ISSN 1063-7761, Journal of Experimental and Theoretical Physics, 2022, Vol. 135, No. 5, pp. 617–631. © Pleiades Publishing, Inc., 2022.
Russian Text © The Author(s), 2022, published in Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki, 2022, Vol. 162, No. 5, pp. 630–645.

ATOMS, MOLECULES, OPTICS

A New View on Spin "Nutation"

K. M. Salikhov

Kazan Physical–Technical Institute, Federal Research Center "Kazan Scientific Center, Russian Academy of Sciences," Kazan, 420029 Russia

e-mail: kevsalikhov@mail.ru

Received May 5, 2022; revised June 24, 2022; accepted June 28, 2022

Abstract—It is shown that Torry's theory of nutation based on the Bloch equations for the magnetization vector cannot be used for describing the "nutation" of interacting spins (including the splitting of spin energy levels in zero magnetic field). The Bloch equations presume that the magnetic moment vector of spins fully determines the spin state. However, this is true of only noninteracting particles with spin $S = 1/2$. Systematic analysis is performed for the response ("nutation") of spins to the instantaneous application of an alternating magnetic field for the simplest system with spin $S = 1$ as an example. The dependence of spin nutation on the spin–spin interaction and the pattern of excitation of spins by an alternating field is analyzed in detail. In the conditions when the spin–spin interactions are comparable with of the spin interaction with the alternating field, the motion of spin magnetization is described as the sum of contributions oscillating with different frequencies, which are equal to the frequencies of transitions between the eigenstates of the spin Hamiltonian in a rotating coordinate system. For the first time, the spin "nutation" is described using the Heisenberg mathematical apparatus. In this approach, the equations of motion are written directly for quantities measured in experiment. The complete orthogonal set of quantities for spins consists of the dipole moment and multipole polarizations. For demonstrating the potential of this description of "nutation," the specific case of paramagnetic particles with spin $S = 1$ is considered. Coupled equations of motion for the dipole and quadrupole moments are obtained with account for the energy of splitting in zero magnetic field. These equations can be referred to as generalized equations for the magnetic polarization of spins. The equations show that in the presence of spin–spin interactions, the reversible mutual conversion of the dipole and quadrupole moments occurs. This leads to oscillations of the length of the spin magnetization vector, the projection of which is usually observed in experiment. Therefore, the experimentally observed oscillations of the magnetization projections reflect the nutation of the magnetization vector as well as the modulation of the length of this vector due to mutual conversion of the dipole and quadrupole polarizations.

DOI: 10.1134/S1063776122110164

1. INTRODUCTION

The methods for studying the spin magnetization in the transition regime under the sudden application or removal of an external ac magnetic field have been proposed even at early stages of evolution of magnetic resonance spectroscopy [1].

After a sudden removal of an ac magnetic field pulse, a free induction signal is observed. This method is widely used mainly in nuclear magnetic resonance (NMR) spectroscopy [2]. The evolution of a free induction signal occurs under the action of the Hamiltonian of a free system in zero ac magnetic field. If the system is initially in equilibrium state and the ac field is strong enough for nonselective spin excitation, the Fourier transform of the free induction signal coincides in form with the stationary spectrum recorded in the linear response conditions [3].

The registration of magnetization in another transient regime (for a sudden application of ac magnetic field $\mathbf{B}_1(t)$ [1, 4–6]) is also of considerable interest. In this approach, the motion of spins is detected in dc magnetic field $\mathbf{B}_0$ (z axis) and in transverse field $\mathbf{B}_1(t)$. This approach attracts attention for the following reasons [4–6].

(i) In the transition region, the amplitude of the observable magnetization can substantially exceed the magnetization in the conditions of a stationary electron paramagnetic resonance (EPR) spectrometer. Therefore, the measurement of magnetization in a transient time interval improves the sensitivity of experiment.

(ii) The time dependence of the magnetization in the transient time interval makes it possible in principle to determine all parameters of the spin Hamiltonian, including the relaxation times for the longitudinal and transverse magnetization components. Naturally, pulsed magnetic resonance methods have been developed for measuring the relaxation time. However, not all laboratories are equipped with pulsed EPR facilities. At the same time, widely used EPR spectrometers intended for recording spectra in the stationary conditions can be modified relatively easily for detecting magnetization under the sudden application of ac field $\mathbf{B}_1(t)$ [6–8].

(iii) The fact that the detection of the time dependence of the spin magnetization upon a sudden application of ac magnetic field $\mathbf{B}_1(t)$ makes it possible in principle to determine the multiplicity of electron spins of isolated paramagnetic particles or spin clusters [4–6].

The proposition to use the nutation method for determining the spin multiplicity of spin clusters attracts considerable attention [4, 5, 8]. To such system, we can attribute, for example, fullerene molecules with an adjoint free radical. A fullerene molecule that has absorbed a light quantum is excited to the singlet electron state of fullerene with zero spin. Owing to the spin–orbit interaction, excited fullerene molecules can pass to the triplet state with unit spin. The triplet fullerene molecule and the adjoint radical with a spin of 1/2 can be in the state with a total spin of 1/2 and 3/2. In the case considered here, the total spin of 1/2 can also be observed for fullerene in the singlet excited state with an adjoint free radical. A direct evidence of the formation of a state with a total electron spin of 3/2 in this system is of considerable interest. Another example can be spin-correlated pairs of ion—radicals, which are formed at the primary stage of charge separation in the reaction center of photosynthetic systems.

In the simplest case, the motion of the magnetization vector in dc magnetic field $\mathbf{B}_0$ (z axis) and in circularly polarized transverse field $\mathbf{B}_1(t)$ is nutation [3]. Using the Bloch equations for the magnetization vector, Torry [1] demonstrated, for example, that when the carrier frequency of the ac field coincides with the precession frequency of the magnetic moment in the dc magnetic field, the magnetization vector observed in the rotating coordinate system has the following components:

$$\begin{aligned} M_y &= \langle S_y \rangle = -\sin(\omega_1 t), \\ M_z &= \langle S_z \rangle = \cos(\omega_1 t), \\ M_x &= \langle S_x \rangle = 0, \end{aligned} \tag{1}$$

where $\omega_1 = (g\beta/\hbar)B_1$ is the Rabi frequency of the ac field, g is the spectroscopic splitting factor, and β is the Bohr magneton. According to relations, (1), the end of the magnetization vector circumscribes a circle in the yz plane. In the Torry theory, the spin nutation frequency is equal to the Rabi frequency and is independent of the spin value. Therefore, the Torry nutation theory does not predict the possibility to determine the spin multiplicity from the data on spin “nutation.”

It should be noted that in Eqs. (1), the irreversible phase relaxation that is determined by relaxation time T_2 in the Bloch equation is not taken into account. To detect nutation (1) correctly in experiment, condition $\omega_1 T_2 \gg 1$ must be satisfied, i.e., the Rabi frequency must be high as compared to the relaxation rate.

The Bloch equations for the magnetization vector correctly describe the motion of spins in magnetic fields only for a system of noninteracting paramagnetic particles with spin $S = 1/2$. In the general case, the motion of the magnetization vector after a sudden application of an ac field should be considered using the consistent quantum theory. Then it turns out [4, 5] that upon a sudden application of the field in the transition region, until the stationary state is attained, the observed magnetization demonstrates oscillations; in the general case, more than one oscillation frequencies appear, while in the Tory nutation (1), only one frequency is expected. This means that in the general case, the motion of the spin magnetization is not the nutation described by Torry [3]. Despite this, the motion of spins after the sudden application of an ac field will be referred to as “nutation” for brevity.

At present, the quantum theory of the spin dynamics in experiments on “nutation” is constructed as follows.

We assume that in zero field $\mathbf{B}_1(t)$, the spin system is described by spin Hamiltonian H_0. For particles with spin $S > 1/2$, the spin Hamiltonian contains the Zeeman interaction with dc field B_0 and the zero field splitting term. Upon the application of the ac field, the spin Hamiltonian takes form (the spin Hamiltonian is written in system of units, in which $\hbar = 1$)

$$H = H_0 + 2\omega_1 S_x \cos(\omega t), \tag{2}$$

where ω_1 is the Raby frequency and ω is the carrier frequency of the linearly polarized field. Further analysis is simplified substantially when eigenstates of $\mathbf{H}_0$ in a good approximation are also the eigenstates of operator S_z of the spin projection on quantization axis z parallel to $\mathbf{B}_0$. In many situations, such a secular approximation for the spin Hamiltonian is justified. In this case, taking into account only one circularly polarized field component and passing to a rotating coordinate system, we obtain spin Hamiltonian

$$H_r = H_0 - \omega S_x + \omega_1 S_z. \tag{3}$$

It should be noted that in the basis of eigenfunctions $|m\rangle$ of operator S_z, the nonzero matrix elements of the operators of the x projection of spin are given by [9]

$$(S_x)_{m,m-1} = (S_x)_{m-1,m} = \frac{1}{2}\sqrt{(S+m)(S-m+1)}. \tag{4}$$

It follows hence that the matrix element of a transition from level m to level $m - 1$ depends on particle spin S. This property of the interaction of the spin with the ac field, $\omega_1 S_x$ (see expressions (3) and (4)) makes it possible to determine the value of spin from “nutation.”

