Order Dependence of the Profile of the Intensities of Multiple-Quantum Coherences

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Abstract—A modification of the widespread phenomenological model theory of multiple-quantum (MQ) nuclear magnetic resonance spectra of a single cluster of correlated spins has been developed. In contrast to the mentioned theory, the size distribution of such clusters has been consistently taken into account. To obtain the distribution, solutions for the amplitudes of the expansion in the complete set of orthogonal operators are used. Expressions specifying the dependence of the profile of the intensities of MQ coherences on their number n (order) have been obtained. The total form of the dependence has been evaluated by means of the numerical implementation of the resulting expressions. The asymptotic expressions for large n values (wings of the spectrum) have been obtained analytically by the saddle-point method. It has been shown that the dependence under study has a Gaussian central part and exponential wings. The results obtained are in agreement with the previous calculations for some model systems and existing experimental data.

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1. INTRODUCTION

The rapid development of experimental methods of coherent multiple pulse nuclear magnetic resonance (NMR) spectroscopy of condensed matter at the end of the XX century resulted in the formation of multiple-quantum (MQ) NMR spectroscopy [1−3]. The main factors ensuring the remarkable success of this new field used in numerous applications are methods that were found in the process of development of multiple pulse NMR and appeared to be applicable for almost unlimited transformations of spin Hamiltonians ("spin alchemy").

A significant interest in applications of MQ spectroscopy is due, on one hand, to new possibilities of using these methods to study clusters, local structures, liquid crystals, etc. [4−6]. On the other hand, methods for quantum information processing are tested on nuclear spin systems by the methods based on MQ NMR and the control of MQ coherences are studied in order to create a quantum computer and to implement quantum calculations (see, e.g., [7, 8]). We note that such theoretical and experimental investigations are predominantly performed on systems with a comparatively small number of spins (tens spins) or on model systems, when computers provide successful studies of the multiquantum spectra and dynamics of a spin system [6, 9, 10]. At the same time, in recent, most developed works aimed at studying the behavior of large quantum registers, spin systems containing about 10^4 correlated nuclear spins were created [11−14].

It is noteworthy that MQ NMR methods thus allowed the first experimental observation of an increase in the number of correlated particles at the evolution of a multiple particle dynamic system, which is very important for general physics, e.g., for the development of the statistical mechanics of irreversible processes. The detailed theoretical studies of this kink began with works [15, 16] by the authors of Prigogine's "Brussels school" and, although in a more pragmatic aspect, with works [17−20] by Bogoliubov and his disciples in the process of development and application of two-time Green's function methods.

All particular implementations of multiquantum spectroscopy [1−5, 11−14] involve the irradiation of a spin system by a sequence of radiofrequency pulses, which transform its spin−spin interaction Hamiltonian to a nonsecular (with respect to the equilibrium magnetization) Hamiltonian transferring the initial magnetization to various time correlation functions with a quite complex structure of the product of different numbers (K) of spin operators (multispin correlations). In other words, the equilibrium density matrix ρ_{eq} in a strong magnetic field is transformed to a nonequilibrium density matrix, which is conveniently represented in the form of the sum of off-diagonal elements ρ_n with a certain difference of n magnetic quantum numbers, which are called MQ coherences (n is the order of coherence):

$$\rho(t) = \exp\{iHt\}\rho_{eq}\exp\{-iHt\} = \sum_n \rho_n^0(t). \quad (1a)$$

Here,

$$\rho_n^0(t) = \sum_{K=n}^{K=N} \sum_p g_{Knp}(t)|Knp\rangle,$$

where $|Knp\rangle$ is the basis operator in which K single-spin operators form products coupling Zeeman states differing in n. The index p enumerates different basis states with the same K and n values and N is the total number of spins in the system. The appearing coherences are marked by the phase shift φ proportional to the time. The appearing phase shift is proportional to $n\varphi$, where n is an integer. Thus, K-spin correlations are distinguished in the number of quanta n ($n \leq K$) [1–3]. Then, the system is subjected to a new pulse sequence, which changes the sign of the mentioned nonsecular Hamiltonian, and, thus, "time reversal" is ensured [21, 22]; i.e., the system evolves "backward." The observation of the dependence on the evolution time and phase φ makes it possible to construct one- or two-dimensional Fourier spectrum.

In usual MQ experiments, K-spin correlations are marked by the phase shift about the z axis, i.e., are sorted in terms of the number of quanta in the basis in which the z components of spin operators are diagonal (below, the z basis). However, as was shown in [14], they can also be marked by the phase shift appearing at the rotation about other axes, i.e., x. Such experiments provided additional information in the case of the nonsecular effective Hamiltonian. It is particularly important that the measurement of coherences in the basis different from the convenient z basis makes it possible to study spin dynamics under the action of the Hamiltonian conserving the z projection. Thus, multiple spin dynamics in the process of free induction decay (FID) in NMR of a solid, which is caused by the secular part of the dipole−dipole interaction, was observed in [14] and other works in the x basis. A qualitatively similar picture of the time development of multispin correlations was observed in all bases.

