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ELECTRICAL AND MAGNETIC PROPERTIES OF MATERIALS

Solid-State NMR Free Induction Decay, Simulated by the System of Classical Magnetic Moments and Quantum Correlations

A. A. Lundin[a, *] **and V. E. Zobov**[b, **]

[a] *Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow, Russia*
[b] *Kirensky Institute of Physics, Federal Research Center, Krasnoyarsk Scientific Center,*
Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia
**e-mail: ya-andylun2012@yandex.ru*
***e-mail: rsa@iph.krasn.ru*

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Abstract—In the past decade, nuclear magnetic resonance (NMR) has been actively used to study the basic principles of quantum computers. It is assumed that quantum correlations play a significant role in their performance. They exist at both low and high temperatures. At the same time, the time correlation functions of nuclear spin systems of solids determine the observed signals in traditional NMR implementations. The separation of such signals into quantum and classical components has not previously been carried out and will be performed in this study for the most important of the correlational functions observed in magnetic resonance: the free induction decay (FID).

Keywords: spin, paramagnetic, quantum technology, spin dynamics, quantum computing

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1. INTRODUCTION

The shape of the absorption spectra of nuclear magnetic resonance (NMR) or their Fourier images—free induction decays (FIDs)—since the discovery of NMR has been one of the main sources of information about the structure of matter, mobility in it, electron-nuclear interactions, electronic structure, phase transitions, etc. This has enabled the broadest applications of NMR, ranging from research in the field of physics and chemistry of condensed matter to research in biology and medicine [1–4]. Subsequently, the development and improvement of multipulse NMR methods made it possible to improve the process of extracting actual information about the investigated substance by "editing" the spectra and significantly improve its understanding [3]. In addition, the improvement and development of pulse methods made it possible to significantly deepen and expand research in the field of nonequilibrium statistical mechanics and obtain unique information in this area of fundamental physics. Suffice it to recall the phenomenon of "time reversal" (Loschmidt's echo) [5, 6].

It should be noted that nuclear spin systems studied by NMR methods, which include various multiparticle temporal correlational functions (TCFs), are a suitable base for studying and developing the physics of nonequilibrium processes in quantum multiparticle systems, the dynamic (as opposed to thermodynamic) behavior of multiparticle systems, the development of correlations in them, and the degradation of the latter. In other words, they are (according to N. Blombergen) an excellent "laboratory" of statistical physics, in which we can study in detail processes such as the emergence and growth of interspin correlations, control spin dynamics, and the processes of the redistribution of quantum information over states (scrambling), which is important, for example, for quantum metrology [7, 8].

The intensive development of the experimental technique of multipulse NMR has also given rise to very wide possibilities for transforming spin-spin Hamiltonians. The developed procedures are called *spin alchemy*. Their appearance, in turn, opened up new prospects for research. Thus, the improvement of multiquantum NMR spectroscopy made it possible to create multiparticle quantum registers (up to $\approx 10^5$ correlated spins), study their behavior (relaxation and loss of coherence), and test and develop methods for processing quantum information, which means the emergence and development of new quantum technologies [8].

These circumstances have additionally increased the interest in studying various TCF nuclear spin systems, the most important of which is FID. Since the discovery of NMR, hundreds of papers devoted to this problem have been published. However, we do not consider here all the variety of developed approaches and methods applied to this problem (see, for example, [9, 10] and the literature cited there), but dwell on the most important ones.

In 1973, an article appeared [11], in which the FID of classical magnetic moments placed on a simple cubic lattice was calculated. The specified structure mimicked the structure of a CaF_2 single crystal—a traditional and generally accepted test crystal for studying the shape of the NMR (or FID) spectra. The authors used a fragment of 216 classical magnetic moments with periodic boundary conditions. The results obtained surprisingly well reproduced a number of characteristic features of the FIDs for all the main orientations of the crystal with respect to the external magnetic field. The reasons for the success of this simulation were explained by us in [12] (see also below in the text).

The results of [11] began to arouse particular interest in the past decade, in particular, in relation to purely practical considerations. The possibility of replacing quantum magnetic moments with classical ones radically reduces the requirements for the computer memory used in the calculations. Thus, an N-spin quantum system requires $(2S + 1)^N$ complex numbers; and the classic system, only $2N$ (two polar angles for each spin). At the same time, the TCF calculations for NMR turned out to be in demand in the study of the propagation of correlations in paramagnetic spin systems in the implementation of the numerical register. For example, in [13–15], the possibilities of matching and hybridization of quantum mechanical and classical calculations were considered. In particular, the method developed in these works made it possible to achieve good results for the FID of small quasi-one-dimensional lattices.

Since quantum correlations must play an important role for the speed of quantum computers (both at low and high temperatures) [16, 17], researchers began to show interest not only in direct calculation of correlations but also in their separation into quantum and classical components (see, for example, the review [16]). This separation can also be performed for spin TCFs, which determine signals in traditional NMR techniques for the case of solids, which we have done using the example of an FPS.