Disregarding the paramagnetic spin relaxation, we can define the spin magnetization after a sudden application of field B_1 as [9]

$$M_u = \mathrm{Tr}\{S_u \rho(t)\} \equiv \mathrm{Tr}\{S_u \exp(-iH_r t)\rho(0)\exp(iH_r t)\}, \quad u = x, y, z. \tag{5}$$

Here, $\rho(0)$ is the initial spin density matrix at the instant of sudden application of field B_1. If the spins are in thermodynamic equilibrium, we can set $\rho(0) = H_0$ in expression (5) in the high-temperature approximation [1, 5]. For example, in the case of strong fields B_0, when the Zeeman energy is larger than the zero field splitting, we have

$$\rho(0) = S_z. \tag{6}$$

Then Eq. (5) is reduced to

$$M_u = \mathrm{Tr}\{S_u \exp(-iH_r t)S_z \exp(iH_r t)\}, \quad u = x, y, z. \tag{7}$$

The spin "nutation" was calculated using this expression in a number of publications [4–8, 10]. These calculations have shown that in the case of sudden application of field B_1, oscillations of the observed magnetization (7) are manifested with frequencies that depend on the ac field power. Moreover, in the conditions of selective excitation of a resonant transition, oscillation is observed with a single frequency equal to the doubled matrix element of the transition for operator $\mathbf{V} = \omega_1\mathbf{S}_x$ of the interaction with field B_1; the matrix element of the resonant transition is calculated in the basis of eigenfunctions of operator S_z (see expression (4)). Based on this observation, it has been stated that the nutation frequency for arbitrary spins is determined by the transition matrix element for operator $\mathbf{V} = \omega_1\mathbf{S}_x$ [4, 5]. Since these transition matrix elements depend on spin (see expression (4)), the measurement of the nutation frequency can be used for determining spins of particles.

The calculations of "nutation" with specific magnetoresonance parameters of spins revealed that several contributions to the experimentally observed signal can be manifested in "nutation" simultaneously [4–6, 8, 10]. In this case, it is necessary to find out which of these frequencies should be treated as the "nutation frequency."

In this study, we propose a consistent analysis of this problem. The analysis is performed for systems in which spin Hamiltonian H_0 (see relations (2) and (3)) of free motion preserves the z projection of the spin (i.e., condition $[H_0, S_z] = 0$ is satisfied). This permits the systematization of the description of spin "nutation."

The article has the following structure.

In Section 2, the main results of theoretical calculations in the "nutation" dynamics are summarized using Eqs. (5) and (7). It is shown that upon a sudden application of an ac field, the motion of the magnetization vector is the Torry nutation only when certain relations hold between the energy of spin-dependent interactions of a free spin system and the energy of interaction of spins with an ac field.

In the general case, the motion of the magnetization cannot be reduced to the Torry nutation. The observed signal contains the contributions of oscillations with frequencies of EPR transitions in a rotating coordinate system. The sum of these contributions leads to beats of the "nutation" signal.

Therefore, the quantum theory using Eqs. (5) and (7) predicts a manifestation of several oscillation frequencies of the "nutation" signal. This is in conformity with experimental data. It may appear that everything is fine. However, a new observation has appeared in calculations. Analysis of the "nutation" of model spin systems performed in this study reveals that during "nutation," not only the direction of the magnetic dipole moment of spins (spin magnetization vector), but also the modulus (length) of this vector changes in a quite intricate manner.

This observation is explained visually in Section 3. For this purpose, the Bloch equations for the magnetization vector had to be replaced by more general equations, including (apart from the dipole polarization) the corresponding multipole spin polarizations in explicit form.

2. QUANTUM THEORY OF SPIN DYNAMICS IN THE "NUTATION" CONDITIONS FOR MODEL SITUATIONS

In the general case, the description of spin nutation is a quite complicated problem Here, we consider the results for several simple situations that make it possible to reveal general properties of "nutation" of interacting spins.

2.1. Formalism Conventionally Used for Calculating the Spin Dynamics with "Nutation" (Eq. (5))

In accordance with Eq. (5), the spin dynamics after a sudden application of an ac magnetic field is determined by the eigenvalues and eigenvectors of spin Hamiltonian H_r (3) in a rotating coordinate system. In the basis of eigenfunction of H_r (3), the diagonal elements of the density matrix (populations of the eigenstates of the spin Hamiltonian) remain unchanged with time if we disregard paramagnetic relaxation. The nondiagonal matrix elements of the spin density matrix (i.e., the coherence of spins) in the basis of eigenstates of spins in the rotating coordinate system vary with time in the familiar way [9]:

$$\rho_{k,n}(t) = (\rho_0)_{k,n} \exp(-i(E_n - E_k)t). \tag{8}$$

Here, E_n and E_k are the energy levels of spin Hamiltonian (3) in the rotating coordinate system.

In accordance with expressions (5), (7), and (8), the experimentally observed dipole moment (magnetization) of spins is the sum of the contributions oscillating with frequencies equal to energy difference $E_n - E_k$ for a pair of levels, of the eigenstates of spin Hamiltonian (3) in the rotating coordinate system.

After a sudden application of field $\mathbf{B}_1$, oscillations of the observed signal with different frequencies have different amplitudes, and some frequencies (associated with certain quantum coherences) may not be manifested. This depends on the following two factors.

First, this depends on the initial values of spin coherences $(\rho_0)_{k,\ n}$ (5) and (8) in the basis of eigenstates of Hamiltonian H_r in the rotating coordinate system. If the spins are in the thermodynamic equilibrium at the instant of sudden application of a microwave (see expression (5)), we are dealing with nondiagonal elements of operator S_z in the representation of eigenfunctions of spin Hamiltonian H_r (3).

Other initial states of spins are also possible. In the case of pulsed photoexcitation of molecules due to spin-selective nonradiative singlet–triplet transitions, there appear triplet excited molecules with nonequilibrium polarization of spins. For example, the situation is possible when triplet molecules are generated only in states with spin projection $m = \pm 1$. In this case, the initial matrix in expression (5) can be represented as $\rho(0) = S_z^2$.

It should be noted that initial condition $\rho(0) = S_z^2$ can also be realized in the thermodynamic equilibrium condition if field B_0 is quite weak and the Zeeman energy is lower than the zero field splitting.

Second, the manifestation of different frequencies in the observed "nutation" signal depends on the coherences that appear in the operator of the experimentally observed magnetization (see operator S_u in expressions (5) and (7)) in the basis of eigenstates of the Hamiltonian in the rotating coordinate system. The observable quantity in the magnetic resonance is usually the x-, y-, or z-component of the spin magnetic dipole moment (i.e., $S_u \equiv S_x$, S_y, S_x in expressions (5) and (7)).

It will be shown below that in the extremal situation of the nonselective excitation by a n ac field, the Torry nutation with the Rabi frequency must be observed in good approximation for any values of paramagnetic particle spin. In this case, experiments on nutation provide no information on the magnitude of spin.

It should be noted that in many situations, nonselective excitation can be realized for nuclear spins. However, it cannot be realized as a rule for electron spins because the inhomogeneous broadening of EPR spectra is usually much larger than the amplitude of field B_1.

In the case of selective excitation of only one resonant transition, nutation with only one frequency is practically observed in a quite good approximation also. In contrast to the previous case of the nonselective spin excitation, the nutation frequency depends on the magnitude of spin.

It may appear at first glance that the observation of nutation in the case of selective excitation of only one resonant transition between spin levels is a convenient and universal method for measuring the spin of paramagnetic particles. However, such a type of excitation requires the fulfillment of certain conditions. First, the Rabi frequency must be substantially lower than the difference between our preferred transition frequency and other frequencies in the EPR spectrum. Second, the Rabi frequency must be high enough for the Torry nutation to perform at least one period of motion during the paramagnetic relaxation time. For example, if the phase relaxation time for electron spins is approximately 1 μs, the Rabi frequency must be not less than 1 G. This means that for the selective excitation of only one transition in the EPR spectrum, the frequency difference between a preferred resonantly excited transition and another spin transition with the closest frequency (another line in the EPR spectrum) must be larger than several gauss.

In EPR spectroscopy, these selective excitation conditions often cannot be satisfied simultaneously. For this reason, the development of the nutation theory is especially topical for electron spins when the type of spin excitation cannot be reduced to the limiting types of spin excitations considered above.

In the general case, the response of the system to the sudden application of an ac field is not the Torry nutation. However, this does not mean that it is impossible in some situations to obtain the value of the particle spin from experimental data on "nutation." The detection of "nutation" makes it possible to determine the value of spin. For this, the results of simulation (theoretical calculations of "nutation") must be compared with experimental data.

2.2. Limiting Case of Nonselective Excitation of Spins

Nonselective excitation of spins is realized in the case of strong field B_1, for which the Rabi frequency is much higher than the frequency spread in transitions between the eigenstates of spin Hamiltonian $H_0 - \omega S_z$. The nonselective excitation of spins by an ac field means that in the applied ac magnetic field, we can retain only one term in the spin Hamiltonian in the rotating coordinate system:

$$H_r \approx \omega_1 S_x. \quad (9)$$

The motion of the spin with such a Hamiltonian can easily be determined. Indeed, the eigenvalues (energy levels) of Hamiltonian (9) are well known for any value of spin S. These eigenstates take values

$$E = \{\omega_1 S, \omega_1(S-1), \ldots, -\omega_1 S\}. \tag{10}$$

For each of such equidistant energy levels, eigenfunctions can be found easily.