The most important characteristics of MQ spectroscopy necessary both for applied (e.g., structure) studies and for the understanding of the physics of irreversible processes are the time dependences of the amplitudes of MQ coherences, which determine in turn the distributions of the intensities of coherences of various orders in the MQ spectrum. With the use of the simplest statistical model [2], a Gaussian shape for the distribution of coherences of various orders is empirically taken in experiments:

$$g_n(\tau) \sim \mathrm{Tr}\{\rho_n(\tau)\rho_{-n}(\tau)\} \sim \exp\left(-\frac{n^2}{N(\tau)}\right). \qquad (1)$$

The variance of the distribution in this model ($N(\tau)/2$) is determined by the number of spins $N(\tau)$ between which dynamic correlation is established in the preparation time τ owing to the dipole−dipole interaction. This number, which is called the number of correlated spins or the effective size of the cluster, increases with the preparation time τ. However, it is noteworthy that the experimentally observed dependences are often not described by Eq. (1) (see, e.g., [23, 24]). At the same time, the order dependence of the intensities of MQ coherences is the most important characteristic of their dynamics. The absence of an adequate theory of this dynamics and understanding of the main characteristics of such phenomena suppresses the further development of experimental studies: prior information on the indicated dependence would make it possible, e.g., to study a larger number of correlated spins (larger quantum registers).

In this work, the corresponding theory describing the profile of the intensities of MQ coherences as a function of the order is formulated for crystals with a quite large number of approximately equivalent neighbors surrounding any spin in the lattice. We note that most of the usual solids satisfy this condition.

2. HAMILTONIAN AND MAIN EQUATIONS FOR CORRELATION FUNCTIONS

The secular part of the nuclear dipole−dipole interactions in nonmetallic diamagnetic solids, which is exclusively responsible for the dynamics of the spin system consisting of light nuclei such as protons or ^{19}F nuclei, under the NMR conditions has the form [25]

$$H = \sum_{i>j}\left\{\frac{3}{2}b_{ij}S_{zi}S_{zj} - \frac{1}{2}b_{ij}\mathbf{S}_i\mathbf{S}_j\right\} = H_{zz}^0 + H_{ex}$$

$$= \sum_{i>j}\left\{b_{ij}S_{zi}S_{zj} - \frac{1}{4}b_{ij}(S_i^+S_j^- + S_i^-S_j^+)\right\} = H_{zz} + H_{ff}, \qquad (2)$$

where

$$b_{ij} = \frac{\gamma^2\hbar(1 - 3\cos^2\theta_{ij})}{2r_{ij}^3},$$

$\mathbf{r}_{ij}$ is the vector connecting the ith and jth spins, θ_{ij} is the angle between the vector $\mathbf{r}_{ij}$ and a static external magnetic field, and $S_{\alpha i}$ is the α component ($\alpha = x, y, z$) of the vector spin operator at the ith site. Here and below, the energy is expressed in frequency units.

In traditional experiments using magnetic resonance, the spin temperature is usually much higher than the energy of the Zeeman and other interactions in the spin system. In view of this circumstance, we study, as usual, the time correlation function in the high-temperature approximation. The equilibrium high-temperature density matrix in a strong static magnetic field H_0 is given by the expression [25]

$$\rho_0 \propto 1 + \frac{\gamma\hbar H_0}{kT}\sum_{j=1}^{N}S_{zj},$$

where k is the Boltzmann constant, T is the temperature, and N is the total number of spins in the sample.

We note that Hamiltonian (2) is the basis for spin alchemy and is transformed under the action of radiofrequency pulses to other Hamiltonians, which are of interest for study. For example, traditional MQ NMR [1–3] is usually described by the effective Hamiltonian

$$H_{eff} = (-1/4)\sum_{i \neq j} b_{ij}(S_{+i}S_{+j} + S_{-i}S_{-j}). \quad (3)$$

However, a number of measurements (see, e.g., [14]) of the intensities of coherences of various orders in the multiquantum spectrum as functions of the time were performed for samples with the usual dipole–dipole Hamiltonian given by Eq. (2). It was demonstrated that the behavior of systems described by Hamiltonians (2) and (3), as well as by other Hamiltonians appearing, e.g., by means of multiple pulse narrowing of the NMR spectrum, is the same [12, 14]. This coincidence is due to the adequacy of the conditions for the applicability of the central limit theorem of probability theory, at least for clusters containing a large number of correlated spins K [26]. In view of the mentioned circumstance, all calculations in this work are performed with Hamiltonian (2) in order to avoid too long expressions.

