that the sample is diamagnetic or weakly paramagnetic), and it is also assumed that the sample does not conduct an electric current, then the magnetic field $\mathbf{H}(\mathbf{r})$ satisfies the Maxwell equations

$$\operatorname{div}\mathbf{H}(\mathbf{r})=0; \quad \operatorname{curl}\mathbf{H}(\mathbf{r})=\frac{1}{c}\dot{\mathbf{E}}. \quad (206)$$

It follows from this that in the considered case a solenoidal field will exist only in the presence of a displacement current.

We consider in more detail the conditions of excitation of toroidal resonance by an electric field. We shall assume that the sample is in a planar capacitor in which an alternating field $\mathscr{E}\sim(3\cdot10^4$ V/cm) is generated at a frequency of magnetic resonance, $\omega\sim10^9$ Hz. In this case, the amplitude g of the solenoidal field is estimated as $\omega\mathscr{E}/c$ and in order of magnitude is $g\sim10$ Oe/cm. The alternating field δh that acts on each spin in a certain "averaged" molecule having linear scale l can be estimated as $\delta h\sim gl$. In accordance with the conditions for observation of resonance, this field must be not less than the sensitivity threshold of the NMR method, which we estimate as $\delta h\sim1$ Oe. From this we find the resolution of the method, i.e., the characteristic linear scale of "molecules" or "grains" that can be distinguished: $l\sim\delta h/g\sim10^{-1}$ cm. In the general case, this estimate is changed little by taking into account the polarization of the electrons. We shall assume that the polarization coefficient is proportional to l^3, and therefore the electric dipole moment of the molecule is $P\sim l^3\mathscr{E}$. The polarized electrons create at the nuclei a field $E\sim P/l^3$, from which we find that $E\sim\mathscr{E}$.

An appreciable increase in the resolution can be achieved under conditions close to the linear Stark effect. Namely, we assume that the electrons in the atoms can occupy states Ψ_1 and Ψ_2 separated in energy by a small amount $\Delta\varepsilon=ea\mathscr{E}^*$, where e is the electron charge, a is the atomic linear dimension, and $\mathscr{E}^*$ is a parameter of the order of the amplitude $\mathscr{E}$ of the external field (in the case of complete degeneracy, when $\Delta\varepsilon=0$, in the estimates given below it is necessary to replace $\Delta\varepsilon$ by the thermal energy k_BT). The external field $\mathscr{E}(t)$ can be assumed to be quasistatic, and, as is readily calculated (cf. Ref. 20), using perturbation theory for a degenerate spectrum, in this case the dipole moment of an atom is $P_a\sim(ea)^2\mathscr{E}/\Delta\varepsilon=ea\mathscr{E}/\mathscr{E}^*$, and the electric field acting on a nucleus at distance a is $E\sim P_a/a^3\sim e\mathscr{E}/a^2\mathscr{E}^*$. For $a\sim10^{-8}$ cm and $\mathscr{E}^*\sim10^3$, we obtain $E\sim10^3\mathscr{E}$. Therefore, in this case the external field $\mathscr{E}$ plays the role of a factor that controls the large field at the nuclei created by the electrons. Thus, it is possible to achieve a significant improvement of the spatial resolution: $d\sim(c/\omega)10^3\mathscr{E}\sim10^{-4}$ cm.

The considered method of excitation of toroidal resonance has obvious limitations. Because of the low sensitivity of NMR, it is necessary to produce a field of sufficiently large amplitude. However, under ordinary conditions the strength of the displacement current is bounded above, since at the least the electric field must not exceed the breakdown field of the insulator, which for the majority of insulating materials is at the most 10^5 V/cm. In addition, the frequency of the field variation is also bounded, since it is equal to the NMR resonance frequency, which in turn is determined by

the strength of the homogeneous magnetic field that forms the energy levels of the spin system. Even in modern NMR spectrometers that use superconducting magnets, this frequency does not exceed 10^8–10^9 Hz. Thus, the gradient of the magnetic field is bounded in magnitude by the maximum value $g \sim 10^2$ Oe/cm.