Substituting expression (9) into (7), we obtain a very simple relation for the nutation signal in the case of a nonselective spin excitation:

$$M_u = \mathrm{Tr}\{S_u \exp(-i\omega_1 S_x t) S_z \exp(i\omega_1 S_x t)\}, \quad u = x, y, z. \tag{11}$$

This relation implies that in the thermodynamic equilibrium conditions, the quantum coherence in the initial state exists only between adjacent energy levels m, $m \pm 1$, for which the transition frequency is ω_1 (see expression (10)). As a result, in the transient nutation signal, there appear oscillations only with Rabi frequency ω_1, and we obtain

$$\begin{aligned} M_y &= -2\sin(\omega_1 t), \\ M_z &= 2\cos(\omega_1 t), \\ M_x &= 0. \end{aligned} \tag{12}$$

Therefore, in the conditions of nonselective excitation of spins, the nutation can be described by the Torry theory if the spins have been in thermodynamic equilibrium at the instant of a sudden application of an ac field, and the spin state can be defined by operator (6).

In accordance with the above arguments, in the case of nonselective excitation of spins (9), coherences with frequencies ω_1, $2\omega_1$, ..., $2\omega_1 S$ can be manifested in nutation. The frequencies that can be manifested depend on two factors. First, this depends on coherences in the basis of eigenstates of the spin Hamiltonian in the rotating coordinate system, which are present in the spin system at the initial instant of a sudden application of an ac field. Second, this depends on the specific physical quantity, which is measured in experiment. When the M_y or M_z component of the spin magnetization is the observable and the initial spin state is defined by Eq. (6), only single-quantum coherence defined by spin Hamiltonian (9) is manifested in "nutation."

2.3. Limiting Case of Frequency-Selective Spin Excitation

A spin excitation selective in one of frequencies can be realized in the case of relatively weak field B_1, when the Rabi frequency ω_1 is much smaller than the spread in the frequencies of transitions between the eigenstates of spin Hamiltonian $H_0 - \omega S_z$. In this case of frequency-selective spin excitation, the "nutation" frequency depends on the spin of paramagnetic particles.

To visually demonstrate how the dependence of the spin nutation frequency on spin appears in the selective spin excitation conditions, we consider a system of particles with spin $S = 1$ and an isotropic g tensor and assume that the spin Hamiltonian consists of the energy of the Zeeman interaction of spins with dc magnetic field B_0 and the energy of splitting of spin levels in zero magnetic field. For further calculations, we choose the splitting energy in simplest form DS_z^2; i.e., the spin Hamiltonian in a rotating coordinate system has form [10]

$$H_r = (\omega_0 - \omega)S_z + DS_z^2 + \omega_1 S_x. \tag{13}$$

For example, the term with D in this expression can be associated with the dipole–dipole interaction of two spins. It should be noted that the emergence of splitting of spin energy levels in zero magnetic field ($B_0 = 0$) is a consequence of the spin-dependent interaction. For example, the statement that a paramagnetic particle has electron spin $S = 1$ implies the presence of at least two electrons. The total spin of two electrons can have a multiplicity of 1 (total spin $S = 0$, singlet state of a pair of spins) or a multiplicity of 3 ($S = 1$, triplet state of a pair of spins). For example, owing to the exchange interaction, the singlet state can be highly excited, while the triplet state can be the ground state as in the case of oxygen molecules.

In the basis of eigenfunctions S_z, we have the representation of spin Hamiltonian (13) in form

$$H_r = \begin{pmatrix} \omega_0 - \omega + D & \omega_1/\sqrt{2} & 0 \\ \omega_1/\sqrt{2} & 0 & \omega_1/\sqrt{2} \\ 0 & \omega_1/\sqrt{2} & -(\omega_0 - \omega) + D \end{pmatrix}. \tag{14}$$

This matrix takes a simpler form if we choose the ac field frequency equal to the resonance frequency of one of transitions (e.g., $\omega = \omega_0 + D$). If this resonance condition for the frequencies of the selective excitation situation considered here is satisfied, when $\omega_1 < D$, spin Hamiltonian (14) can be written in the approximation linear in ω_1/D in form [4, 11]

$$H_r = \begin{pmatrix} 0 & \omega_1/\sqrt{2} & 0 \\ \omega_1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 2D \end{pmatrix}. \tag{15}$$

In this approximation, weak field B_1 does not affect the state of the spin with projection $m = -1$. However, even very weak field B_1 effectively mixes two degenerate states of the spin with projections $m = 1$ and $m = 0$. The eigenvalues and eigenstates of H_r (15) are given by

$$\begin{aligned} E_1 &= \frac{\omega_1}{\sqrt{2}}, \quad \Psi_1 = \frac{1}{\sqrt{2}}(|+1\rangle + |0\rangle), \\ E_2 &= -\frac{\omega_1}{\sqrt{2}}, \quad \Psi_2 = \frac{1}{\sqrt{2}}(-|+1\rangle + |0\rangle), \\ E_3 &= 2D, \quad \Psi_3 = |-1\rangle. \end{aligned} \tag{16}$$

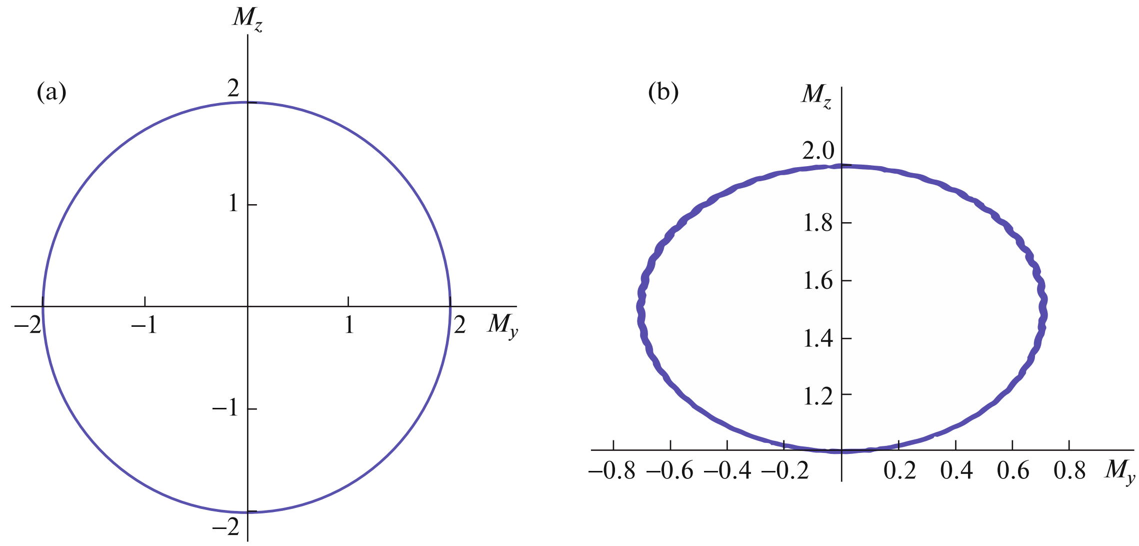

Fig. 1. Trajectories of the tip of the magnetization vector for (a) nonselective and (b) selective spin excitations. Calculations are performed for $\omega_1 = 1$ G, $D = 0$ (a) and 40 G (b). In this article, the frequencies are measured in gauss. To transform frequencies into rad/s, the value in gauss must be multiplied by the gyromagnetic ratio. For example, for a free electron, the multiplication factor is 1.76×10^7.

Using relations (7), (15), and (16), we obtain

$$M_y = -\frac{1}{\sqrt{2}}\sin(\sqrt{2}\omega_1 t),$$
$$M_z = \frac{1}{2}(3 + \cos(\sqrt{2}\omega_1 t)). \quad (17)$$

It can be seen that the difference between the first two eigenvalues (16) gives nutation frequency $\sqrt{2}\omega_1$.

Therefore, in the two limiting situations (nonselective excitation and selective resonant excitation of one of transitions), nutation occurs with different frequencies ω_1 (12) and $\sqrt{2}\omega_1$ (17), respectively. However, it turns out that there is one more difference between nutations in these limiting cases. In the selective excitation, the tip of the magnetization vector circumscribes a circle in the plane perpendicular to $\mathbf{B}_1$ (see expression (12)), while in selective excitation, it circumscribes an ellipse (see expression (17)). In this case, the semimajor axis (along M_y) is $\sqrt{2}$ times larger than the semiminor axis of the ellipse (along M_z) (Fig. 1).

Oscillations with a small amplitude in Fig. 1b are due to the fact that the ac field slightly excites a nonresonant transition also. When we speak of "selective resonant excitation of spins," this does not mean that only one resonant transition is excited. In actual practice, other (nonresonant) transitions are also excited (true, with a much lower effectiveness than a resonant transition).