As is known [25], FID appearing after the application of a $\pi/2$ pulse to the equilibrium nuclear spin system is proportional to the time correlation function defined in the reference frame rotating with the Larmor frequency by the expression

$$A_0(t) = \frac{Tr\{S_x(t)S_x\}}{Tr\{S_x^2\}} = \frac{Tr\{S^+(t)S^-\}}{Tr\{S^+S^-\}},$$

$$A_0(t) = \sum_{n=0}^{\infty} i^{2n}\frac{M_{2n}}{2n!}t^{2n}. \quad (4)$$

Here, $\{M_n\}$ are the moments, i.e., the coefficients in the expansion in the time power series of the FID; since the temperature is very high as compared to the nuclear dipole–dipole interaction, only even-order moments are nonzero; and $S_x = \sum_{i=1}^{N} S_{xi}$ is the total x component of the spin of the system. The dependence $S_x(t)$ is determined by the Heisenberg equation

$$dS_x/dt = i[H, S_x] = iLS_x,$$

where L is the Liouville operator and N is the total number of nuclear spins in the sample. As was shown in [27], the problem of calculating FID (3) is completely equivalent to the solution of almost infinite (dimension on the order of 10^{23}) system of differential equations:

$$\dot{A}_0(t) = v_0^2 A_1(t),$$

$$\dot{A}_1(t) = A_0(t) - v_1^2 A_2(t),$$

$$\dots \quad (5)$$

$$\dot{A}_n(t) = A_{n-1}(t) - v_n^2 A_{n+1}(t),$$

$$\dots$$

with the initial conditions $A_0(0) = 1$, $A_n(0) = 0$, $n \geq 1$. The functions $\{A_j(t)\}$ are "multicommutator" (multiple particle) time correlation functions [27]:

$$A_j(t) = \frac{\langle j|S_x(t)\rangle}{\langle j|j\rangle},$$

$$|j\rangle = (i)^j L^j|0\rangle - (i)^j \sum_{k=0}^{j-1} \frac{\langle k|L^j|0\rangle}{\langle k|k\rangle}|k\rangle, \quad (5a)$$

$$|0\rangle = |S_x(0)\rangle.$$

Here, the jth power of the Liouville operator traditionally means the calculation of j commutators:

$$L^j = \underbrace{[H, [H, \dots[H, \dots]]]}_{j}.$$

In the above expressions, the angular brackets mean the statistical average, which in the accepted high-temperature approximation means the calculation of trace [25, 27]. The parameters $\{v_n^2\}$, which determine the solution of the system, are unambiguously related to the moments of the absorption line [27]: $v_n^2 = D_{n-1}D_{n+1}/D_n^2$ and $\{D_n\}$ are the determinants having the form

$$D_n = \begin{vmatrix} 1 M_1 \dots M_n \\ M_1 M_2 \dots M_{n+1} \\ \dots \\ M_n M_{n+1} \dots M_{2n} \end{vmatrix}.$$

For convenience, we present the expressions for several first coefficients:

$$D_{-1} = D_0 = 1, \quad D_1 = M_2,$$

$$D_2 = M_2(M_4 - M_2^2),$$

$$D_3 = (M_4 - M_2^2)(M_2M_6 - M_4^2),$$

$$v_0^2 = M_2 = \frac{9}{4}\sum_j b_{ij}^2, \quad v_1^2 = \frac{M_4 - M_2^2}{M_2},$$

$$v_2^2 = \frac{M_2M_6 - M_4^2}{(M_4 - M_2^2)M_2}.$$

Here and below, we set the nuclear spin $S = 1/2$ without restriction of generality [28].

The experimentally observed intensity of MQ coherences is determined by the time correlation function:

$$\Gamma_\varphi(t, \tau) = \frac{\mathrm{Tr}\{U^+(\tau)\,U_\varphi U(t)\,S_x U^+(t)\,U_\varphi^+ U(\tau)\,S_x\}}{\mathrm{Tr}\{S_x^2\}}. \quad (6)$$

Here, $U(t)$ is the operator of evolution with the Hamiltonian of the internal interaction H from Eq. (2) (or this interaction transformed by radiofrequency pulses to a certain new nonsecular effective Hamiltonian, e.g., H_{eff} from Eq. (3)) and $U_\varphi = \exp(i\varphi S_x)$ is the operator of rotation by the angle τ about the x axis. For generality, we introduce the notation τ for evolution in "reverse time." Below, we set $t = \tau$ and $\Gamma_\phi(t) \equiv \Gamma_\phi(t, t)$ according to the experimental conditions.

The direct calculation of four-spin time correlation functions in Eq. (6) is a very difficult and cumbersome problem, which is also significantly complicated by the necessity of an additional Fourier transform for the determination of desired amplitudes:

$$g_n(t) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\phi \exp(in\phi)\Gamma_\phi(t).$$

In view of the mentioned circumstances, the indicated problem was solved only for certain specific models [6, 9, 10, 29], which have exact solutions. Even in these situations, numerical calculations were often necessary for obtaining the final result.

3. EXPANSION OF TIME CORRELATION FUNCTIONS IN THE COMPLETE SET OF ORTHOGONAL OPERATORS AND INTENSITIES OF MULTIPLE-QUANTUM COHERENCES