2. HAMILTONIAN AND BASIC EQUATIONS FOR CORRELATIONAL FUNCTIONS

The secular part of internuclear dipole-dipole interactions, which is practically the only one responsible for the dynamics of the spin system under NMR conditions in nonmetallic diamagnetic solids, has the form [2]

$$\begin{aligned} H &= \sum_{i>j}\{(3/2)b_{ij}S_{zi}S_{zj} - (1/2)b_{ij}\mathbf{S}_i\mathbf{S}_j\} = H_{zz}^0 + H_{ex} \\ &= \sum_{i>j}\left\{b_{ij}S_{zi}S_{zj} - (1/4)b_{ij}\left(S_i^+S_j^- + S_i^-S_j^+\right)\right\} = H_{zz} + H_{ff}, \end{aligned} \tag{1}$$

where $b_{ij} = \gamma^2\hbar(1 - 3\cos^2\theta_{ij})/2r_{ij}^3$; $\mathbf{r}_{ij}$ is the vector connecting spins i and j; θ_{ij} is the angle made by vector $\mathbf{r}_{ij}$ with a static external magnetic field; and $S_{\alpha i}$ is the α-component ($\alpha = x, y, z$) of the vector spin operator at site i. Hereinafter, energy is expressed in frequency units.

The equilibrium density matrix in a strong static magnetic field H_0 is described by the expression [2]

$$\hat{\rho}_{eq} = \frac{\exp(-H/kT)}{\mathrm{Sp}\{\exp(-H/kT)\}} = \exp\left(-\frac{\gamma\hbar H_0}{kT}\sum_{j=1}^{N}S_{zj}\right)L^{-1}, \tag{2}$$

where k is the Boltzmann constant, T is temperature, H is the Hamiltonian of the system, N is the total number of spins in the sample, and L is the partition function.

As is known [2], the FID arising after the application of the $\pi/2$-pulse to the equilibrium nuclear spin system is proportional to the TCF, which is determined in the reference frame rotating with the Larmor frequency by the relation

$$\begin{gathered} \Gamma_0(t) = \mathrm{Sp}\{\rho(t)S_x\}/L_0, \\ \text{or } \Gamma_0(t) = \sum_{n=0}^{\infty} i^n(M_n/n!)t^n. \end{gathered} \tag{3}$$

Here L_0 is the normalization factor providing the initial condition $\Gamma_0(0) = 1$ and $\{M_n\}$ are moments, i.e., expansion coefficients in powers of time for FID. In traditional experiments that use magnetic resonance, the spin temperature usually significantly exceeds the energy of the Zeeman and other interactions in the spin system. In relation to this, we, as usual, restrict ourselves to study the TCF in the high-temperature approximation, and since the temperature is very high compared to the internuclear dipole–dipole interaction, only the moments of even order are nonzero, and the FID, therefore, is an even function of time; moreover, the FID and the equilibrium density matrix in the accepted high-temperature approximation, respectively, are described by the formulas

$$\begin{aligned} \Gamma_0(t) &\to \mathrm{Sp}\{S_x(t)S_x\}/\mathrm{Sp}\{S_x^2\} \\ &= \mathrm{Sp}\{S^+(t)S^-\}/\mathrm{Sp}\{S^+S^-\}, \end{aligned} \tag{3a}$$

$$\rho_{eq} \sim 1 + \frac{\gamma\hbar H_0}{kT}\sum_{j=1}^{N}S_{zj},$$

where $S_x = \sum_{i=1}^{N}S_{xi}$ is the total of the x component of the spin of the system. Dependence $S_x(t)$ is given by the Heisenberg equation:

$$dS_x/dt = i[H, S_x]. \tag{4}$$

Using relations (3) and (4) leads to the well-known expression for the moments:

$$M_n = (i/\hbar)^n \mathrm{Sp}\{\underbrace{[H,[H,\ldots[H,S_x]]]}_{n}S_x\} \Big/ \mathrm{Sp}\left(S_x^2\right). \quad (5)$$

Expressions that are completely analogous to relations (3)–(5) can be written for classical mechanical moments [12]. In this case, the quantum moment $\hbar S_x$ is replaced by the classic moment l. Function $\Gamma_0^{cl} = \langle l_x(t) l_x \rangle \big/ l_x^2$ fully corresponds to the TCF from relation (3a), and $\langle\ldots\rangle$ is the ensemble's mean, which is equivalent to averaging over the initial orientations of each spin l. The quantity is defined as $l_x(t) = \sum_{i=1}^{N} l_{xi}(t)$, where $l_x(t)$ is the solution of the equation of motion for classical moments, which in vector form can be written in the form

$$\begin{aligned} \frac{d}{dt} l_x(t) &= \sum_{j=1}^{N} \left[\mathbf{H}_{\mathrm{loc}}^{j} \gamma \mathbf{l}_j(t)\right]_x \\ &= \sum_{j \neq j_1} \gamma^2 b_{j,j_1} (l_{zj} l_{yj_1} + 0.5 l_{y,j_1} l_{z,j}). \end{aligned} \quad (6)$$

The local field acting on the jth spin in a crystal is a vector with three components:

$$\left(H_{\mathrm{loc}}^{j}\right)_x = -\frac{1}{2}\sum_i b_{ij} l_{xi}, \quad \left(H_{\mathrm{loc}}^{j}\right)_y = -\frac{1}{2}\sum_i b_{ij} l_{yi},$$
$$\left(H_{\mathrm{loc}}^{j}\right)_z = \sum_i b_{ij} l_{zi}.$$