The arguments put forth for spin $S = 1$ can easily be generalized to arbitrary spins. For this, we propose that because of a quite strong splitting of spin energy levels in zero magnetic field B_0 for a given frequency of the ac field, only a resonant transition with a change in spin projection m is effectively excited (m, $m - 1$, see relation (4)). If the resonant excitation condition for one of possible lines in the EPR spectrum is satisfied for Hamiltonian H_0 as well as conditions of negligibly small excitation for other (nonresonant) lines, there appears nutation with frequency [4, 5]

$$\Omega_{\text{nut}} = 2\omega_1(S_x)_{m,m-1} = \omega_1\sqrt{(S+m)(S-m+1)}. \quad (18)$$

Thus, in the case of selective resonant excitation of transitions between two levels with quantum numbers m, $(m - 1)$, nutation with frequency equal to doubled matrix element of the resonant transition induced by the interaction of field B_1 with spins can be manifested. This nutation frequency is maximal for minimal values of m. Indeed, for the maximal value of $m = S$, we have $\Omega_{\text{nut}} = \omega_1\sqrt{2S}$ (see expression (18)). For the minimal value of m, the nutation frequencies are different for integer and half-integer spins. For integer values of S, we have $\Omega_{\text{nut}} = \omega_1\sqrt{S(S+1)}$, while for half-integer S, we obtain $\omega_{\text{nut}} = \omega_1(S + 1/2)$. The dependence of the nutation frequency on the resonant transition that is excited by the ac field makes it possible to determine the spin value by comparing the results obtained for the excitation of different transitions.

2.4. General Case of Spin Excitation

In the general case, it is necessary to determine the eigenvalues and eigenstates of spin Hamiltonian H_r (3) in the rotating coordinate system and ultimately to calculate the time dependence of "nutation" only numerically.

By way of illustration, Fig. 2 shows the calculated dependences of the M_y magnetization components for spin $S = 1$ with spin Hamiltonian (13) after a sudden application of an ac field for spin $S = 1$.

It should be noted that the period of oscillations is $T = 2\pi/\omega$. All curves in Fig. 2 are calculated for $\omega_1 = 1$ G. In these units, for oscillations with frequency $\omega_1 = 1$ G, the period of oscillations is $T = 2\pi = 6.28$ in the units of 1/G. The period of oscillations with frequency $\sqrt{2}\omega_1$ is $T = 4.44$ 1/G.

It can be seen from Fig. 2 that in the absence of splitting in zero field ($D = 0$, blue curve in Fig. 2a), the nutation period is 6.28, i.e., the nutation frequency is $\omega_1 = 1$ G. This result is expected because in this case, nonselective spin excitation is realized and, hence, $\Omega_{nut} = \omega_1$ (see relation (14)).

When the splitting in zero field is much stronger than ω_1 (red curve for $D = 20$ G in Fig. 2a), the period of oscillations almost coincides with the expected result for the selective excitation of spins: the nutation period is 4.44 1/G, i.e., the nutation frequency coincides with $\sqrt{2}\omega_1$ (see relation (19) below).

In both aforementioned limiting situations, the observable quantity oscillates with single frequency ω_1 or $\sqrt{2}\omega_1$ for the nonselective or selective resonant spin excitation, respectively.

For an intermedium value of $D = 0.5$ G (see Figs. 2a and 2b), not one, but all three possible coherences (one-quantum and two-quantum oscillating terms of the observable magnetization component) contribute to the observed signal.

Using numerical calculations, the dependence of experimentally observed quantity has been determined in the situation when $D = 0.5$ G, $\omega_1 = 1$ G, and $\omega = \omega_0 + D$:

$$M_y = -0.76\sin(1.05t) - 0.9\sin(1.25t) - 0.024\sin(2.3t). \quad (19)$$

For these parameters, the eigenvalues of the spin Hamiltonian in the rotating coordinate system are

$$E_1 = 1.45 \text{ G}, \quad E_2 = -0.85 \text{ G}, \quad E_3 = 0.40 \text{ G}. \quad (20)$$

In this specific example, the main contribution to the observed "nutation" comes from coherences between states $1 \leftrightarrow 3$ and $2 \leftrightarrow 3$, while the coherence of states $1 \leftrightarrow 2$ makes a negligibly small contribution.

In the limiting situation with $D \gg \omega_1$, for the selective resonant excitation of the spin transition, the nutation frequency depends on spin (see relation (19)). For spin $S = 1$, the nutation frequency is equal to $\sqrt{2}\omega_1$ (see expression (19)).

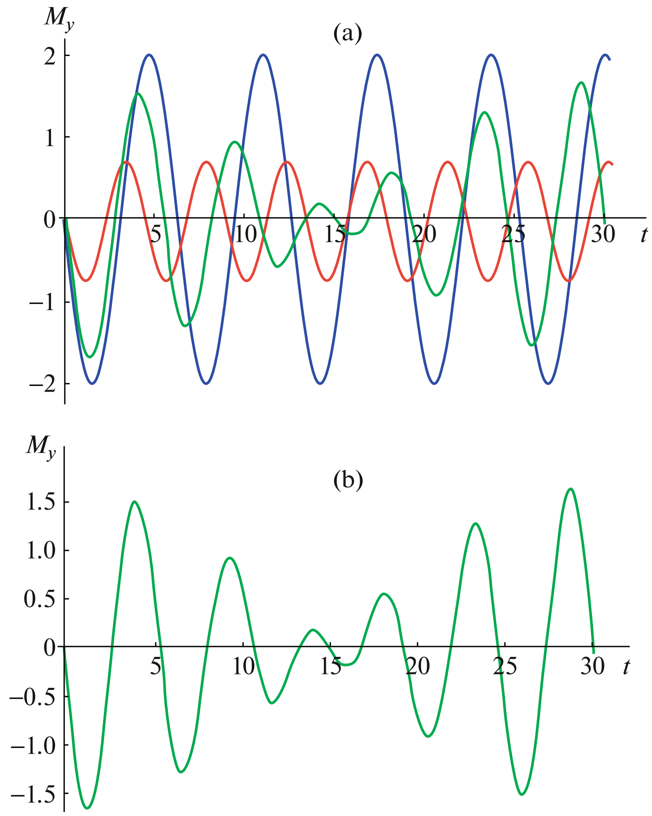

Fig. 2. (a) Time dependences of the M_y component of the magnetization after a sudden application of am ac field with amplitude $\omega_1 = 1$ G (blue, green, and red curves correspond to $D = 0$, 0.5, and 20 G). (b) The curve for $D = 0.5$ G is plotted separately to elucidate better the beats of two oscillating contributions with different frequencies. All calculations have been performed for the case when the carrier frequency of the alternating field coincides with one of resonance frequencies of spins; in these calculations, the resonant transition at frequency $\omega = \omega_0 + D$ has been selected. The time laid on the abscissa axis in Figs. 2–4, 7, and 8 must be multiplied by $(2\pi/1.76) \times 10^{-7}$ to convert it into seconds. For a field of 1 G, the angular frequency is $\omega_1 = 1.76 \times 10^7$ rad/s, or $\nu_1 = 2.8$ MHz.

In interval $|D| \le \sqrt{2}\omega_1$, oscillations with two or three frequencies can appear. When the contributions of two oscillations are comparable, their beats can be observed, as shown by the curve in Fig. 2b.

In actual situations, only such oscillations are observed in experiment, the period of which is shorter than the spin decoherence time. Therefore, only a few periods of oscillations can be observed in experiment. In this case, the time of the first passage of the observed signal through zero can be erroneously interpreted as the "nutation" period.

In Fig. 2a, instants t^* at which the observable signal passes through zero for the first time in limiting case when $D = 0$ and $D \gg \omega_1$ are equal to the nutation period in the relevant limiting cases.

In the intermediate case with $D = 0.5$ G and $\omega_1 = 1$ G, instant t^* at which the observed signal passes through zero for the first time does not give the period of oscillations for any coherence. For example, in the case when two coherences make almost identical contributions to the nutation signal, time t^* is equal to the period of oscillations with the frequency equal to half the sum of the frequencies for two spin coherences.

Therefore, in the general case, the determination of the spin from the data on "nutation" is not so straightforward as in the limiting cases of very weak and very strong splittings in zero magnetic field. However, this does not mean that it is impossible to determine the value of spin from experimental data on "nutation." It is possible to measure "nutation" for several values of ω_1, which correspond to a certain degree of selectivity of excitation, and to simulate of experimental data by numerical calculations.

2.5. Variation of the Length of the Magnetization Vector during "Nutation" Due to Spin Dynamics Even in the Absence of Paramagnetic Relaxation

In this study, the behavior of "nutation" only due to spin dynamics is considered, while spin relaxation to the thermodynamic equilibrium state is not considered. In such a situation, it turns out that the projections of the dipole magnetization vector onto the x, y, and z coordinate axes, which are calculated using Eq. (7), give a vector with a length oscillating with time in an intricate manner. This observation will be illustrated below.

This observation impels to consider the spin dynamics during "nutation" from a different standpoint.

It is well known that quantum systems can be described using the Heisenberg mathematical apparatus. In this approach, the equations of motion are written directly for experimentally measured quantities. In the problem considered here, such quantities are the projections of the dipole polarization and the components of multipole spin polarizations [12, 13]. It can be noted that the Heisenberg approach has been successfully used, for example, in the theory of spin polarization induced by the spin-dependent recombination of radical pairs [14, 15]. In the next section, this approach is realized in analysis of the effect of the spin–spin interaction on spin "nutation."