In [29], we solved the problem under discussion for the exactly solvable model with an infinite radius of interaction ($b_{ij} = b = $ const for all i and j values in Hamiltonian (2)). In [30], we calculated only the second derivative with respect to φ at $\varphi = 0$ in Eq. (6), i.e., the second moment of time correlation function (6), which presents the total rate of an increase in the number of correlated spins in a MQ experiment as a function of the time. To solve this very difficult and cumbersome problem, the leading sequences of contributions (diagrams) were separated in the expansion of the four-spin correlation function in the power series of time and were summed in the approximation of lattices of a large spatial dimension (the dimension of space is $d \longrightarrow \infty$). To solve the problem formulated in the Introduction, we use the analysis of the amplitudes of the expansion of $S_x(t)$ in the complete set of orthonormalized operators (5a) [27]:

$$S_x(t) = \sum_{j=0}^{\infty} A_j(t)|j\rangle. \quad (7)$$

Such expansions were often used in nonequilibrium statistical mechanics and previously (see, e.g., [30–35]) to describe various time correlation functions. It is easy to see that Eq. (7) can be represented in the form of the sum of operators such that each term of this sum refers to a cluster with K spins (cf. Eq. (1a)):

$$S_x(t) = \sum_{K=1}^{\infty} \rho_K(t). \quad (8)$$

We note that contributions to the orthogonal operator with the number j in Eq. (7) can obviously contain maximum $j + 1$ spin operators and, correspondingly, $j + 1$ summation indices over the lattice [30]. Indeed, the transition from the operator $|j-1\rangle$ to the operator $|j\rangle$ by commutation with Hamiltonian (2), which results in the addition of no more than one spin operator (lattice index) in each step. The operator $|j\rangle$ obviously contains contributions with a smaller number of spins (lattice indices). Therefore, if $j \geq K$, this vector can also make contributions to the K-spin cluster. However, these contributions can be neglected because they are small. Indeed, they increase at small times as tj. At large times ($t > T_2 = 1/M_2^{1/2} \propto 1/Z^{1/2}$, where Z is the number of approximately equivalent nearest neighbors), the functions $A_j(t)$ decrease rapidly. Consequently, their amplitude decreases as $A_j(t) \sim Z^{-j/2}$ with an increase in the number. Thus, comparison of Eqs. (7) and (8) indicates that, at least for systems where the number of neighbors is large,

$$\rho_K(t) \approx A_{K-1}(t)|K-1\rangle. \quad (9)$$

The substitution of Eq. (8) into time correlation function (6) gives

$$\Gamma_\varphi(t) = \frac{\mathrm{Tr}\left\{U_\varphi \sum_K \rho_K(t) U_\varphi^+ \sum_j \rho_j(t)\right\}}{\mathrm{Tr}\{S_x^2\}}. \quad (10)$$

Since Eq. (9) is valid for a large number of equivalent nearest neighbors (see [30]), only terms with $K = j$ retain in Eq. (10), because the rotation operator U_φ does not change the number of spin operators in the vector. As a result,

$$\Gamma_\varphi(t) = \sum_K \Gamma_{\varphi, K}(t), \quad (11a)$$

where

$$\Gamma_{\varphi, K}(t) = \frac{\mathrm{Tr}\{U_\varphi \rho_K(t) U_\varphi^+ \rho_K(t)\}}{\mathrm{Tr}(S_x^2)}. \quad (11)$$

At $\varphi = 0$, we obtain

$$P(K, t) = \Gamma_{0, K}(t) = \frac{A_{K-1}^2(t)\langle K-1||K-1\rangle}{\mathrm{Tr}(S_x^2)}, \quad (12)$$

and the condition

$$\Gamma_{\varphi=0}(t) = \sum_{K=1}^{\infty} \Gamma_{\varphi=0,K}(t) = \sum_{K=1}^{\infty} P(K,t) = 1$$

is satisfied. A new notation was introduced in Eq. (12) in order to emphasize that $P(K,t)$ is in essence a distribution in the number of clusters with K spins. The substitution of $\rho_K(t)$ (9) in the form of the sum with certain orders of coherence,

$$\rho_K(t) = \Sigma_n \rho_{Kn}(t), \quad \text{where}$$

$$\rho_{Kn}(t) = A_{K-1}(t)|K-1\rangle_n,$$

into Eq. (11) yields

$$\Gamma_{\varphi,K}(t) = \sum_n \frac{\text{Tr}\{\exp(i\varphi n)\rho_{Kn}(t)\rho_{K(-n)}(t)\}}{\text{Tr}(S_x^2)}$$

$$\tag{13}$$

$$= \Gamma_{0,K}(t)\sum_n \exp(i\varphi n)g_{Kn},$$

where

$$g_{Kn} = \frac{\langle K-1|K-1\rangle_n}{\langle K-1|K-1\rangle}. \tag{14}$$

It is taken into account in Eq. (13) that the contribution to the trace from the terms where the coherence of the second operator differs from $-n$ is zero. Thus, Eq. (13) specifies the required Fourier series where the coefficients are the desired intensities of the multi-quantum coherences.