Expression (6) can be rewritten in a form completely equivalent to the quantum mechanical relation (4) if we use the equations of classical mechanics in the Hamilton form and take into account the rules for calculating Poisson brackets for the components of the angular momentum [18] ($[l_x, l_y]_p = l_z$, with the corresponding cyclic permutation):

$$dl_x/dt = [H, l_x]_p. \quad (6a)$$

Thus [12],

$$\begin{aligned} \Gamma_0^{cl} &= \sum_0^{\infty} M_n^{cl} \frac{t^n}{n!}, \\ M_n^{cl} &= \frac{1}{\left\langle l_x^2 \right\rangle} \left\langle \underbrace{[H,[H,\ldots[H,l_x]_p]_p]_p}_{n} l_x \right\rangle. \end{aligned} \quad (7)$$

Expression (7) fully corresponds to formulas (3) and (5) both in form and in content (compare the commutator $[S_x, S_y] = iS_z$ and the Poisson bracket $[l_x, l_y]_p = l_z$). The difference arises only when averaging. For example, for the quantum mechanical case, it is necessary to calculate the trace, and in the classical case, to integrate over polar coordinates (angles ϑ_i, φ_i) of each of the spins.

When calculating the moments in relations (5) and (7), first of all, it is necessary to calculate the commutators (Poisson brackets). In order for the result to be nonzero, it is necessary that in the process of calculations the commutated expressions coincide each time with at least one lattice index. Moreover, if at each stage of successive commutations exactly one index coincides, the final expression is the maximum number of summations over lattice indices, and the operator part will contain, after pairing, only squares of the operators (moments). As a result of averaging, the corresponding contributions from the operators and the classical moments in this approximation completely coincide, and the lattice sums turn out to be proportional to the number of approximately equivalent nearest neighbors surrounding the spin in the lattice [12]. Thus, for a moment of the order of $2n$ with a large number of equivalent neighbors ($Z \to \infty$), the following estimate holds: $b^{2n}Z^n$ [12]. If a larger number of indices coincide, the number of nearest neighbors is increased to a lesser degree. From what has been said it follows [12] that a discrepancy between the moments of quantum and classical systems arises only after averaging in lower orders over the number of neighbors Z, which explains the success of the work [11]. At the same time, pairing corresponding to lower orders in the number of neighbors leads to the appearance of spin operators (classical moments) to a greater second degree; as a result, there is a difference in the mean values obtained for constructions composed of spins and classical moments.

In [12], we were able to determine the quantum corrections only to the first eight moments due to the knowledge of their exact expressions [19]. Thus, in general, the fraction of quantum correlations in the FPS was not estimated in [12]. The corresponding assessment is carried out in the next section.

3. DIVISION INTO QUANTUM AND CLASSICAL CORRELATIONS

One of the possible approaches to solve the formulated problem is the reduction of the multispin density matrix. They are usually limited to the lowest approximation: a two-spin density matrix with the subsequent analysis of pair correlations [16]. In [20, 21], this approach was applied to the one-dimensional XY-chain; and in [22], to spins in a nanocavity with equal dipole interactions between any two spins. In both cases, spins with a spin quantum number $S = 1/2$ were taken. In this paper, we consider lattices of spins with the spin quantum number S of arbitrary value (quadrupole effects are not considered). We will reduce the multispin density matrix to a two-spin matrix. Then, following [23], we calculate the fractions of quantum and classical correlations: for $S = 1/2$, by using the Neumann orthogonal measurement, while for $S > 1/2$, by using generalized POVMs (positive-operator-valuedmeasurements) with a basis from the spin coherent states (SCSs) [24]. In addition to systems with dipole-dipole interaction, we will consider model lattices with interactions only between spin components parallel to a static magnetic field (a type of Ising interaction (see Hamiltonian (1)). The latter allows us to get an exact solution to the problem.

To observe the NMR signal, the system is exposed to an RF magnetic field pulse, which causes the spins to rotate through an angle of 90° around the y axis of the rotating reference frame:

$$\hat\rho(0) = \hat Y\hat\rho_{eq}\hat Y^{-1} = (1+\beta\hat S_x)/L.$$

This initial density matrix will change over time,

$$\begin{aligned}\hat\rho(t) &= \hat U(t)\hat\rho(0)\hat U^{-1}(t) = \left[1+\beta\hat U(t)\hat S_x\hat U^{-1}(t)\right]/L\\ &= [1+\beta\Delta\hat\rho(t)]/L,\end{aligned} \tag{8}$$

ultimately generating FPS, determined by relationship (3). Here $\hat U(t) = \exp(-iHt/\hbar)$ is the evolution operator with Hamiltonian H.