3. GENERALIZED EQUATIONS FOR SPIN POLARIZATION AND SPIN "NUTATION"

It has been mentioned above more than once that Torry's theory fails to describe spin "nutation" in the general case. This is not surprising. Torry used the Bloch equations for magnetization. These equations imply that three projections of the magnetization provide a complete description of the spin system. In the quantum theory, three spin projections give a comprehensive description only for noninteracting particles with spin $S = 1/2$. For example, for a particle with spin $S = 1$, not only three projections of the spin moment, but also five components of the spin quadrupole moment must be specified to obtain a complete description [12].

For this reason, in analysis of the motion of spins in the conditions when spin interactions are manifested, the attempts at using the Bloch equations as an equivalent model for describing the spin dynamics are not justified. To elucidate the role of multipole moments in the motion of the dipole moment, it is expedient to write the quantum equations of motion for a complete set of physical quantities (for the dipole and multipole moments).

To demonstrate this approach to the description of the spin dynamics, we consider in detail the simplest model system of paramagnetic particles with spin $S = 1$, which do not interact with one another; however, for each spin, we take into account the so-called splitting energy levels in zero magnetic field.

For particles with spin $S = 1$, we obtain a system of equations for the complete set of physical quantities describing the spin state. The spin dynamics is calculated numerically for each projection of the spin dipole moment and for each component of the quadrupole moment after the sudden application of an ac field.

It is shown that in the conditions when the energy of spin–spin interactions is commensurate with the energy of interaction of spins with an ac magnetic field, the reversible mutual transformation of the dipole and quadrupole spin polarizations plays an important role.

3.1. Mutual Transformations of the Dipole and Quadrupole Moments for Paramagnetic Particles with Spin S = 1

Let us consider a system of particles with spin $S = 1$ and an isotropic g tensor and assume that the spin Hamiltonian includes the energy of the Zeeman interaction of spins with a dc magnetic field B_0 and the splitting of energy levels in form DS_z^2; i.e., the spin Hamiltonian in a rotating coordinate system has form (see expression (13))

$$\mathbf{H}_r = (\omega_0 - \omega)\mathbf{S}_z + D\mathbf{S}_z^2 + \omega_1\mathbf{S}_x.$$

All calculations have been performed under the assumption that the ac field frequency is $\omega = \omega_0 + D$. This frequency of the ac field is the resonance frequency for one of transitions in the stationary EPR spectrum in the conditions of a linear response for spin $S = 1$ with spin Hamiltonian

$$\mathbf{H}_0 = \omega_0\mathbf{S}_z + D\mathbf{S}_z^2.$$

Any state of spin $S = 1$ is defined by a 3×3 density matrix (i.e., by nine numbers). Taking into account the normalization condition and the hermiticity of density matrix ($\rho_{km} = \rho^*_{mk}$ [9]), we find that eight experimentally measured physical quantities can also provide a complete description of the state of spin $S = 1$. These quantities are three projections of the spin and five components of the quadrupole tensor (quadrupole moment) [12]:

$$\begin{aligned}
&\mathbf{S}_x, \mathbf{S}_y, \mathbf{S}_z, \\
\mathbf{Q}_{xxyy} &= \mathbf{S}_x\mathbf{S}_x - \mathbf{S}_y\mathbf{S}_y, \\
\mathbf{Q}_{zz} &= \mathbf{S}_z\mathbf{S}_z - \frac{2}{3}\mathbf{F}, \\
\mathbf{Q}_{xy} &= \mathbf{S}_x\mathbf{S}_y + \mathbf{S}_y\mathbf{S}_x, \\
\mathbf{Q}_{xz} &= \mathbf{S}_x\mathbf{S}_z + \mathbf{S}_z\mathbf{S}_x, \\
\mathbf{Q}_{yz} &= \mathbf{S}_y\mathbf{S}_z + \mathbf{S}_z\mathbf{S}_y.
\end{aligned} \tag{21}$$

Here, $\mathbf{F}$ is a unit operator. These operators together with the unit operator form a complete orthogonal basis of the operators.

For all projections of spin moment ($\mathbf{S}_x$, $\mathbf{S}_y$, and $\mathbf{S}_z$) and quadrupole tensors components $\mathbf{Q}_{km}$, we can write the Heisenberg equation of motion. For arbitrary operator $\mathbf{A}$, we have equation

$$\frac{\partial \mathbf{A}}{\partial t} = i[H, \mathbf{A}]. \tag{22}$$

For operators (21), we obtain the following system of linear equations:

$$\begin{aligned}
\frac{\partial \mathbf{S}_x}{\partial t} &= D\mathbf{S}_y - D\mathbf{Q}_{yz}, \\
\frac{\partial \mathbf{S}_y}{\partial t} &= -D\mathbf{S}_x - \omega_1\mathbf{S}_z + D\mathbf{Q}_{xz}, \\
\frac{\partial \mathbf{S}_z}{\partial t} &= \omega_1\mathbf{S}_y, \\
\frac{\partial \mathbf{Q}_{xy}}{\partial t} &= -2D\mathbf{Q}_{xxyy} - \omega_1\mathbf{Q}_{xz}, \\
\frac{\partial \mathbf{Q}_{xz}}{\partial t} &= -D\mathbf{S}_y + \omega_1\mathbf{Q}_{xy} + D\mathbf{Q}_{yz}, \\
\frac{\partial \mathbf{Q}_{yz}}{\partial t} &= D\mathbf{S}_x - \omega_1\mathbf{Q}_{xxyy} - 3\omega_1\mathbf{Q}_{zz} - D\mathbf{Q}_{xz}, \\
\frac{\partial \mathbf{Q}_{zz}}{\partial t} &= \omega_1\mathbf{Q}_{yz}, \\
\frac{\partial \mathbf{Q}_{xxyy}}{\partial t} &= 2D\mathbf{Q}_{xy} + \omega_1\mathbf{Q}_{yz}.
\end{aligned} \tag{23}$$

It can be seen from this equations that for $D = 0$, there is no mutual conversion of the dipole and quadrupole moments; the alternating field does not induce such transformations. Spin–spin interactions ($D \neq 0$) induce the reversible conversion of the dipole and quadrupole moments.

It should be noted that for $D = 0$, Eqs. (23) for the dipole moment projections coincide with the Bloch equations with no account for paramagnetic relaxation.

The experimentally measured mean values of spin (magnetization) projections and the quadrupole moment components are given by

$$\begin{aligned}
S_u &\equiv \langle S_u \rangle = \mathrm{Tr}(S_u\rho(0)), \\
Q_{uv} &\equiv \langle Q_{uv} \rangle = \mathrm{Tr}(Q_{uv}\rho(0)), \\
&u, v = x, y, z.
\end{aligned} \tag{24}$$

Here, $\rho(0)$ is the initial spin density matrix at the instant of sudden application of field B_1. If the spins are in thermodynamic equilibrium, in the high-temperature approximation in expressions (24), we can assume that $\rho(0)$ is equal to S_z (6).

It can be seen from Eqs. (23) and (24) that the average values of physical quantities (24) satisfy the same equations (23) for the operators of corresponding physical quantities.

System (23) of linear differential equations for average values (24) must be solved for the initial conditions that are defined by the spin density matrix at the instant of sudden application of an ac field. If the spins are in the state of thermodynamic equilibrium and the initial state of spins is defined by expression (6), the spin "nutation" starts from the state in which there is only one nonzero initial condition ($S_z(0) = 2$), while all remaining projections of the dipole moment and all components of the quadrupole moment are equal to zero.

In the case of photoexcitation, molecule can be obtained in the triplet state with a nonequilibrium polarization of electron spins. For example, the initial state of the spin can be described by density matrix $\rho(0) = S_z^2$ [5, 15]. In this case, Eqs. (23) for mean values (24) should be solved with the initial conditions $Q_{zz}(0) = 2/3$, and the remaining quantities are equal to zero. Spin "nutation" starts from the state in which the dipole moment is zero, and only one of the quadrupole moment components differs from zero. In this case, in the experiment on "nutation," first the signal is equal to zero, and a nonzero signal is observed only upon the conversion of the quadrupole moment into the dipole moment because one of the dipole moment projection is usually registered in experiment. Therefore, if an enhancement of the signal is observed in experiment over short time intervals, this means that by the instant of microwave field application, the spin has been in the state with nonzero quadrupole polarization. Precisely such a behavior of "nutation" is observed in experiments with the polarization of electron spins in electron-excited organic molecules in accordance with the so-called triplet mechanism of spin polarization [5, 8, 15].

It is worth noting that the second derivatives of the observable quantities also satisfy the following system of linear equations:

$$\frac{\partial^2 S_x}{\partial t^2} = D(2D(-S_x + S_{xz}) + (S_{xxyy} - S_z + 3S_{zz})\omega_1),$$
$$\frac{\partial^2 S_y}{\partial t^2} = 2D^2(-S_y + S_{yz}) + S_{xy}D\omega_1 - S_y\omega_1^2,$$
$$\frac{\partial^2 S_z}{\partial t^2} = -\omega_1(D(S_x - S_{xz}) + S_z\omega_1),$$
$$\frac{\partial^2 S_{xxyy}}{\partial t^2} = -4D^2 S_{xxyy}$$
$$+ D\omega_1(S_x - 3S_{xz}) - (S_{xxyy} + 3S_{zz})\omega_1^2, \tag{25}$$
$$\frac{\partial^2 S_{zz}}{\partial t^2} = -\omega_1(D(-S_x + S_{xz}) + (S_{xxyy} + 3S_{zz})\omega_1),$$
$$\frac{\partial^2 S_{xy}}{\partial t^2} = -4D^2 S_{xy} + D\omega_1(S_y - 3S_{yz}) - S_{xy}\omega_1^2,$$
$$\frac{\partial^2 S_{xz}}{\partial t^2} = 2D^2(S_x - S_{xz}) + D\omega_1(-3S_{xxyy} + S_z - 3S_{zz}) - S_{xz}\omega_1^2,$$
$$\frac{\partial^2 S_{yz}}{\partial t^2} = 2D^2(S_y - S_{yz}) - 3D\omega_1 S_{xy} - 4S_{yz}\omega_1^2.$$

The initial conditions required for solving these equations are defined by the initial values of the observable quantities at instant $t = 0$; the first derivatives at $t = 0$ are given by Eqs. (24).