We consider briefly the conditions of measurement of the toroidal susceptibility of the spin system. In Sec. 3.1, it was introduced phenomenologically as the "generalized susceptibility" of the system[21] with respect to the curl of the magnetic field $\mathbf{g}(t)$. In accordance with the form of the Hamiltonian (160), the response of the system to the action of the field $\mathbf{g}(t)$ is the mean toroidal moment $\langle \hat{\mathscr{T}} \rangle$ of the system, and the Fourier transforms of the field and of the response are related by a linear equation of the form

$$\langle \hat{\mathscr{T}} \rangle = \kappa(\omega)\mathbf{g}_\omega . \tag{207}$$

As a simplification, we have restricted ourselves here to the case of an isotropic medium. The imaginary part of the toroidal susceptibility $\kappa''(\omega)$ determines the absorption of energy, while the real part $\kappa'(\omega)$ makes a contribution to the change of the reactive part of the resistance to the alternating current of the element of the electrical circuit that contains the polarizable matter.

Suppose, for example, that a field is produced in a sample by means of a parallel-plate capacitor having capacitance C and separation d between the plates. In accordance with the form of the Hamiltonian (160) and the expression (207), the mean energy of the sample in the field $\mathbf{g}$ can be expressed as

$$U = -(\langle \mathbf{T} \rangle \mathbf{g}) = -\kappa g^2 . \tag{208}$$

Bearing in mind that the electric field E in a parallel-plate capacitor can be expressed in terms of the charge q on its plates as $E = q/Cd$, and remembering that $\mathbf{g} = \text{curl}\, \mathbf{H} = \dot{\mathbf{E}}/c$, we can rewrite the expression (208) in the form

$$U = -\frac{L_T \dot{q}^2}{2c^2}, \tag{209}$$

where we have introduced the coefficient of effective "toroidal" inductance of the parallel-plate capacitor:

$$L_T = \frac{2\kappa}{C^2 d^2}. \tag{210}$$

Thus, in the ac circuit the capacitor filled with a toroidally polarizable medium will possess complex impedance $\mathscr{Z}$, which can be expressed in terms of its capacitance C and effective inductance L_T as

$$\mathscr{Z} = -i\left(\omega L_T - \frac{1}{\omega C}\right). \tag{211}$$

The oscillation circuit obtained in this manner has resonance frequency $\omega_0 = \sqrt{L_T C}$.

In the case when the effective solenoidal field is produced by a system of conductors with currents J_A flowing through them, the mean value of the curl of the magnetic field at the sample can be assumed to be proportional to the current strengths J_A, namely,

$$\mathbf{g} = \frac{1}{c} \sum_A \mathbf{K}_A J_A , \tag{212}$$

where $\mathbf{K}_A$ are certain generalized coefficients of "solenoidal inductance," which are determined by the geometrical arrangement of the conductors. Substituting the expression (212) in (208), we can represent the toroidal contribution to the energy of the system in the form

$$U = \frac{1}{2c^2} \sum L_{AB} J_A J_B , \tag{213}$$

where we have introduced effective coefficients of mutual inductance of the conductors with current associated with the presence of the polarizable medium:

$$L_{AB} = 2\kappa(\mathbf{K}_A \mathbf{K}_B). \tag{214}$$

Thus, in this case too the presence of the medium can be noted as a change in the inductance of the circuit.

4. TOROIDAL RESPONSE OF A SPIN SYSTEM

As is well known,[1–7] there exist two main methods of observing magnetic resonance in nuclear spin systems—stationary and pulsed. The first method (also called the method of slow passage through the lines) is associated with obtaining the absorption curve in the case of prolonged action of an rf field $\mathbf{h}(t)$ on the system. The pulsed methods are based on the interaction of a spin system with pulses of an rf field and observation of the shape of the signal of the free-induction damping that follows the pulses. In the previous section, we considered the stationary method. In this section, we shall investigate the response of the system to a pulsed solenoidal field.