As noted above, we assume that the system is in equilibrium in a strong static magnetic field, which exceeds the spin-spin interaction (1) with the density matrix (2). There are no correlations in this initial state. During the evolution of state (8), dynamic correlations are formed in the system. Further, in accordance with the program outlined above, we should reduce the multispin density matrix (8) to a two-spin matrix with the subsequent analysis of pair correlations and their division into quantum and classical parts (components) [16, 20–24]. For the reduction, we choose two spins at sites i and j and calculate the trace in expression (8) with respect to all the other spin variables. In the resulting density matrix $\hat\rho_{ij}(t)$ only the dependence on the spin states of the two spins remains, i and j (see, for example, formulas (21) and (34) below). In the general formulas (9)–(16) of this section, we assign numbers 1 and 2 to spins i and j, respectively, thus passing to the reduced density matrix:

$$\hat\rho_{12}(t) = [1+\beta\Delta\hat\rho_{12}(t)]/L. \tag{8a}$$

Mutual information can serve as a measure of the correlation between spins [16, 25]

$$I(\hat\rho_{12}) = S_N(\hat\rho_1) + S_N(\hat\rho_2) - S_N(\hat\rho_{12}), \tag{9}$$

where $S_N(\hat\rho) = -Sp\{\hat\rho\log_2\hat\rho\}$ is the von Neumann entropy; and $\hat\rho_1 = \mathrm{Sp}_2\hat\rho_{12}$, and $\hat\rho_2 = \mathrm{Sp}_1\hat\rho_{12}$ are the density matrices reduced to one spin. We will calculate the von Neumann entropy in the lowest order in β [17, 23]:

$$S_N(\hat\rho) = -\mathrm{Sp}\{\hat\rho\log_2\hat\rho\} \approx \log_2 L - \frac{\beta^2}{2L\ln 2}\mathrm{Sp}(\Delta\hat\rho)^2.$$

In the indicated high-temperature approximation, for mutual information (9), we obtain

$$\begin{aligned}I(\hat\rho_{12}) = \frac{\beta^2}{2\ln 2}\Bigg\{&\frac{1}{L_{12}}\mathrm{Sp}(\Delta\hat\rho_{12})^2 - \frac{1}{d}\mathrm{Sp}_1(\Delta\hat\rho_1)^2\\ &- \frac{1}{d}\mathrm{Sp}_2(\Delta\hat\rho_2)^2\Bigg\}, \quad L_{12} = d^2, \quad d = 2S+1.\end{aligned} \tag{10}$$

Mutual information (9) is a measure of the total correlations, which are the sum of the classical and quantum correlations. To calculate the classical correlations of two random variables—the orientations of two magnetic moments in our case—it is necessary to find the probability distribution of their values. In quantum mechanics [16, 25], such a distribution can be obtained from the density matrix $\hat\rho_{12}(t)$ of a quantum system by measuring the corresponding observables. Measurement means establishing a connection between a microscopic quantum observable and a "pointer variable" measurable on a macroscopic device. For $S = 1/2$ we will perform an orthogonal Neumann measurement, whereas for $S > 1/2$, we will apply generalized POVMs [16, 25], which allow us to extract most of the classical correlations in this case.

In the orthogonal von Neumann measurement, the state $\hat\rho_{12}(t)$ is projected to some complete basis of orthogonal wave functions $|\Psi_m\rangle$ with a complete projector system:

$$\hat\Pi_m = |\Psi_m\rangle\langle\Psi_m|, \quad \sum_m \hat\Pi_m = 1. \tag{11}$$

For a system with $S = 1/2$, the complete set of mutually orthogonal projectors of the first spin consists of two general projectors:

$$\hat\Pi_{1\pm} = \frac{1}{2}[1 \pm (n_x\hat\sigma_{1x} + n_y\hat\sigma_{1y} + n_z\hat\sigma_{1z})], \tag{12}$$

where n_α are the direction cosines and $\hat\sigma_\alpha$ are the Pauli matrices, $\alpha = x, y, z$.

After projection along the first spin, the reduced density matrix $\hat\rho_{12}(t)$, defined by relation (8a) is transformed to the form

$$\begin{aligned}&\hat\Pi_1(\hat\rho_{12})\\ &= \frac{1}{L}\left[1+\beta\sum_m(\hat\Pi_{1m}\otimes\hat E_2)\Delta\hat\rho_{12}(t)(\hat\Pi_{1m}\otimes\hat E_2)\right],\end{aligned} \tag{13}$$

where $\hat E_2$ is the identity matrix. Thus, we presented it as an ensemble of pure states describing the measurement results. Since in each state the observed quantity now has a quite definite value, it behaves like a classical variable necessary for calculating classical correlations.

In generalized POVMs, the functions $|\Psi_m\rangle$ in operators (11) can be nonorthogonal. Then these operators, strictly speaking, are no longer projectors [25]. It is believed that the closest states to the states of the classical moment are spin coherent states (Bloch states) [24]:

$$\left|\theta,\phi\right\rangle = R(\theta,\phi)\left|S\right\rangle = \sum_{m=-S}^{m=S}\left(C_{2S}^{S+m}\right)^{1/2}(\cos\theta/2)^{S+m}\left(e^{i\phi}\sin\theta/2\right)^{S-m}\left|m\right\rangle, \quad (14)$$

where θ is the polar angle and φ is the azimuthal angles on the unit sphere (Bloch sphere) C is the binomial coefficient; and $\left|m\right\rangle$ is the basis from the operator S_z eigenstates with a certain value m of the projection on the z axis, which takes $2S + 1$ values: $-S, -S + 1, \ldots, S - 1, S$.