Following the traditional phenomenological model [1, 2], we take Gaussian shape (1) for the distribution of coherences of various orders of the cluster with K spin in the form

$$g_{Kn} = \frac{1}{\sqrt{\pi K}}\exp\left(-\frac{n^2}{K}\right). \tag{15}$$

Thus, taking into account Eqs. (11a) and (13), we obtain

$$g(n,t) = \sum_K \Gamma_{0,K}(t)g_{Kn}. \tag{16}$$

The substitution of Eqs. (12) and (15) into Eq. (16) gives the final expression

$$g(n,t) = \sum_{K=1}^{\infty} \frac{1}{\sqrt{\pi K}}\exp\left(-\frac{n^2}{K}\right)P(K,t). \tag{17}$$

4. ORDER DEPENDENCE OF THE INTENSITY OF MULTIPLE-QUANTUM COHERENCES

According to Eq. (17), to calculate the profile of coherences as functions of the order, it is necessary to determine the distribution function in the number of clusters with K spins, $P(K,t)$, or, according to Eq. (12), the amplitudes $A_j(t)$ and parameters $\{v_j^2\}$. The exact calculation of these parameters is very difficult and was performed only for several simple model systems. For the general case, the authors of [33, 36] presented only the relation between the shape of the wing of the Fourier spectrum of the time correlation function $A_0(t)$,

$$\Phi(\omega) \propto \exp\{-|\omega/\omega_0|^{2/\lambda}\} \tag{18}$$

and the dependence of the parameters $\{v_j^2\}$ on their number j,

$$v_j^2 \propto \omega_0^2 j^{\lambda}. \tag{19}$$

Here, the growth rate λ [33, 36] characterizes the average asymptotic growth of the sequence $\{v_j^2\}$ and ω_0 is the frequency unit in the model under consideration [33, 36]. The corrections to Eq. (19) with smaller exponents are responsible for the form of the pre-exponential factor in Eq. (18).

The experimental measurements showed that the wings of the NMR spectra and the spectra of other correlation functions in crystals [37−41] are well described by a simple exponential corresponding to $\lambda = 2$ in Eq. (18). At the same time, a quadratic dependence of parameters (19) was obtained from the first eight known moments in [36, 42]. Finally, for the case $\lambda = 2$, the theory developed in [30] predicts the exponential growth of the average size of the cluster of correlated spins with the time, which is in good agreement with the results of the MQ experiments [11−14, 24].

The theoretical correlation functions with the simple exponential wings of the spectrum were obtained in the self-consistent fluctuating field approximation, which is a development of Anderson's statistical theory [25]. Anderson demonstrated that the fluctuating resonance frequency of the spin at a large number of neighbors can be described by a Gaussian random process. On the basis of this property, Blume and Hubburd [43] proposed the following equation for a paramagnetic spin system with the isotropic Heisenberg interaction:

$$\Gamma_1(t) = \exp\left\{-\int_0^t (t-\tau)\Gamma_1(\tau)d\tau\right\}, \tag{20}$$

where

$$\Gamma_1(t) = \Gamma_x(t) = \Gamma_y(t) = \Gamma_z(t),$$

$$\Gamma_\alpha(t) = \frac{\text{Tr}\{S_{\alpha i}(t)S_{\alpha i}\}}{\text{Tr}\{S_{\alpha i}^2\}}, \quad \alpha = x,y,z, \tag{21}$$

are the autocorrelation functions of different projections of one of the spins, which coincide with each other because the Hamiltonian is isotropic. The time in Eq. (20) and formulas below in this section is measured in units of the inverse square root of the second moment of the function $A_0(t)$. Equation (20) physically means that the spin rotates in a time-dependent local field produced by surrounding spins; the correlation function of this spin is expressed in terms of the

autocorrelation functions of individual spins. Equation (20) has the simple solution

$$A_0(t) = \frac{1}{\cosh^2(t/\sqrt{2})}, \qquad (22)$$

whose Fourier transform has the form

$$\Phi(\omega) = \frac{1}{\sinh(\pi\omega/\sqrt{2})}. \qquad (23)$$

It is easy to see that the continuation of $A_0(t) = \Gamma_1(t)$ (5) in the complex plane of the variable t has second-order poles at the points of the imaginary axis satisfying the condition

$$t_k = \frac{i\pi(2k+1)}{\sqrt{2}}, \quad k = 0, \pm 1, \pm 2, \dots . \qquad (24)$$

The Hamiltonian of the secular part of the dipole–dipole interaction given by Eq. (2) is anisotropic with respect to the spin components parallel and perpendicular to the direction of the external magnetic field. In the self-consistent fluctuating field approximation, the autocorrelation functions $\Gamma_\alpha(t)$ of these spin components are described by equations of different forms. The first variant of such equations was derived in [44]. In [45], it was shown that the self-consistent fluctuating field approximation is exact in the limit of infinite-dimensional lattices, $d \longrightarrow \infty$, and self-consistent equations were refined. It was established that the nearest singular points of their solutions are second-order poles and their coordinates in the imaginary-time axis were found [37, 45]. At the transition from infinite-dimensional lattices to three-dimensional lattices, the coordinates of singular points increase owing primarily to strong correlation in the motions of neighboring spins; as a result, multiple interactions of neighboring spins and loops of couplings should be taken into account in lattice sums for moments. The found singular points determine the exponential wings of correlation functions. The results of calculation of the corresponding corrections to the coordinate of a singular point [46] demonstrated good agreement with the experimental wing of the NMR spectrum [40].