4.1. General theory of crossed magnetic–toroidal response

We shall seek the response of a spin system to a pulsed spatially inhomogeneous alternating rf field $\mathbf{h}_a(t) = \mathbf{h}(t) + \mathbf{h}(\mathbf{r}_a, t)$. As is well known,[1] the state of the system at an arbitrary time is described by a density matrix $\hat{\rho}(t)$, which satisfies the equation of motion

$$\frac{\partial}{\partial t} \hat{\rho}(t) = i[\hat{\rho}(t), \hat{\mathscr{H}}], \tag{215}$$

where $\hat{\mathscr{H}}$ is the Hamiltonian of the spin system:

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \hat{\mathscr{H}}_{dd} + \hat{\mathscr{V}}(t); \quad \hat{\mathscr{H}}_0 = -H_0 \hat{\mathscr{S}}_z ;$$

$$\hat{\mathscr{V}}(t) = -\sum_a (\hat{\mathscr{S}} \mathbf{h}_a(t)). \tag{216}$$

Here, $\hat{\mathscr{H}}_{dd}$ is the operator of the dipole–dipole interaction (146). The solution of Eq. (215) can be expressed in the form

$$\hat{\rho}(t) = \hat{\mathscr{U}}(t,0)\hat{\rho}(0)\hat{\mathscr{U}}^+(t,0), \tag{217}$$

where $\hat{\mathscr{U}}(t,0)$ is the evolution operator, and $\hat{\rho}(0)$ is the density matrix at the initial time:

$$\hat{\rho}(0) = \frac{1}{Z} e^{-\hat{\mathscr{H}}_0 \beta}; \quad Z = \text{Tr}\{e^{-\hat{\mathscr{H}}_0 \beta}\}; \quad 1/\beta = k_B T^0 . \tag{218}$$

On the time axis of the events, two intervals $(0,t_p)$ and (t_p,t) can be distinguished. The first of them corresponds to the period of preparation of the system, and the second to the period of response or decay of the free precession. In the preparation stage, the spin system is subjected to a pulse of the rf field whose intensity is usually large compared with the strength of the dipole–dipole interaction, $|\hat{\mathscr{V}}| \gg |\hat{\mathscr{H}}_{dd}|$, and at the same time the pulse duration is sufficiently short that the effects associated with the presence of interaction are not manifested and can be ignored. Therefore, in the preparation stage the behavior of the spin system will be determined by the Hamiltonian $\hat{\mathscr{H}}_1(t)=\hat{\mathscr{H}}_0+\hat{\mathscr{V}}(t)$.

One can eliminate the time dependence in the operator $\hat{\mathscr{H}}_1(t)$ by going over to a rotating coordinate system K_{rot} (the procedure of this transition is described in detail in Secs. 1.3 and 1.4):

$$\hat{\mathscr{H}}_{\text{rot}}=\hat{\mathscr{U}}_z^+(t)\hat{\mathscr{H}}_1(t)\hat{\mathscr{U}}_z(t); \quad \hat{\mathscr{U}}_z(t)=e^{i\omega_0\hat{\mathscr{S}}_z t}. \tag{219}$$

Assuming that the frequency ω of the alternating field is equal to the resonance frequency $\omega_0=-H_0$, we obtain

$$\hat{\mathscr{H}}_{\text{rot}}=-\sum_a (\mathbf{H}_{a\ \text{eff}}\cdot\hat{\mathscr{S}}_a), \tag{220}$$

where the effective magnetic field $\mathbf{H}_{a\ \text{eff}}=\omega_{ai}\mathbf{e}_i$ acting on the ath spin is determined by the expression (78).

Despite the large strength of the static magnetic field $\mathbf{H}_0$, in the interval (t_p,t) the interaction cannot be ignored, since, acting over a long period, it is manifested in dephasing of the spins (the behavior of a system of interacting spins was described in detail in Sec. 2), and therefore the behavior of the system during the decay of the free precession will be determined by the Hamiltonian $\hat{\mathscr{H}}_2=\hat{\mathscr{H}}_0+\hat{\mathscr{H}}_{dd}$.

Since the behaviors of the system during the time of action of the pulse and in the stage of decay of the free precession are determined by the different Hamiltonians $\hat{\mathscr{H}}_{\text{rot}}$ and $\hat{\mathscr{H}}_2$, the operator $\hat{\mathscr{U}}(t,0)$ in the expression (217) can be represented as the product of two evolution operators $\hat{\mathscr{U}}(t_p,0)$ and $\hat{\mathscr{U}}(t,t_p)$, which act in the intervals $(0,t_p)$ and (t_p,t), respectively:

$$\hat{\mathscr{U}}(t,0)=\hat{\mathscr{U}}(t,t_p)\hat{\mathscr{U}}_z(t_p)\hat{\mathscr{U}}(t_p,0), \tag{221}$$