States (14) are obtained from the ground state $\left|S\right\rangle$ using the rotation operator $\hat{R}(\theta,\varphi)$ and are a superposition of states with different projections m. In state (14), the average values of the spin projections

$$\left\langle\theta,\varphi\right|\hat{S}_z\left|\theta,\varphi\right\rangle = S\cos\theta,\ \left\langle\theta,\varphi\right|\hat{S}_x\left|\theta,\varphi\right\rangle = S\sin\theta\cos\varphi,$$
$$\left\langle\theta,\varphi\right|\hat{S}_y\left|\theta,\varphi\right\rangle = S\sin\theta\sin\varphi,$$

are the same as in the classic moment. For a basis from the SPS the completeness condition is satisfied:

$$\frac{2S+1}{4\pi}\int\left|\theta,\varphi\right\rangle\left\langle\theta,\varphi\right|\sin\theta d\theta d\varphi = 1;$$

however, the basis is not orthogonal.

We take the SPS system as a measuring basis in (11) and perform a POVM on the first spin, which reduces to multiplying $\hat{\rho}_{12}(t)$ on the SPS and computing the trace. As a result, we obtain the classical probability density function of the distribution over the values of the angles:

$$\hat{\rho}_2(\theta_1\varphi_1;t) = \frac{(2S+1)}{4\pi}\mathrm{Sp}_1\{\hat{\rho}_{12}(t)\left|\theta_1,\varphi_1\right\rangle\left\langle\theta_1,\varphi_1\right|\otimes E_2\} = \frac{(2S+1)}{4\pi}\left\langle\theta_1,\varphi_1\right|\hat{\rho}_{12}(t)\left|\theta_1,\varphi_1\right\rangle. \quad (15)$$

Now, to calculate the Shannon entropy, we have to calculate the integral over the Bloch sphere:

$$S_{ShN}(\hat{\rho}_2(\theta_1\varphi_1;t)) = -\int\mathrm{Sp}_2\{\hat{\rho}_2(\theta_1\varphi_1;t)\log_2\hat{\rho}_2(\theta_1\varphi_1;t)\}\sin\theta_1 d\theta_1 d\varphi_1.$$

The mutual information $I(\hat{\Pi}_1(\hat{\rho}_{12}))$, calculated by formulas (10), (13), and (15) for this matrix will serve as a measure of the classical correlations. However, the obtained value depends on the chosen basis (11). In accordance with the formula from [16], it is proposed to sort out all the bases and take the maximum value of the correlation $I(\hat{\Pi}_1(\hat{\rho}_{12}))$ as a universal measure. Such a program can be executed only in some simple cases, for example, for a two-level system. If we subtract the classical part from all correlations (9), then we get their quantum part:

$$Q_{12} = I(\hat{\rho}_{12}) - I(\hat{\Pi}_1(\hat{\rho}_{12})). \quad (16)$$

After minimizing this quantity over the measurement bases, we obtain the entropy measure of the quantum correlations: the quantum discord D_{12} [16]. The measurement from relation (16) without optimization is called a measurement dependent discord [16].

The general case of the total dipole–dipole interaction with Hamiltonian (1) is discussed below. Let us first consider the situation when the system interacts only through the Ising part of Hamiltonian (1) (when there is no transverse interaction). In this case, since an exact solution of the problem is possible, the time evolution of matrix (2) can be written explicitly:

$$\hat{\rho}(t) = \frac{1}{L}\left[1 + \frac{\beta}{2}\left\{\sum_i \hat{S}_{i+}\prod_{j(\neq i)}\exp(-it2b_{ij}\hat{S}_{jz}) + \sum_i \hat{S}_{i-}\prod_{j(\neq i)}\exp(it2b_{ij}\hat{S}_{jz})\right\}\right]. \quad (17)$$

The observed FPS signal (3) has the form

$$\Gamma_{zz}(t) = \prod_{j(\neq i)}\frac{\sin(db_{ij}t)}{d\sin(b_{ij}t)}. \quad (18)$$

With a large number of neighbors Z, the resulting expression for the FPS is closely approximated by the Gaussian function:

$$\Gamma_G(t) = \exp\left\{-M_2^{zz}t^2/2\right\},\quad M_2^{zz} = \frac{4}{3}S(S+1)\sum_j b_{ij}^2. \quad (19)$$

In the implemented limit, the shape of the FPS does not depend on S and therefore coincides with the FPS form of the system of classical magnetic moments $\mu = \gamma\hbar\sqrt{S(S+1)}$, obtained upon passing to the limit $S \to \infty$.

The difference between functions (19) and (18) can be estimated by the difference between their fourth moments:

$$M_{G4} = 3\left(M_2^{zz}\right)^2 = 3\left[\frac{4}{3}S(S+1)\sum_j b_{ij}^2\right]^2,$$
$$M_4^{zz} = 3\left(M_2^{zz}\right)^2 - \frac{48}{45}S(S+1)\sum_j b_{ij}^4(2S^2 - 3S + 6). \quad (20)$$

The difference ΔM_4 that appears is expressed in terms of the lattice sum with one summation over the lattice sites, while the value of moment (20) is determined by the lattice sum with two such summations contained in $\left(M_2^{zz}\right)^2$, and therefore, $\Delta M_4/M_4^{zz} \sim 1/Z$.