Since the dipole–dipole interaction is a long-range interaction, we developed a physically more transparent method to take into account strong correlations in the motion of nearby spins [47–50]. The region around any spin is separated into two regions: nearby and remote spins. The nearby spins form the so-called "cell," where the number of spins depends on the orientation of the crystal in the magnetic field [47, 48]. The function $A_{0(\text{int})}(t)$, which well describes the oscillations of FID [51] responsible for the central part of the NMR spectrum, was found with allowance for the correlated motion of the spins of the cell. Motions of remote spins are assumed independent of the spins of the cell; as a result, the total free precession relaxation can be written as the product of contributions from two regions [47]:

$$A_0(t) = A_{0(\text{int})}(t)A_{0(\text{ext})}(t), \qquad (25)$$

where

$$A_{0(\text{ext})}(t) = \exp\left\{-a^2\int_0^t (t-\tau)k(\tau)d\tau\right\} \qquad (26)$$

is the FID component that is caused by the spins of remote environment and is described within Anderson's statistical theory [25]. The motion of each spin of the remote environment is in turn determined predominantly by the interaction of the spin with the spins in the same cell, and the correlation function of the field from remote spins $k(t)$ can be self-consistently expressed in terms of the autocorrelation functions of spins. Consequently, function (26) ensures the correct wings of the NMR spectrum and an unlimited increase in parameters (19) with $\lambda = 2$, whereas the oscillating function $A_{0(\text{int})}(t)$ determined by the spins of the cell has a finite spectrum and the corresponding parameters ν_j cease to increase (are frozen) beginning with a certain number [35, 49, 50].

A linear increase in parameters (19) with $\lambda = 1$,

$$\nu_j^2 = (j+1)\nu_0^2, \qquad (27)$$

corresponds to Gaussian frequency dependence (18). Such a situation occurs in an exactly solvable model with a fixed dipole–dipole coupling constant independent of the angles and distances (van der Waals model) for which it was found [29]:

$$A_0(t) = \exp(-t^2/2). \qquad (28)$$

Furthermore, a Gaussian dependence was found for the autocorrelation function of the transverse spin components in an xx chain of spins [52]. In this case, the autocorrelation functions of the z component in the chain are described by the Bessel functions and have a limited spectrum and "frozen" parameters ν_j.

We now analyze the profiles of MQ spectra corresponding to different cases of an increase in parameters (19). As was shown above, a quadratic increase is characteristic of real systems. Unfortunately, analytical solutions are unknown for equations for autocorrelation functions in the case of the anisotropic dipole–dipole interaction; for this reason, for analysis, we take function (22) with the known amplitudes [34]

$$A_j(t) = \frac{1}{\cosh^2(t/\sqrt{2})}\frac{\tanh^j(t/\sqrt{2})}{j!} \qquad (29)$$

and parameters

$$\nu_j^2 = (j+1)(j+2)\nu_0^2. \qquad (30)$$

Taking into account normalization (see Eq. (12)), we find

$$P(K,t) = \frac{(\tanh^2(t/\sqrt{2}))^{K-1}K}{\cosh^4(t/\sqrt{2})}. \qquad (31)$$

To derive Eq. (31), we used the general relation [27]

$$\frac{\langle K-1||K-1\rangle}{\mathrm{Tr}(S_x^2)} = \prod_j^{K-2} v_j^2. \tag{32}$$

The substitution of Eq. (31) into Eq. (17) gives

$$g(n, t) = \sum_{j=0}^{\infty} P(j+1, t)\frac{\exp\{-n^2/(j+1)\}}{\sqrt{2\pi(j+1)}}$$

$$\approx \int_0^{\infty} dj\, P(j+1, t)\frac{\exp\{-n^2/(j+1)\}}{\sqrt{2\pi(j+1)}}. \tag{33}$$

We note that, since summation in Eq. (33) begins with zero rather than with unity, the number K is replaced by $j + 1$. The beginning of summation with zero allows the transition to the "traditional" form of integral in Eq. (33).

Although sums in Eqs. (33) can be quite simply calculated numerically (the results will be presented below), the approximate replacement of the sum by an integral, which is valid at least for large K values, was performed to obtain an analytical estimate of Eq. (33). This estimate can be obtained by the saddle-point method [53]. Thus, for the case under consideration, we find the exponential shape of the wings of the MQ spectrum as a function of the order of coherence:

$$g(n, t) \propto \frac{\bar{K}(n^2/2)^{1/2}}{\cosh^4(t/\sqrt{2})} \exp(-2|n|/\sqrt{\bar{K}}). \tag{34}$$

Here, $\bar{K} = \sinh^2(t/\sqrt{2})$ is the average size of a cluster of correlated spins.

As the second example with a quadratic increase in parameters (19), we take the function

$$A_0(t) = \frac{1}{\cosh(t)}, \tag{35}$$

for which

$$P^{(1)}(K, t) = \frac{(\tanh^2(t))^{K-1}}{\cosh^2(t)}. \tag{36}$$

The substitution of Eq. (36) into Eq. (17) yields

$$g^{(1)}(n, t) \approx \sum_{j=0}^{\infty} P^{(1)}(j+1)\frac{\exp\{-n^2/(j+1)\}}{\sqrt{2\pi(j+1)}}$$

$$\approx \int_0^{\infty} dj\, P^{(1)}(j+1)\frac{\exp\{-n^2/(j+1)\}}{\sqrt{2\pi(j+1)}}. \tag{37}$$

The saddle-point method gives the following estimate for Eq. (37):

$$g^{(1)}(n, t) \propto \frac{(\bar{K}/2)^{1/2}}{\cosh^2 t} \exp\left(-\frac{2|n|}{\sqrt{\bar{K}}}\right), \tag{38}$$

i.e., the dependence on n is exponential, as in the preceding case. Here, $\bar{K} = \sinh^2(t)$.