where the operators $\hat{\mathscr{U}}(t_p,0)\equiv\hat{\mathscr{U}}(t_p)$ and $\hat{\mathscr{U}}(t,t_p)=\hat{\mathscr{U}}(t-t_p)\equiv\hat{\mathscr{U}}(\tau)$ have the form

$$\hat{\mathscr{U}}(t_p)=\exp\{-i\hat{\mathscr{H}}_{\text{rot}}t_p\}; \quad \hat{\mathscr{U}}(\tau)=\exp\{-i\hat{\mathscr{H}}_2\tau\};$$

$$\tau=t-t_p, \tag{222}$$

and $\hat{\mathscr{U}}_z(t_p)$ describes a transition from the rotating coordinate system to the laboratory system at the end of the pulse. Substituting the explicit form of the operator $\hat{\mathscr{U}}(t,0)$ in the expression (217), we obtain

$$\hat{\rho}(t)=\hat{\mathscr{U}}(\tau)\hat{\mathscr{U}}_z(t_p)\hat{\mathscr{U}}(t_p)\hat{\rho}(0)\hat{\mathscr{U}}^+(t_p)\hat{\mathscr{U}}_z^+(t_p)\hat{\mathscr{U}}^+(\tau). \tag{223}$$

Using the high-temperature approximation $\omega_0\beta\ll 1$ (which is usually valid for a system of nuclear spins), we can represent the density matrix $\hat{\rho}(0)$ (218) in the form of a series, retaining only the first terms of the expansion:

$$\hat{\rho}(0)=\frac{1}{\text{Tr}\{\hat{1}\}}\{\hat{1}-\hat{\mathscr{H}}_0\beta\}. \tag{224}$$

Applying the evolution operators $\hat{\mathscr{U}}(t_p)$ and $\hat{\mathscr{U}}_z(t_p)$ to the density matrix (224), we obtain an expression for the density matrix at the time t_p:

$$\hat{\rho}(t_p)=\frac{1}{\text{Tr}\{\hat{1}\}}\left\{\hat{1}-H_0\beta\sum_a\left[\hat{\mathscr{S}}_{az}\cos\lambda_a t_p+\frac{\omega_{ai}}{\lambda_a}\sin\lambda_a t_p\right.\right.$$
$$\left.\left.\times(e_{zik}\hat{\mathscr{S}}_{ak}\cos\omega_0 t_p+\hat{\mathscr{S}}_{ai}\sin\omega_0 t_p)\right]\right\}, \tag{225}$$

where we have introduced the notation $\lambda_a\equiv\sqrt{\omega_{ai}\omega_{ai}}$.

To obtain a clear picture of the spin dynamics, we consider the secular approximation, in which the operator $\hat{\mathscr{H}}_{dd}$ of the dipole interaction commutes with the operator $\hat{\mathscr{H}}_Z$; then in accordance with the expressions obtained above, the expectation values of the operators of the toroidal moment $\hat{\mathscr{T}}$ and $\hat{\mathscr{S}}$ in the stage of free precession will be determined by the expressions

$$\langle\hat{\mathscr{S}}_j\rangle=\frac{-H_0\beta}{\text{Tr}\{\hat{1}\}}\left\{\sum_a \text{Tr}\{\hat{\mathscr{S}}_{az}^2\}\delta_{zj}\cos\lambda_a t_p\right.$$
$$+\sum_a\frac{\omega_{ai}}{\lambda_a}\sin\lambda_a t_p[e_{zik}\,\text{Tr}\{\hat{\mathscr{S}}'_{ak}\hat{\mathscr{S}}_{aj}\}\cos\omega_0 t$$
$$\left.+\text{Tr}\{\hat{\mathscr{S}}'_{ai}\hat{\mathscr{S}}_{aj}\}\sin\omega_0 t]\right\}; \tag{226}$$

$$\langle\hat{\mathscr{T}}_j\rangle=\frac{-H_0\beta}{\text{Tr}\{\hat{1}\}}\left\{\sum_a e_{ljz}x_{al}\text{Tr}\{\hat{\mathscr{S}}_{az}^2\}\cos\lambda_a t_p\right.$$
$$+\sum_a\frac{\omega_{ai}}{\lambda_a}e_{jlm}x_{al}\sin\lambda_a t_p[e_{zik}\text{Tr}\{\hat{\mathscr{S}}'_{ak}\hat{\mathscr{S}}_{am}\}$$
$$\left.\times\cos\omega_0 t+\text{Tr}\{\hat{\mathscr{S}}'_{ai}\hat{\mathscr{S}}_{am}\}\sin\omega_0 t]\right\}. \tag{227}$$