Does this mean that the quantum correlations disappear if the FPS shapes match at $Z \to \infty$? To answer this question, we reduce the density matrix (17) [20–22]. We choose two spins at sites i and j and calculate the trace in (17) in all the other spin variables. We find

$$\begin{aligned}\hat{\rho}_{ij}(t) = \frac{1}{L_{ij}}\Big[1 + \frac{\beta}{2}\{G_{i(j)}(t)\hat{S}_{i+}\exp(-it2b_{ij}\hat{S}_{jz}) \\ + G_{i(j)}(t)\hat{S}_{i-}\exp(it2b_{ij}\hat{S}_{jz}) + G_{j(i)}(t)\hat{S}_{j+} \\ \times \exp(-it2b_{ij}\hat{S}_{iz}) + G_{j(i)}(t)\hat{S}_{j-}\exp(it2b_{ij}\hat{S}_{iz})\}\Big],\end{aligned} \quad (21)$$

$$G_{i(j)}(t) = \prod_{f(\neq i,j)}\frac{\sin(db_{if}t)}{d\sin(b_{if}t)}, \quad G_{j(i)}(t) = \prod_{f(\neq i,j)}\frac{\sin(db_{jf}t)}{d\sin(b_{jf}t)}.$$

To simplify the analysis, we assume that all spins occupy equivalent positions in the lattice, then

$$G_{i(j)}(t) = G_{j(i)}(t) \equiv G_{ij}(t).$$

In this case

$$\begin{aligned}\hat{\rho}_{ij}(t) = \frac{1}{L_{ij}}\Big[1 + \frac{\beta}{2}G_{ij}(t)\{\hat{S}_{i+}\exp(-it2b_{ij}\hat{S}_{jz}) \\ + \hat{S}_{i-}\exp(it2b_{ij}\hat{S}_{jz}) + \hat{S}_{j+}\exp(-it2b_{ij}\hat{S}_{iz}) \\ + \hat{S}_{j-}\exp(it2b_{ij}\hat{S}_{iz})\}\Big],\end{aligned} \quad (22)$$

Expression (22) differs from the analogous expression for an isolated pair of spins obtained in [23] by replacing τ by $t2b_{ij}$ and β by $\beta G_{ij}(t)$. Therefore, omitting the intermediate calculations, we present the final results at once. First, for the mutual information (10), we obtain

$$I(\hat{\rho}_{ij}) = \frac{(\beta G_{ij}(t))^2}{3\ln 2}S(S+1)\left[1 - g_{ij}^2(t)\right], \quad (23)$$

where

$$g_{ij}(t) = \frac{\sin(db_{ij}t)}{d\sin(b_{ij}t)}.$$

Secondly, for the classical (C_{ij}) and quantum (quantum discord D_{ij}) parts of the correlations at $S = 1/2$ we have

$$C_{ij} = D_{ij} = \frac{1}{2}I(\hat{\rho}_{ij}) = \frac{(\beta G_{ij}(t))^2}{8\ln 2}\sin^2(tb_{ij}). \quad (24)$$

Result (24) was obtained using the Neumann orthogonal measurement (13) along one of the spins with projectors (12). Finally, for the classical (J_{ij}) and quantum (Q_{ij}) parts of the correlations at $S > 1/2$, we find

$$\begin{aligned}J_{ij} = \frac{(\beta G_{ij}(t))^2}{6\ln 2} \\ \times\left\{S(S+1)\left[f_{ij}(t) - g_{ij}^2(t)\right] + S^2\left[1 - g_{ij}^2(t)\right]\right\},\end{aligned} \quad (25)$$

$$\begin{aligned}Q_{ij} = I(\hat{\rho}_{ij}) - J_{ij} = \frac{(\beta G_{ij}(t))^2}{6\ln 2} \\ \times\left\{S(S+1)[1 - f_{ij}(t)] + S\left[1 - g_{ij}^2(t)\right]\right\},\end{aligned} \quad (26)$$

where

$$f_{ij}(t) = \sum_{n=0}^{n=2S} C_{2S}^n\frac{(2n)!!}{(2n+1)!!}(-1)^n\left(\sin tb_{ij}\right)^{2n}.$$

Here C_{2S}^n is the binomial coefficient (number of combinations).

Formula (25) was obtained using generalized POVMs (15) with a basis from SPS (14).

Expressions (25) and (26) describe the time evolution of the sought parts of the correlations. For a qualitative analysis of their behavior with a large number of neighbors Z, we note that in this case the function $G_{ij}(t)$ from formula (21) rapidly decays at times of the order $t \geq 1/\sqrt{M_2^{zz}}$. In this time scale,

$$|b_{ij}t| \sim \sqrt{b_{ij}^2/M_2^{zz}} \sim 1/\sqrt{Z} \ll 1.$$

Therefore, in (23), (25), and (26), in the functions $f_{ij}(t)$, $g_{ij}(t)$, and $\sin tb_{ij}$, we can leave the first terms of the expansion in time:

$$I(\hat{\rho}_{ij}) \approx \frac{(\beta G_{ij}(t))^2}{9\ln 2}4[S(S+1)b_{ij}t]^2, \quad (27)$$

$$Q_{ij} \approx \frac{(\beta G_{ij}(t))^2}{9\ln 2}4\left(Sb_{ij}t\right)^2(S+1). \quad (28)$$

We again note that formulas (27) and (28) are adequate not only for small but also for large times, since their growing terms arising from the above-mentioned expansion of functions are cut off by the rapidly decaying function $G_{ij}(t)$.