Finally, we obtain the corresponding estimate for the Gaussian case given by Eqs. (27) and (28) for which

$$A_j(t) = \frac{t^j}{j!}\exp\left(-\frac{t^2}{2}\right), \tag{39}$$

$$P^{(2)}(K, t) = \frac{t^{2(K-1)}}{(K-1)!}\exp(-t^2). \tag{40}$$

The MQ spectrum $g^{(2)}(n, t)$ is given by Eq. (37) with the corresponding replacement of $P^{(1)}$ by $P^{(2)}$. Then, the saddle-point method for large K values gives

$$g^{(2)}(n, t) \propto \frac{1}{\exp(t^2)}\exp\left\{-\frac{2|n|}{1+1/\ln(|n|/\bar{K})}\right.$$

$$\left. -0.5|n|\left[1+\frac{1}{\ln(|n|/\bar{K})}\right]\ln\frac{|n|}{2e\bar{K}}\right\} \tag{41}$$

where the dependence $\exp(-0.5|n|\ln|n|)$ is not exponential, but is very close to exponential. Here, $\bar{K} = t^2$.

The numerical calculations allowed the determination both of the error at the replacement of summation in Eqs. (33) and (37) by integration and of n values at which a transition to an exponential asymptotic behavior occurs. For each of three above functions $(1/\cosh^2(t/\sqrt{2})$, $1/\cosh t$, and $\exp(-t^2/2))$, the calculations were performed for three times, 0.2, 1, and 3, in units of the inverse square of the second moment. Some of the results of the calculations are shown in Figs. 1−3. We note that sums are adequately approximated by integrals in all cases, but it is noteworthy that the best agreement was reached at large values of the time parameter. This also refers to the transition of the spectrum to the asymptotic exponential regime.

5. DISCUSSION OF THE RESULTS

According to the analytical and numerical calculations, the order dependence of the profile of the intensities of MQ coherences has a Gaussian central part and quite rapidly approaches exponential wings (see Fig. 2). A similar dependence was predicted for some model systems, e.g., nanopores [6, 10] and for the exactly solvable model with an infinite radius of interaction [29, 54]. The exponential wings of the MQ spectrum as a function of the order were apparently observed in experimental works [23, 24].

The above consideration indicates that spins of the remote environment of any individual spin are fundamentally responsible for the formation of the wings of the spectrum of interest. The main processes are certainly developed because of complex perturbations in the cell of each spin; the consequence of these perturbations is the appearance of rapidly grown phase (apparently) correlations involving large spatial regions of the crystal, which in turn ensures, in partic-
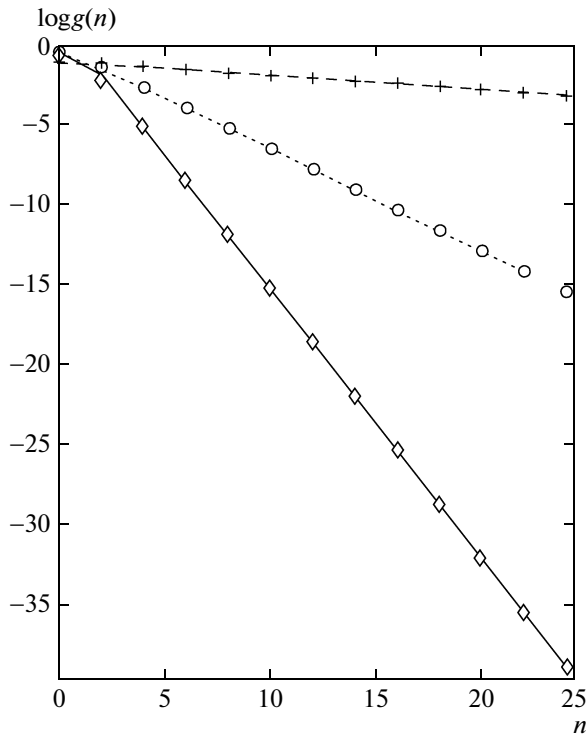
Fig. 1. Numerical results obtained with integration and summation in Eqs. (33) and (37). The solid line and diamonds are obtained with summation and integration in Eq. (33), respectively, for a time of 0.2 in units of the square root of the second moment. The dotted line and circles are obtained with summation and integration in Eq. (37), respectively, for a time of 1. The dashed line and crosses are obtained with summation and integration in Eq. (37), respectively, for a time of 3.
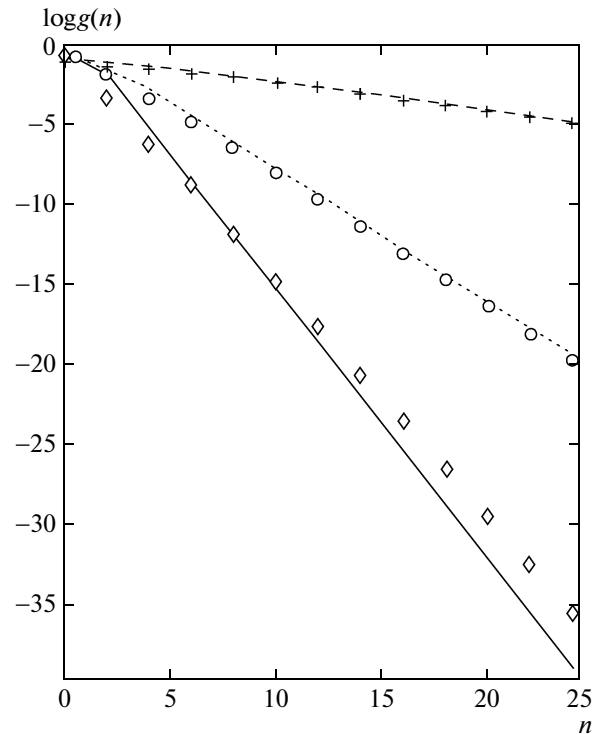
Fig. 2. Spectra obtained by the saddle-point method and by complete summation. The solid line and diamonds are obtained by summation according to exact formula (33) and by the saddle-point method (34), respectively, for a time of 0.2. The dotted line and circles are obtained by summation according to exact formula (33) and by the saddle-point method (34), respectively, for a time of 1. The dashed line and crosses are obtained by summation according to exact formula (33) and by the saddle-point method (34), respectively, for a time of 3.