In this and the following expressions, we have used for brevity the notation $\hat{\mathscr{S}}'_{ak}=e^{i\hat{\mathscr{H}}_{dd}t}\hat{\mathscr{S}}_{ak}e^{-i\hat{\mathscr{H}}_{dd}t}$. The expressions obtained here enable us to construct a scheme for describing the responses in magnetic resonance on the basis of the magnetic and toroidal moments, leading to the conclusion that any pulses of an alternating field, homogeneous or solenoidal, not only form a "pure" (magnetic or toroidal) moment but also, by virtue of the interaction between the spins, create the basis for the formation of "crossed" moments (the process of formation of crossed moments was considered in detail in Sec. 2).

We consider the process of formation of the toroidal moment at the end of a pulse of a homogeneous magnetic field directed along the Y axis and with duration satisfying the condition $\lambda t_p=\pi/2$ [we also take a phase difference $\delta=0$ (78)]. Then the expressions (226) and (227) take the form

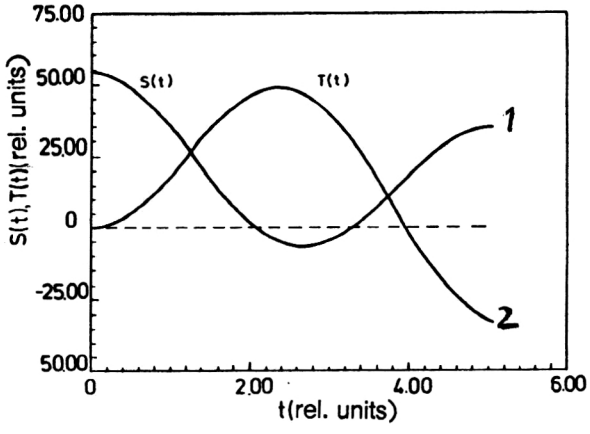


FIG. 10. Envelopes of the signal of the decay of free precession of the magnetic (*1*) and toroidal (*2*) moments after a pulse. For clarity, the scale for curve *2* has been increased in the vertical direction by a factor *5*.

$$\langle \hat{\mathscr{S}}_x \rangle = -\frac{H_0\beta}{\mathrm{Tr}\{\hat{1}\}} \sum_a \mathrm{Tr}\{\hat{\mathscr{S}}'_{ax}\hat{\mathscr{S}}_{ax}\}\cos\,\omega_0 t;$$

$$\langle \hat{\mathscr{S}}_y \rangle = \frac{H_0\beta}{\mathrm{Tr}\{\hat{1}\}} \sum_a \mathrm{Tr}\{\hat{\mathscr{S}}'_{ay}\hat{\mathscr{S}}_{ay}\}\sin\,\omega_0 t, \tag{228}$$

$$\langle \hat{\mathscr{T}}_j \rangle = \frac{H_0\beta}{\mathrm{Tr}\{\hat{1}\}} \sum_a x_{al}\{-e_{ljx}\mathrm{Tr}\{\hat{\mathscr{S}}'_{ax}\hat{\mathscr{S}}_{ax}\}\cos\,\omega_0 t$$

$$+ e_{jly}\mathrm{Tr}\{\hat{\mathscr{S}}'_{ay}\hat{\mathscr{S}}_{ay}\}\sin\,\omega_0 t\}. \tag{229}$$