These equations are very interesting because their form coincides with the equations of coupled oscillations of harmonic oscillators. However, a peculiarity also exists. The coupling coefficients of different pairs of oscillators can have different signs.

For any system of spins with the spin Hamiltonian that does not change with time, we can obviously write a system of coupled equations of “harmonic oscillators’ for the complete set of experimentally measured physical quantities, which is analogous to system (25).

In limiting cases, Eqs. (23) and (25) are simplified significantly. In the absence of zero field splitting, we must set $D = 0$ in these equations. Then the dipole and quadrupole moments are not exchanged. For example, Eqs. (25) for the dipole moments give

$$\frac{\partial^2 \langle S_x\rangle}{\partial t^2} = 0,$$
$$\frac{\partial^2 \langle S_y\rangle}{\partial t^2} = -\omega_1^2\langle S_y\rangle, \tag{26}$$
$$\frac{\partial^2 \langle S_z\rangle}{\partial t^2} = -\omega_1^2\langle S_z\rangle.$$

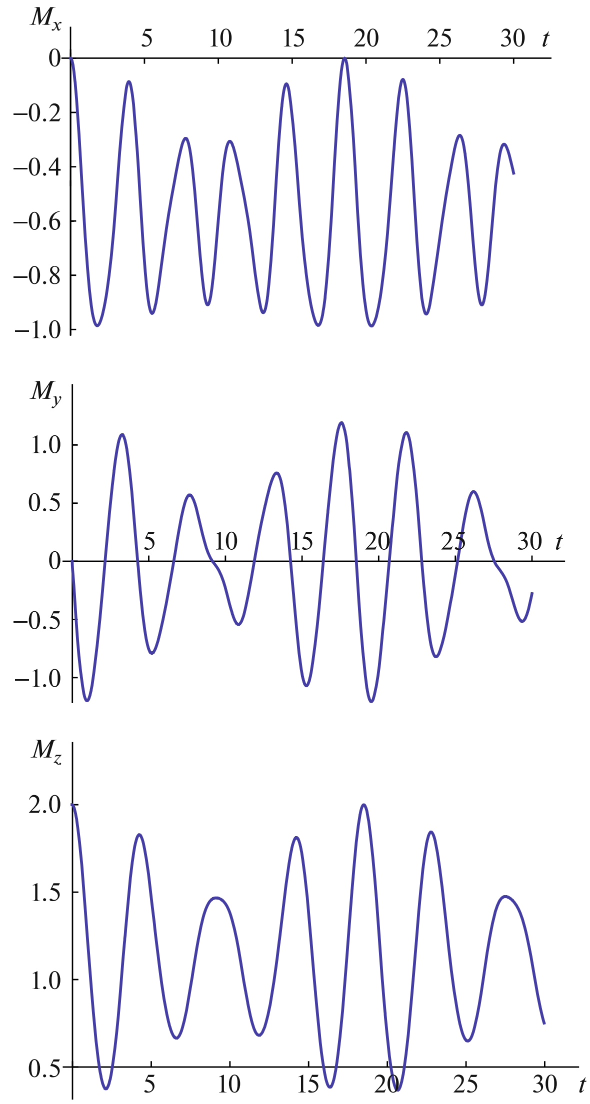

Fig. 3. Time dependences of the spin magnetization projections after a sudden application of an ac field. It is considered that the spin is initially in the equilibrium state (6). Parameters of calculations: $\omega = \omega_0 + D$, $\omega_1 = 1$ G, and $D = 1$ G.

As expected, the dipole moment vector rotates in this case in a circle in the yz plane with frequency ω_1 in a rotating coordinate system and performs the Torry nutation in the laboratory coordinate system.

In the presence of zero field splitting, the motion of the dipole moment vector occurs in accordance with Eqs. (23), (25) in a much more complicated trajectory. To demonstrate this, we consider below the results of numerical solution of Eqs. (23).

3.2. Manifestations of Zero Field Splitting in “Nutation” of Spin $S = 1$

Spin “nutation” depends on the relation between parameters ω_1 and D. In the limiting cases, $\omega_1/|D| \gg 1$

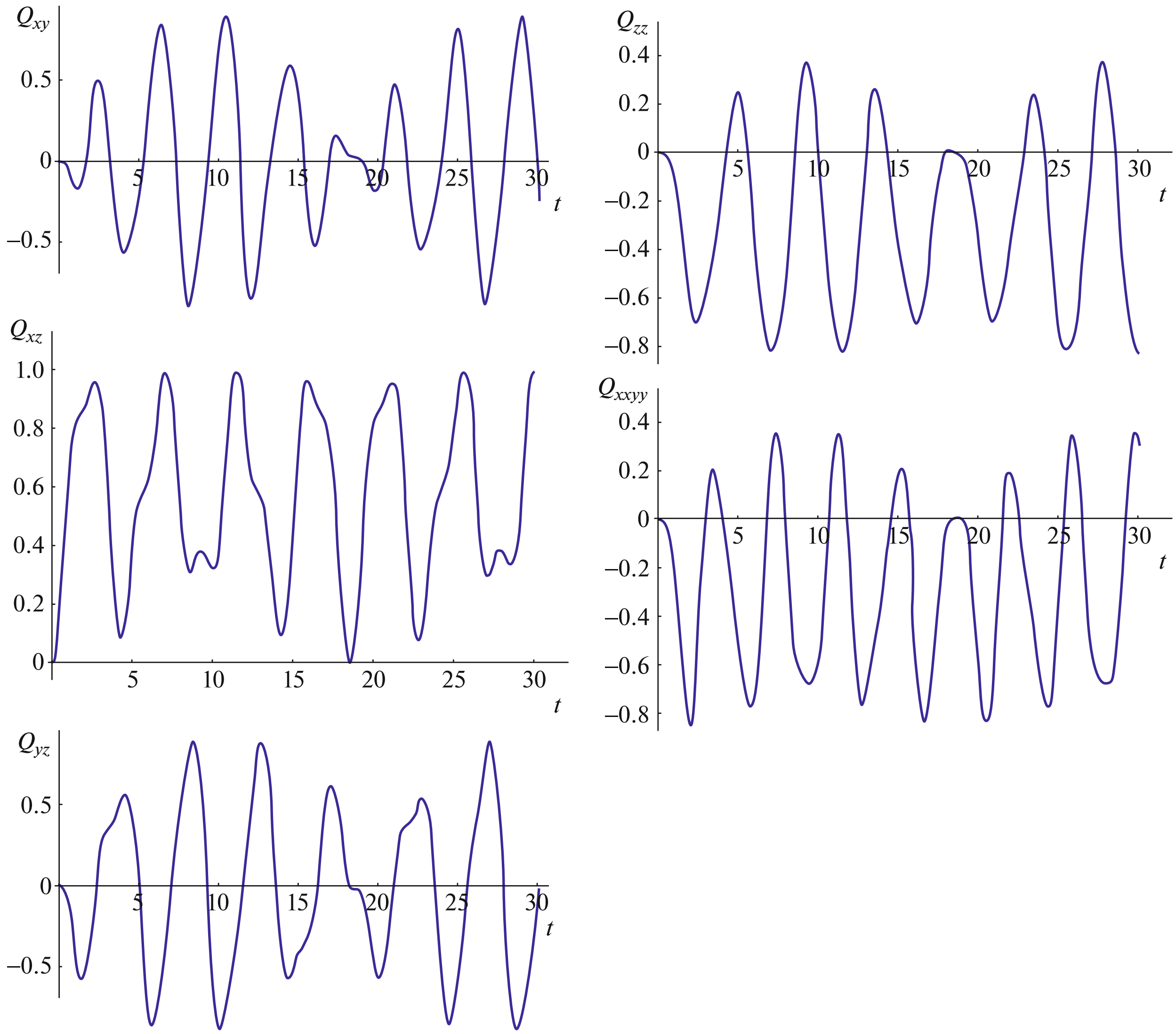

Fig. 4. Time dependences of the quadrupole moment of spins after a sudden application of an ac field. The initial spin state is considered the equilibrium state (6). Parameters of calculations: $\omega = \omega_0 + D$, $\omega_1 = 1$ G, and $D = 1$ G.

and $\omega_1/|D| \ll 1$, the motion of the magnetization vector is the Torry nutation with frequencies ω_1 and $\sqrt{2}\omega_1$, respectively, in a good approximation. When ω_1 and D are comparable, the motion of the spin is much more complicated. Figure 3 shows for illustration the calculated dependences of dipole moment (magnetization) projection of spin for $\omega_1 = 1$ G and $D = 1$ G.