ular, the process of exponential growth of clusters of correlated spins with the time [11−14, 30].

As was indicated in [50], the closeness of the exponential relaxation constant of the FID component cause by the spins of the remote environment to the exponential growth constant of the number of correlated spins, as well as the loss of the dependence of the shape of the time correlation functions on the initial conditions observed in experiments [55] at least for the lowest-order time correlation function, is not accidental and follows from the exponential randomization of the dynamic system because of its instability [16]. As was often emphasized in the literature (see, e.g., [16] and references therein), the connection between statistical mechanics and physics of chaotic systems is one of the most fundamental, but contradictory current problems of theoretical physics. Statistical mechanics is based on probabilistic (statistical) laws characteristic of the microscopic scale of a multiparticle system. At the same time, the relation of these laws to the actual (in the mathematical meaning) theory of chaos, which is well justified and tested for systems with a small number of degrees of freedom and is based on Lyapunov's theory of stability, is still unclear:

in systems with a macroscopic number of degrees of freedom, it is very difficult to separate the effects of "true" chaos from the effects of randomization because of the multiparticle character of the system. One of the most characteristic manifestations of this regime is the mutual correspondence between the exponential damping component of FID and the exponential increase in the number of correlated spins at the development of MQ multiple spin coherences under the conditions of MQ NMR, which is a manifestation of the dynamic instability in such systems.

The growth (damping) constant is a Lyapunov exponent, which corresponds to the known fact: these constants for a dynamic system always exist pairwise $(-\lambda_i, \lambda_i)$ [16]. In the problem considered in this work, the same constant and the same time correlation function given by Eq. (21) are of primary importance in the study of basic dynamic processes that should be described for the investigation of interest and should be taken into account for the adequate description of the spectrum under study. Thus, the universal (irrespective of the crystal structure [6, 10−12, 24, 54] of the object under investigation) character of the order
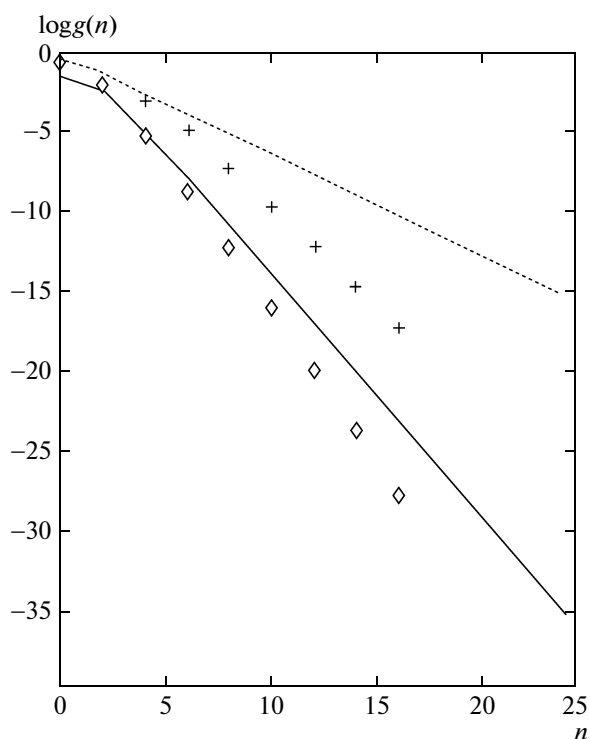
$\log g(n)$

Fig. 3. Spectra (17) obtained with the use of (solid and dotted lines for times of 0.2 and 1, respectively) distribution function (31) and (diamonds and crosses for times of 0.2 and 1, respectively) Gaussian (40).

dependence of the profile of intensities of MQ coherences is possibly due to the development of dynamic chaos in the paramagnetic spin system.

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