On the basis of these expressions, we can make a qualitative analysis of the conditions of occurrence of a "crossed" toroidal response in pulsed NMR experiments. As can be seen from the expression (229), the main reason why the sample acquires a toroidal moment is the presence of the dipole–dipole interaction between the spins, which disturbs the original parallel orientation of the spins, forcing them to precess with different frequencies around the static magnetic field. If $\hat{\mathscr{H}}_{dd}=0$ in the expression (229), then $\langle \hat{\mathscr{T}}_j \rangle = 0$. Since the trace $\mathrm{Tr}\{\hat{\mathscr{S}}_{ay}\hat{\mathscr{S}}_{ay}\}=\mathrm{Tr}\{\hat{1}\}$ is also independent of a, it can be taken in front of the summation sign. In this case, there remains a summation only over the coordinates of the spins, and this sum is equal to zero, since the origin is taken at the geometrical center of the system. The situation is analogous immediately after the end of the pulse at the time $t=t_p$. A distinctive feature of the toroidal response is that the expression for $\langle \hat{\mathscr{T}}_j \rangle$ contains explicitly the coordinates of the spins, and this makes it possible to extract significantly more information by the NMR methods, especially in the investigation of asymmetric "chiral" systems.

Analytic calculations, by means of perturbation theory,[17] and numerical calculations were made of the toroidal response for model systems consisting of three or four particles; they agree well with each other. As an illustration, Fig.

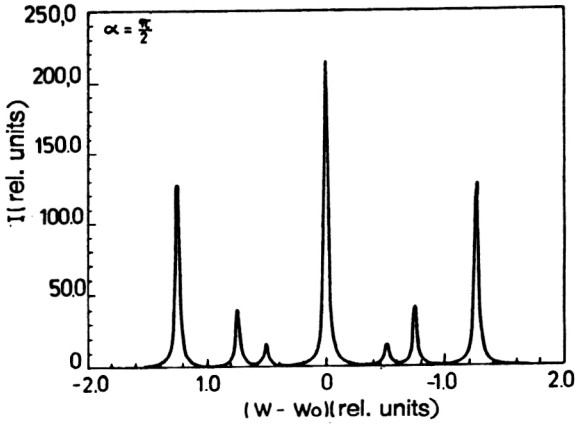


FIG. 11. Spectral lines obtained after Fourier transformation of the signals of the free precession of the magnetic moment. For clarity, a line width has been introduced artificially into the spectra. The origin corresponds to the ground frequency of the resonance.

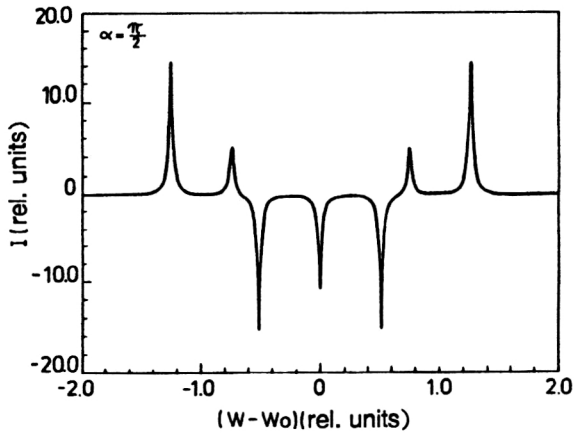


FIG. 12. Spectral lines obtained after Fourier transformation of the free-precession signals of the toroidal moment.

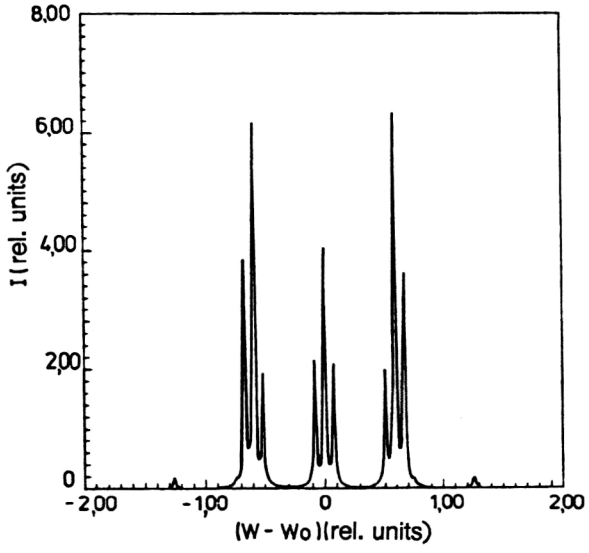


FIG. 13. Absorption spectrum for a system of three particles at the vertices of an equilateral triangle (toroidal resonance).