Thus, for the relative fraction of the quantum correlation, we find

$$Q_{ij}/I(\hat{\rho}_{ij}) \approx 1/(S+1). \quad (29)$$

As follows from (29), as S increases, the proportion of quantum correlations decreases. Note that for $S = 1/2$ relation (29) gives a value of 2/3, while from (24) we obtain 1/2. The discrepancy is due to the differences in the measurement methods.

Let us now consider a system with a complete Hamiltonian (1). The interaction between the transverse spin components no longer allows us to write the explicit time dependence of the density matrix in a simple form (17). To find it, we use the method of expansion in terms of the complete system of orthogonal operators $[k)$ [26–28]. In this view

$$\hat{S}_x(t) = \hat{U}(t)\hat{S}_x\hat{U}^{-1}(t) = \sum_{k=0}^{\infty}A_k(t)[k). \quad (30)$$

The original operator $[0) = \hat{S}_x$. Each subsequent basis operator is obtained from the previous one by calculating the commutator with the Hamiltonian in accordance with the recurrent equation

$$[1) = i\left[\hat{H}_d,[0)\right], \quad [k+1) = i\left[\hat{H}_d,[k)\right] + \nu_{k-1}^2[k-1) \text{ at } k \geq 1, \quad \nu_k^2 = \mathrm{Sp}\{(k+1|k+1)\}/\mathrm{Sp}\{(k|k)\}. \tag{31}$$

For amplitudes $A_k(t)$ in [26, 27], a (actually infinite) system of interlocking differential equations was obtained:

$$\dot{A}_0(t) = -\nu_0^2 A_1(t), \quad \dot{A}_k(t) = A_{k-1}(t) - \nu_k^2 A_{k+1}(t) \text{ at } k \geq 1. \tag{32}$$

To avoid confusion, let us pay attention to some difference in the definition of amplitudes $A_k(t)$ in [26] and [27]. The difference lies in the factor $(i)^k$. We have chosen the version of [27] in which amplitudes $A_k(t)$ do not contain an imaginary part since the factor $(i)^k$ is included in the definition of operators $[k)$. Parameters $\{\nu_k\}$, the values of which determine the solution of system (28), are expressed unambiguously in terms of the moments of the NMR absorption line [26]. In particular,

$$\nu_0^2 = M_2 = \frac{9}{4}\sum_j b_{ij}^2, \quad \nu_1^2 = \left(M_4 - M_2^2\right)/M_2, \quad \nu_2^2 = \left(M_2 M_6 - M_4^2\right)/\left(M_4 - M_2^2\right)M_2, \tag{33}$$

where M_2, M_4, and M_6 are the second, fourth, and sixth moments of the NMR absorption line.

Substituting (30) into (8), we carry out a reduction. We choose two spins at sites i and j and calculate the trace in (8) in all the other spin variables. As a result, we get

$$\hat{\rho}_{ij}(t) = \frac{1}{L_{ij}}\left[1 + \beta\sum_{k=0}^{\infty} A_k(t)\frac{L_{ij}}{L}\mathop{\mathrm{Sp}}_{\neq i,j}[k)\right]. \tag{34}$$

For the first two orthogonal operators

$$\frac{1}{L}\mathop{\mathrm{Sp}}_{\neq i,j}[0) = \frac{1}{L}\mathop{\mathrm{Sp}}_{\neq i,j}\sum_f \hat{S}_{xf} = \frac{1}{L_{ij}}(\hat{S}_{xi} + \hat{S}_{xj}), \tag{35}$$

$$\frac{1}{L}\mathop{\mathrm{Sp}}_{\neq i,j}[1) = \frac{i}{L}\mathop{\mathrm{Sp}}_{\neq i,j}[\hat{H}_d, \hat{S}_x] = -\frac{2}{L_{ij}}(b_{ij} - a_{ij}) \times (\hat{S}_{yi}\hat{S}_{zj} + \hat{S}_{yj}\hat{S}_{zi}), \quad a_{ij} = -b_{ij}/2. \tag{36}$$

A contribution to (34) from the orthogonal operators of a higher order is possible in two cases: if, between the chosen spins i and j, direct interaction vanishes, which corresponds, for example, to the situation when the angle of vector r_{ij} with the magnetic field θ_{ij} equals the "magical" value of 54°44′. In this case, the contribution of vector $[3)$ through the intermediate spin f with constant $b_{if}b_{jf}^2$ is nonzero. At $S > 1/2$ higher-order orthogonal operators are formed from the products of spin operators not only of different sites but also of the same site. For example, $\hat{S}_{xi}\left\{\hat{S}_{zj}^2 - S(S+1)/3\right\}$ will contribute in $[2)$ and $\hat{S}_{yi}\left\{\hat{S}_{zj}^3 - \hat{S}_{zj}(3S^2 + 3S - 1)/5\right\}$ will contribute in $[3)$. We will neglect these contributions in (34), since they do not contain new qualitative properties but are small corrections to the contributions from the traces in expressions (35) and (36). The insignificance of the corrections is related to the difference in the time dependence at the small times of the amplitudes of different orders: $A_k(t) \sim t^k$ due to the rapid decay of the amplitudes at times of the order of $t \geq 1/\sqrt{M_2}$ every degree t adds a small multiplier $|b_{ij}t| \sim \sqrt{b_{ij}^2/M_2} \sim 1/\sqrt{Z} \ll 1$. Thus, the performed reduction to a two-particle density matrix seems to be a correct approximation for systems containing a large number of equivalent nearest neighbors Z. This is also fully consistent with the results of the FID calculations for crystals with large Z numbers based on the model of "pairwise interactions" [29, 30].