The motion in this can be described by the Torry nutation only when the magnetization projections in a rotating coordinate system vary with time with a certain nutation frequency Ω_{nut} (see expression (12)) [1, 2].

The curves in Fig. 3 show that the spin dynamics cannot be described in any way with one frequency of oscillations of the spin moment projections. Figure 3 also clearly demonstrate that beats of frequency are manifested in the time dependence of projections. For the given specific set of parameters, the main contribution comes from two oscillations with different frequencies.

To demonstrate the reversible mutual conversion of the dipole and quadrupole spin moments in the nutation conditions, Fig. 4 shows the time dependence of the quadrupole moment components for the same values of parameters of the system, for which the time dependences of the dipole moment projections are given in Fig. 3.

Comparison of the time dependences of the dipole (see Fig. 3) and quadrupole (see Fig. 4) moments shows that for the chosen parameters with a period of about 1 μs, the mutual conversion of the dipole and quadrupole moments takes place.

The strong difference of the trajectory of the tip of the spin dipole moment vector in space for the given

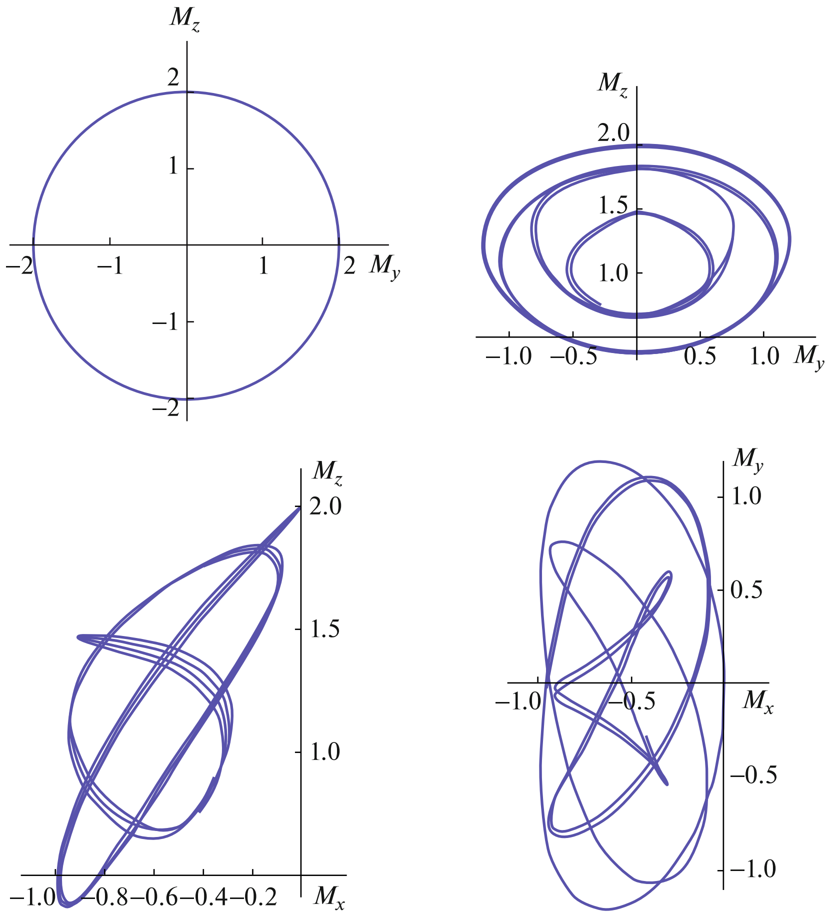

Fig. 5. Trajectories of the tip of the dipole moment vector in the projection onto different planes, which are plotted based on the time dependences from Fig. 3.

set of parameters, which has been obtained from the solution of Eq. (23), from the trajectory predicted by the Torry theory is clearly seen from the parametric curves of projections of these trajectories on different planes (Fig. 5) and the 3D representation (Fig. 6).

Figure 5 also shows for comparison the projection of the dipole moment onto the *yz* plane in the hypothetic case when the dipole moment projections onto the axes are given by Eqs. (12) that correspond to the Torry nutation; it is a circle (see the curve in the upper left panel). In the case of Torry nutation (12), the projection onto the *xy* or *xz* plane degenerate into a line on the *y* or *z* axis, respectively. The clearest idea of the motion of the dipole moment vector is given by its 3D representation (Fig. 6).

It should be noted that in the absence of zero field splitting (for $D = 0$), the Torry nutation is realized. It can clearly be seen from Figs. 3, 5, and 6 that the inclusion of splitting in zero magnetic field B_0 radically changes the trajectory of the tip of the spin dipole moment vector.

This is obvious. However, the results of calculations considered here lead to one more less obvious, but important observation. It turns out that not only the direction of the dipole moment vector, but also its length changes with time. Using the results represented in Fig. 3 and expression

$$M = \sqrt{M_x^2 + M_y^2 + M_z^2}$$

it is possible to calculate the length of this vector at any instant (Fig. 7). This figure shows that oscillations with at least two frequencies are manifested because the effect of oscillation beats is clearly seen.

The oscillations of the length of the dipole moment vector in the presence of splitting in zero field ($D \neq 0$) are explained by reversible transformations of the dipole and quadrupole moments, which are described by Eqs. (23).

The observed "nutation" of the magnetization vector depends on the initial state of spins. The numerical calculations considered above have been performed for the situation when the spins are in thermodynamic equilibrium at the instant of sudden ac field application (see expression (6)). However, as noted above, the spins can initially be in a nonequilibrium state. For example, in the case of photoexcitation of organic

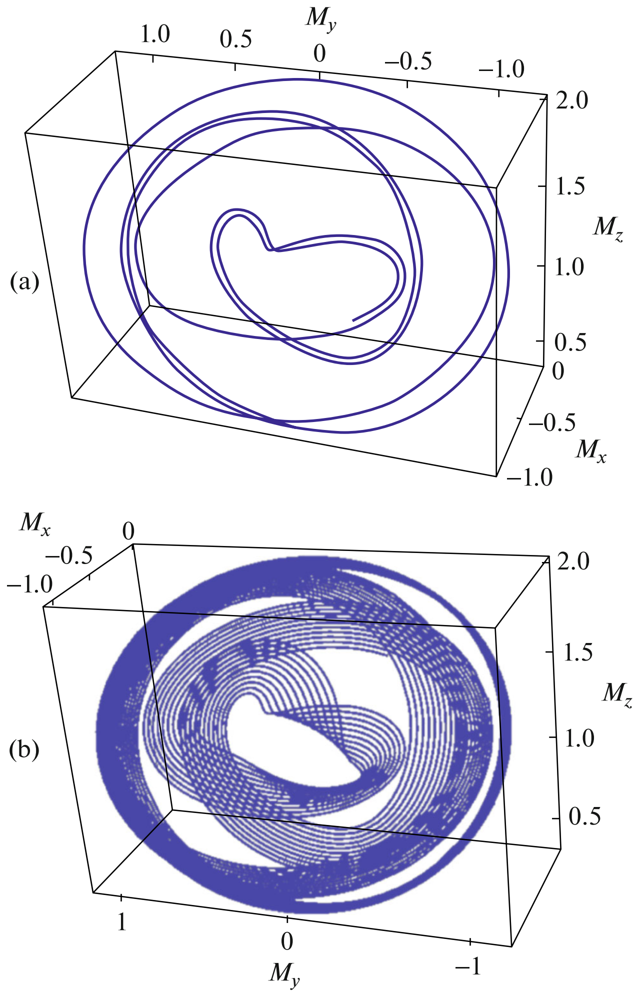

Fig. 6. Three-dimensional representation of the motion of the spin dipole moment vector for (a) t = 30 and (b) t = 200. Parameters of calculation are the same as in Fig. 3.

molecules, the molecules in the triplet excited state are often characterized by a large quadrupole spin moment [4, 5]. Solving Eqs. (3) for the initial state with a nonzero quadrupole spin polarization component, $\rho(0) = S_z^2$, we find the dipole moment projections. The results are shown in Fig. 8.

The results shown in Figs. 3 and 8 differ only in that they have been obtained for different initial states of spins. In the case depicted in Fig. 3, the spins have only dipole polarization at the initial instant, while in the case represented in Fig. 8, only the quadrupole polarization component differs from zero. It can be seen that the temporal behavior of the experimentally observed spin dipole moment depends very strongly on the initial state of spins. It can be observed that the z projection of the magnetization in Fig. 3 at the initial instant has the highest value, while in the conditions of Fig. 8, all projections of the dipole moment start from zero value. In both cases, the observed projection of the dipole moment is the sum of the contributions of oscillating terms. However, these oscillations with different frequencies can appear in the observable quantity with quite different amplitudes.