10 shows the free-induction decay and the toroidal response for a system of spins at the vertices of an isosceles triangle with angle $\alpha=\pi/2$ placed at right angles to the static magnetic field (in this case, only the z component of the toroidal moment is nonzero). Figures 11 and 12 give spectra obtained after Fourier transformation of the signals of the magnetic and toroidal responses for $\alpha=\pi/2$. For comparison, Fig. 13 gives the spectrum of the toroidal absorption for $\alpha=\pi/3$.

4.2. Estimate of the conditions of observations of toroidal response

In the investigation of magnetic resonance, the magnetic moment $\mathbf{M}$ of some distinguished system of spins is usually an observable quantity, and it is the mean value of the total spin operator $\hat{\mathscr{S}}=\Sigma_a\hat{\mathscr{S}}_a$: $\mathbf{M}=\langle\hat{\mathscr{S}}\rangle$; the angular brackets here denote an average over both the quantum state and an "ensemble" of spin systems. However, it is obvious that a system of spins distributed in space—and such a system is in reality a nuclear subsystem (for definiteness, in what follows we discuss a system of nuclear spins)—can also be described by (in addition to the dipole moment $\mathbf{M}$) other multipoles—quadrupole, octupole, etc., which are more sensitive to the details of the spatial distribution of the spins. Nevertheless, in nuclear resonance the fields of the higher multipoles are usually ignored. The point is that the magnetic field H_l of a multipole of rank l depends on the coordinates as $1/r^{2+l}$. Considering a macroscopic sample of length L and adding the fields produced by each multipole, we see that in the dipole case (corresponding to $l=1$) the total dipole moment increases as ML^3 (here, M is the density of the dipole moment), and its field H_1 at the boundary of the sample, which is usually observed in an experiment, varies as ML^3/L^3, i.e., it is proportional to the magnetization M. At the same time, the field H_l of a multipole of higher rank $l>1$ and possessing volume density Q_l decreases at the boundary of the sample as $H_l\sim Q_l/L^{l-1}$, and this makes it possible to ignore this field.

However, there exists one important case in which the field of a multipole that describes a system of nuclear spins behaves like the field of a magnetic dipole. We have in mind the field of the toroidal moment that was introduced and investigated in detail in Refs. 13–15. We shall regard the nuclear spins as a set of classical magnetic dipoles $\mathbf{m}_a=\langle\hat{\mathscr{S}}_a\rangle$ (we assume here the same averaging process as in the introduction of the total magnetic moment), which are situated at the points $\mathbf{r}_a$ in space. The toroidal moment of the system is defined as the sum of products of the form

$$\mathbf{T}=\tfrac{1}{2}\sum_a[\mathbf{r}_a\mathbf{m}_a]. \tag{230}$$

As was shown in Refs. 13–15, the static (i.e., time-independent) toroidal moment produces neither an electric nor a magnetic field, but only a vector-potential field of the form

$$\mathbf{A}=\frac{3\mathbf{r}(\mathbf{Tr})-\mathbf{T}r^2}{r^5}. \tag{231}$$

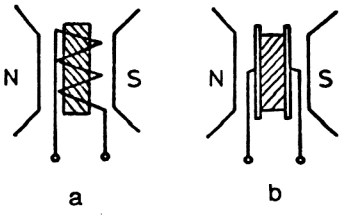


FIG. 14. Basic arrangement of an instrument for observing magnetic (a) and toroidal (b) responses of a nuclear spin system.

This expression can be obtained by summing the potentials $\mathbf{A}_a$ that are produced by the individual magnetic dipoles $\mathbf{m}_a$ and then using an ordinary multipole expansion in powers of the ratio of the diameter of the system to the distance to the point of observation. One of the contributions to this expansion is determined by the toroidal moment (230) and has the form (231). In nuclear magnetic resonance, the mean values of the spins $\mathbf{m}_a$ are functions of the time and, like them, the toroidal moment $\mathbf{T}(t)$ will also depend on the time, and so will the field of the vector potential (231) produced by it. However, as is well known, the time derivative of the vector potential is proportional to the electric field:

$$\mathbf{E}=-\frac{1}{c}\dot{\mathbf{A}}=\frac{\dot{\mathbf{T}}r^2-3\mathbf{r}(\dot{\mathbf{T}}\mathbf{r})}{cr^5}. \tag{232}$$