Keeping two contributions, (35) and (36), in (34), we find

$$\hat{\rho}_{ij}(t) \approx \frac{1}{L_{ij}}\left[1 + \beta A_0(t)(\hat{S}_{xi} + \hat{S}_{xj}) + \beta A_1(t)B_{ij}(\hat{S}_{yi}\hat{S}_{zj} + \hat{S}_{yj}\hat{S}_{zi})\right], \tag{37}$$

where $B_{ij} = -2(b_{ij} - a_{ij}) = -3b_{ij}$ for Hamiltonian (1). Finally, upon further reduction to one spin, we obtain

$$\hat{\rho}_{i(j)}(t) \approx \frac{1}{d}\left[1 + \beta A_0(t)\hat{S}_{xi(j)}\right]. \tag{38}$$

Substituting (37) into (3), we find $A_0(t) = \Gamma_0(t)$ and, as follows from relations (32), $A_1(t)$ is the FPS derivative.

The formula for the density matrix (37) is quite similar to the expression obtained in [23] at small times for an isolated pair of spins. Therefore, omitting the intermediate calculations, we present the final results at once. For the mutual information, we get

$$I(\hat{\rho}_{ij}) \approx \frac{\beta^2}{9\ln 2}[S(S+1)B_{ij}A_1(t)]^2 = \frac{\beta^2 b_{ij}^2}{M_2 \ln 2}[S(S+1)\dot{A}_0(t)]^2. \tag{39}$$

When transforming in (39), we used formulas (32) and (34). The quantum discord D_{ij} (at $S = 1/2$) and the quantum part of the correlations Q_{ij} (at $S > 1/2$) are related to $I(\hat{\rho}_{ij})$ from (39) with the same relations (24) and (29) as in the previous example:

$$C_{ij} = D_{ij} = I(\hat{\rho}_{ij})/2, \quad Q_{ij} \approx I(\hat{\rho}_{ij})/(S+1).$$

Based on the results obtained, we conclude that the time dependence of the mutual information (39) and the quantum part of the correlations is determined through the derivative of the FID. In this case, the rapid decay of the pairwise correlations and a decrease in their maximum values with an increase in the number of neighbors Z does not mean a weakening of the correlation, but only means the overflow of pairwise correlations into more complex multispin correlations. The complete mutual information can serve as a measure of a complete correlation [16, 31]:

$$T(\rho) = \sum_i S_N(\rho_i) - S_N(\rho) \approx \frac{\beta^2}{3\ln 2} S(S+1)\left[1 - A_0^2(t)\right]. \tag{40}$$

At the initial moment of time $A_0^2(0) = 1$ and $T(\rho) = 0$. At large times $A_0^2(t)$ vanishes; thus, $T(\rho)$ reaches the limiting value determined by the initial conditions: polarization of β at the given temperature and magnetic field.

3. CONCLUSIONS

As is well known, the semiclassical description of quantum systems is valid [32] if the wave function has a large number of nodes, i.e., within large quantum numbers. In particular, for the angular momentum, the semiclassical transition has the form [32]

$$\Lambda^2 = \lim_{\hbar \to 0, l \to \infty} \hbar^2 l(l+1) = \text{const.}$$

In the case when the angular momentum has a spin origin, the situation is somewhat complicated, since spin is a purely quantum property. Nevertheless, since particles have a spin-related magnetic moment, it is usually assumed that the indicated passage to the limit is, at a certain ratio, also valid for spins.

The mentioned passage to the limit has another aspect. Fischer's work [33] can be cited here. An indispensable attribute for spin operators consists of the commutation relations

$$S_x S_y - S_y S_x = iS_z, \ldots$$

According to Fischer's formula [33], the length of spin S should be taken out of the brackets in the commutation relations and both parts should be divided by S^2; at $S \to \infty$, the commutation relations vanish, which is valid only for the classical particles (see also [32]). This underlines that spin is a purely quantum property. However, as follows from the points made above, this somewhat primitive interpretation of the semiclassical transition should be improved at least for describing the dynamics of multiparticle systems.

The conducted research has shown the following points. Although, with a large number of neighbors Z, the FPS of quantum spins and classical magnetic moments largely coincide in shape, this does not mean that the quantum properties are completely lost. In each pair of spins of the system, the fraction of quantum correlations varies from 1/2 to $1/(S+1)$ for large values S. The quantum properties completely disappear only with an additional passage to the limit: $S \to \infty$. Limit $Z \to \infty$ is insufficient. The closeness of the FPS forms means that measurable classical correlations and immeasurable (lost in measurement) quantum correlations affect the FID in the same way. Thus, the simultaneously unobservable spin components $\hat{S}_x, \hat{S}_y$, and $\hat{S}_z$ can, however, simultaneously contribute to the dynamics of the spin system. As a result, the scale of the time dependence is set by value $S(S+1)$, but not S^2, where S is the maximum value of the observed projection onto any axis.

In conclusion, we note that in recent years important relationships have been established and confirmed experimentally, allowing one to study quantum correlations not only by measuring the TCF but also, for example, by the data on magnetic susceptibility and other physical parameters [34].

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