4. CONCLUSIONS

Analysis of the response of the spin system to a sudden application of an ac magnetic field ("nutation") makes it possible in principle to determine all magnetoresonance parameters of spins. The registration of "nutation" can be a convenient method for determining the total electron spins of paramagnetic particles. Despite the rich potential of this method, it is employed quite seldom (e.g., in EPR spectroscopy). This is probably due to the fact that the theory of "nutation" has not attracted sufficient attention. In

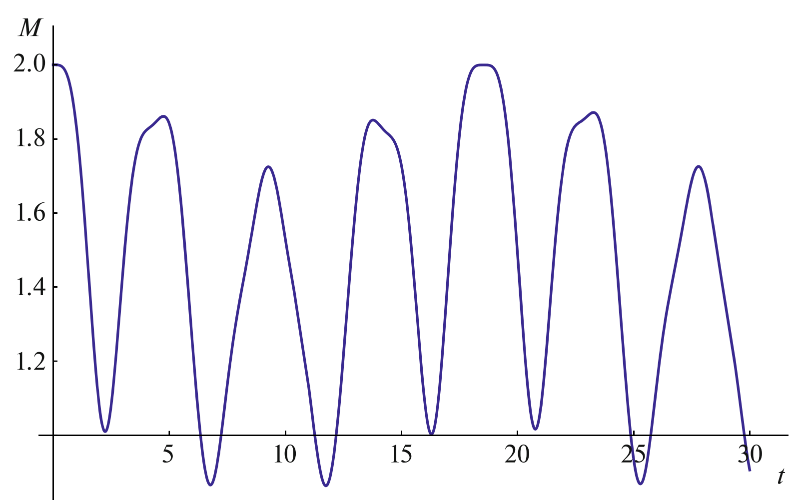

Fig. 7. Time dependence of the length of the dipole moment vector of spin magnetization $M = \sqrt{M_x^2 + M_y^2 + M_z^2}$. Parameters of calculation are the same as in Fig. 3.

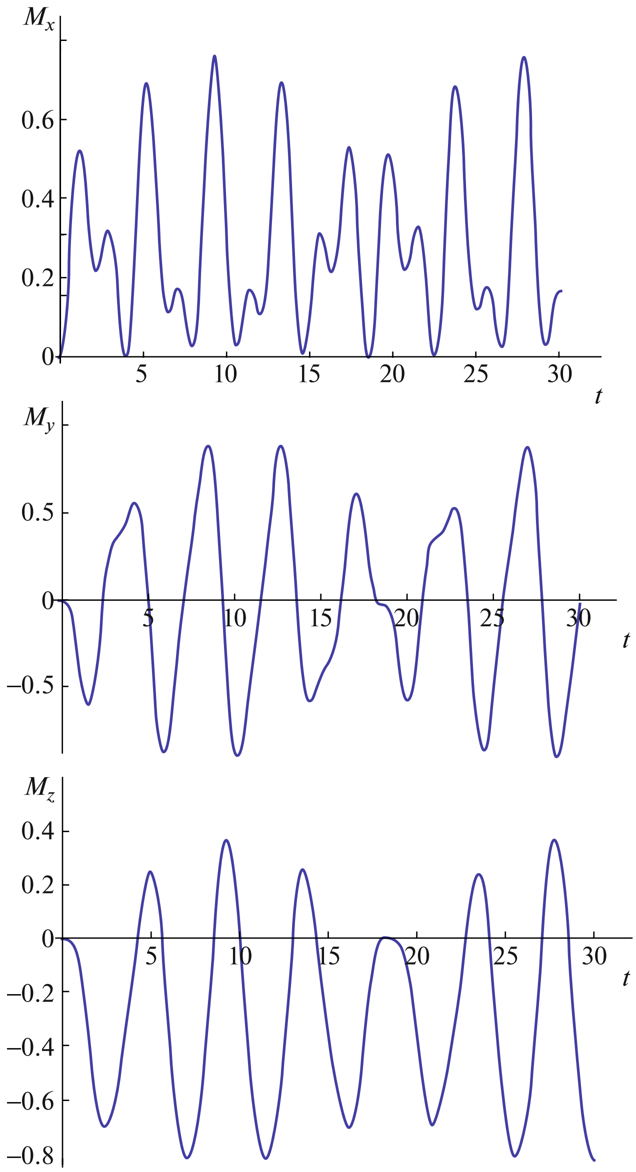

Fig. 8. Time dependences of the spin magnetization projections after the sudden application of an ac field. The initial state of spins is assumed to be $\rho(0) = S_z^2$. Parameters of calculations: $\omega = \omega_0 + D$, $\omega_1 = 1$ G, and $D = 1$ G.

fact, the present level of the theory of spin dynamics makes it possible to simulate numerically the expected "nutation" of spins in many cases.

This study was aimed at revealing some general features of the dynamics of spins during their "nutation." To simplify the problem, the effect of paramagnetic spin relaxation was not considered; attention was concentrated on analysis of the spin dynamics with account for the spin–spin interaction and the interaction of spins with an external ac magnetic field of an arbitrary intensity. Analysis was performed in two representations: using the quantum mechanics in the Schrödinger formulation and in the Heisenberg formulation. In the Schrödinger formulation, the complete description of the spin system is obtained using the wavefunction (or density matrix). According to Heisenberg, the state of the system is determined by the complete set of experimentally measurable physical quantities. Both approaches ultimately lead to completely identical results. However, at intermediate stages, these approaches operate with different concept using different "languages." Different approaches makes it possible to better understand the behavior of spins during their motion in different conditions (in particular, during "nutation").

The traditional quantum theory of "nutation" is constructed using the Schrödinger approach [5, 6, 13]. In this case, a complex nutation signal, which is the sum of the contributions oscillating with different frequencies, is interpreted as a manifestation of different one-quantum and multiquantum coherences. It is shown in this study that the Heisenberg approach makes it possible to obtain a different interpretation of a complex behavior of the "nutation" signal and gives a more visual description of the behavior of the observed signal. In experiments on "nutation," the measured quantity is one of the projections of the spin dipole moment. However, the spin dipole moments do not provide a full description of the spin state in a system of interacting spins. Apart from the dipole polarization of spins, the corresponding multipole polarizations (moments) of spins must be taken into account. When the spin–spin interactions have time to be manifested in the interval of transient "nutation" regime, apart from the proper nutation of the dipole moment in magnetic fields, periodic variations of the magnitude of the dipole moments are manifested in the time dependence of the magnetization due to reversible conversion of the dipole moment into multipole moments on the one hand and, on the other hand, periodic variations of the components of multipole moments can be observed.

The results of this study make it possible to formulate the following conclusions.

1, The Bloch equations cannot be used for describing "nutation" of interacting spins (including the splitting of the spin energy levels in zero magnetic field).

2. "Nutation" of the spin dipole moment with account for the spin–spin interaction cannot in principle be reduced to the Tory nutation.

3. "Nutation" of spins in the presence of the spin–spin interaction cannot be explained disregarding multipole spin moments.

4. For spin $S = 1$, the system of coupled linear differential equations for the projections of the dipole magnetic moment and the components of the quadrupole magnetic moment is obtained in explicit form. These equations clearly show that in the "nutation" conditions, reversible transformations of the dipole

moment (magnetization vector) and multipole moments of the spin system occur.

5. In "nutation" conditions, the length of the magnetization vector does not remain constant even with the disregard of paramagnetic relaxation.

In this study, an isolated systems of spins have been considered, in which the spin Hamiltonian parameters are preset constants, and the contribution of the paramagnetic relaxation to the motion of spins is not taken into account. Therefore, the results of this study are applicable above all to paramagnetic centers in solid matrices. These results pave new ways in the application of spin "nutation" for analysis of spin dynamics, in the development of pulsed EPR spectroscopy, and, in particular, in quantum calculations and quantum informatics, where electron spins are used as cubits.

ACKNOWLEDGMENTS

The author's interest in this problem was induced by experiments performed by his colleagues R.B. Zaripov, A.A. Sukhanov, and V.F. Tarasov at the Kazan Physico-Technical Institute. Thanks are also due to R.T. Galeev and A.G. Mar'yasov for numerous fruitful discussions.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. H. C. Torry, Phys. Rev. **76**, 1059 (1949).
2. R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Clarendon, Oxford, 1987).
3. I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).
4. A. V. Astashkin and A. Schweiger, Chem. Phys. Lett. **174**, 595 (1990).
5. A. Schweiger and G. Jeschke, *Principle of Pulse Electron Paramagnetic Resonance* (Oxford Univ. Press, Oxford, 2001).
6. S. S. Kim and S. I. Weissman, J. Magn. Reson. **24**, 167 (1976).
7. R. Furrer, E. Fujara, C. Lange, et al., Chem. Phys. Lett. **75**, 332 (1980).
8. R. Hanaishi, Ya. Ohba, K. Akiyama, et al., J. Chem. Phys. **103**, 4819 (1995).
9. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics,* Vol. 3: *Quantum Mechanics: Non-Relativistic Theory* (Pergamon, New York, 1977; Fizmatlit, Moscow, 2004).
10. R. Janssen and W. S. Veeman, J. Chem. Soc., Faraday Trans. 1 **84**, 3747 (1988).
11. G. M. Zhidomirov and K. M. Salikhov, Sov. Phys. JETP **29**, 1037 (1969).
12. D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (Nauka, Leningrad, 1975; World Scientific, Singapore, 1988).
13. H.-J. Stoeckmann and D. Dubbers, New J. Phys. **16**, 1 (2014).
14. K. M. Salikhov, F. S. Sarvarov, and R. Z. Sagdeev, Chem. Phys. **16**, 41 (1976).
15. K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, and A. L. Buchachenko, *Spin Polarization and Magnetic Effects in Radical Reactions* (Academic Kiado, Budapest; Elsevier, Amsterdam, 1984).

Translated by N. Wadhwa