This field is formally equivalent to the field of an electric dipole $\mathbf{P}$ that has strength $\mathbf{P}=-\dot{\mathbf{T}}/c$, and its "toroidal origin" can be detected only in interference experiments in a study of spectral characteristics (see Ref. 12, Appendix 3). As for the magnetic dipole moment, the field of a sample of macroscopic dimensions L will not depend on L and will be entirely determined by the density of the electric dipole moment $\mathbf{P}$. Estimating the time derivative in (232) as a quantity proportional to the frequency ω of magnetic resonance, one can see that the electric component of the field differs from the magnetic component by a factor equal to the dimensionless parameter $a\omega/c$, where a is the diameter of the spin system, or, if it is remembered that $\lambda=c/\omega$, by the factor a/λ. The NMR frequencies usually lie in the range $\omega\sim10^6$–10^9 Hz, corresponding to wavelengths $\lambda\sim10$–10^4 cm. For sample dimensions $a\sim1$ cm, the electric field is weaker by several orders of magnitude than the magnetic field, but it increases linearly with increasing resonance frequency.

Our discussions show clearly that, after the magnetic moment $\mathbf{M}$, the "pretender" for observation in NMR is the toroidal moment $\mathbf{T}$ of the spin system. It is this moment that determines the electric component of the electromagnetic field induced by the magnetic-dipole system in the surrounding space (we say here that the fields are induced rather than radiated, since throughout we consider the field in the "near zone," which is the one usually measured in magnetic resonance). An experimental method of high-precision measurement of the electric field in magnetic resonance was recently developed and used to measure the back reaction of the quadrupole field of nuclei on the electron subsystem by Hahn *et al.*[14]

CONCLUSIONS

We have considered one of the ways of exciting magnetic resonance in a spatially distributed spin system by means of an inhomogeneous magnetic field. It is based on the interaction of a solenoidal field with the toroidal moment of the spin system. In this case, the spatial configuration of the field is "compared" with the configuration of the system, and this makes it possible to "recognize" the distribution of the nuclei. The method can be helpful, for example, in the investigation of the changes in the shape of oriented macromolecules in solutions or the behavior of microscopic particles of a suspension under the influence of external factors. It is obvious that for the same purpose one can take into account different types of multipole interactions of higher orders, which were considered in Refs. 10–13. This will make it possible to detect finer details in the structure of molecules (higher moments of the distribution function of the spins over space). The detailed study made in this paper shows that in the free-induction process it is possible to observe not only a signal from the precessing magnetic moment of the sample but also a signal from its toroidal moment. The magnetic moment is observed by the standard NMR methods, the basis of which is measurement of the emf induced in the detecting coil (Fig. 14a). As was shown in Sec. 4.2, the strength of the magnetic field in this case is proportional to the magnetization of the sample, $H \sim M$, and the emf φ_M in the coil is proportional to the rate of change of the magnetic flux, i.e.,

$$\varphi_M \approx \frac{\omega}{c} ML^2, \tag{233}$$

where L^2 is the area of the transverse section of the coil, which we assume is equal, in order of magnitude, to the square of the sample linear dimension L. By virtue of the alternating toroidal polarization of the sample, the field acquires an electric component, as was noted in the Introduction. It is easy to show that the potential differences between the plates of the capacitor (Fig. 14b) is, in order of magnitude,

$$\varphi_T \approx 4\pi PL \approx 4\pi TL \frac{\omega}{c}. \tag{234}$$

By means of these expressions, it is possible to estimate the ratio of the magnetic and toroidal signals:

$$\frac{\varphi_T}{\varphi_M} = \frac{4\pi \frac{\omega}{c} TL}{\frac{\omega}{c} ML^2} \sim \frac{a}{L}, \tag{235}$$

where for an estimate we have assumed that $T \sim Ma$, where a is the diameter of the spin system. The value of a is determined by the spatial correlation radius of the system of spins. If the spins are not correlated, the value of the toroidal signal is averaged to zero. If, however, a increases (for example, in the case of an increase of spatial fluctuations of the interacting particles in the process of a liquid–solid phase transition), then, accordingly, the strength of the signal of the toroidal response will also increase.

Thus, our study shows that the observation of toroidal response provides a new possibility for investigating spatial correlations in a spin system, and it thus extends the sphere of applications of nuclear magnetic resonance.

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