

## MODELING MULTIPARTICLE COHERENCES IN SOLID-STATE NUCLEAR SPIN SYSTEMS USING INFINITE-RANGE INTERACTION

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*Using the exactly solvable model known in statistical physics as the infinite-range interaction model (the van der Waals model), we obtain expressions for the hierarchy of multispin multi-quantum time correlation functions for a solid-state paramagnetic nuclear spin system with magnetic dipole–dipole interaction between nuclei. These functions are observed experimentally using contemporary multi-quantum NMR spectroscopy methods. We write the complete set of orthogonal multispin operators explicitly and find the time dependence for amplitudes of multiparticle time correlation functions. The proposed model describes the behavior of multiparticle correlation functions well, at least for not very large numbers  $n$  of expansion harmonics. The theoretical results agree well with the experimental data obtained for hexamethylbenzol.*

**Keywords:** multipulse method, dipole–dipole interaction, multispin coherence, time correlation function, rotating reference frame

### 1. Introduction

A rapid growth of multipulse methods in solid state NMR started at the beginning of the 1970s. These methods now prevail in modern radio-frequency spectroscopy [1], [2]. Just because of these methods, the application of NMR ranges from investigating solid state physics and superconductivity to molecular biology and medicine (including diagnostics).

The main advantage ensuring the success of the new technologies is the possibility of performing almost unlimited transformations of the nuclear spin system Hamiltonian in accordance with the investigation project, which is sometimes even called the “alchemy of spin systems.” At the same time, signals observed using the pulse NMR methods are determined by different time correlation functions (TCF), and these investigations are therefore essential for developing the statistical mechanics of irreversible processes: solid-state nuclear spin subsystems with their exactly known (and often pre-devised) Hamiltonian and practically total isolation from other degrees of freedom of a sample (lattice) are, according to Blombergen, an “excellent statistical-physics laboratory.” We here only recall the “time reversal” in a solid-state spin system experimentally realized in NMR [3], [4] and underlying many modern experimental methods, as well as “quantum computing” (computers) realized using multipulse NMR [5].

One of the most interesting directions of solid-state NMR development is the multi-quantum Fourier spectroscopy [2], [4], [6]–[8]. The whole variety of actual realizations of its methods can be eventually reduced to the fact that irradiating a spin system with a sequence of radio-frequency pulses results in a nonsecular

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(w.r.t. the equilibrium magnetization) Hamiltonian appearing in the system. This Hamiltonian pumps the initial magnetization into various multispin TCF (multispin coherences). The manifested coherences are labeled by a phase shift proportional to time for which one more radio-frequency pulse can be used. The arising phase shift is proportional to  $n\varphi$ , where  $n$  is an integer and  $\varphi$  is the phase corresponding to the pulse. We can therefore distinguish coherences by the parameter  $n$  corresponding to the number of quanta [2]. We can then stimulate the system with a new pulse sequence that changes the sign of the above nonsecular Hamiltonian, thus realizing a “time reversal,” and the system starts to evolve “backward.” Observing the dependence of the evolution on time and the phase  $\varphi$  then allows constructing a one- or two-dimensional Fourier spectrum.

Multiquantum NMR spectroscopy is very convenient, for instance, for studying cluster structures or other local structures [9]. In the case of regular solid bodies, developing the application is hindered, in particular, by the absence of a consistent theory (see, e.g., [6]–[9]). On the other hand, the time evolution of multispin multiquantum TCF chain is very interesting from the standpoint of the statistical mechanics of irreversible processes.

In this paper, we investigate the above problem using the model with infinite-range interaction. The proposed model allows finding an exact solution of the problem under consideration. Our results agree well with the experimental data [4], at least, qualitatively.

## 2. Hamiltonian, model Hamiltonian, and the problem setting

The physical quantity that is directly observed in pulse NMR experiments is the magnetization in the frame of reference rotating with the Larmor frequency  $\gamma H_0$  about the  $Z$  axis of the laboratory frame of reference along which a large constant magnetic field  $H_0$  is applied ( $\gamma$  is the gyromagnetic ratio). In the simplest experiments, this magnetization excited by a single  $\pi/2$  pulse (i.e., a pulse whose duration  $t_p$  in the rotating frame system (RFS) is chosen such that  $\gamma H_1 t_p = \pi/2$ , where  $H_1$  is the amplitude of the radio-frequency field) is called the free precession signal and is proportional to the TCF:

$$\Gamma_0(t) = \frac{\text{Sp}(S_x(t)S_x)}{\text{Sp}S_x^2} = \frac{\text{Sp}(S^+(t)S^-)}{\text{Sp}(S^+S^-)}, \quad (1)$$

where  $S_x = \sum_i S_{x_i}$ , which is the  $x$  component of the total system spin, satisfies the Heisenberg equation

$$\begin{aligned} \dot{S}_x &= i[H_d^0, S_x], \\ S^+ &= S_x + iS_y, \quad S^- = S_x - iS_y. \end{aligned} \quad (2)$$

In Eq. (2) and below, we measure energies in frequency units,  $H_d^0$  is the secular part of the dipole–dipole interaction [10], which is mainly responsible for the widening of the NMR spectra in nonmetallic diamagnetic crystals,

$$H_d^0 = \frac{3}{2} \sum_{i \neq j} b_{ij} S_{z_i} S_{z_j} - \frac{1}{2} \sum_{i \neq j} b_{ij} \vec{S}_i \vec{S}_j = H_{zz} + H_{\text{ex}}, \quad (3)$$

where

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

$\vec{r}_{ij}$  is the vector connecting the spins  $i$  and  $j$ , and  $\theta_{ij}$  is the angle between the vector  $\vec{r}_{ij}$  and the constant external magnetic field. Hamiltonian (3) is basic for “spin alchemy”; a researcher can transform it into other Hamiltonians of interest using radio-frequency pulses.

The problem of calculating even the simplest TCF (1) with Hamiltonian (3) is extremely complex because of the multiparticle nature of the problem and the lack of an explicit small parameter in the Hamiltonian. Essential progress in solving this problem has been achieved only recently (see, e.g., [11], [12] and the references therein). Calculating the TCF that determine the behavior of multiquantum coherences is, as is seen below, an even more complex problem. We must therefore simplify the problem by making an assumption that is basic for the problem under consideration: let the coefficients  $b_{ij}$  be independent of angles and distances, i.e., let  $b_{ij} = b$  for all  $i$  and  $j$ . Such an approach is common in the physics of magnetic phenomena (see, e.g., [13]–[15]). Hamiltonian (3) then becomes

$$H_d^0 = \frac{3}{2} \sum_{i \neq j} b S_{z_i} S_{z_j} - \frac{1}{2} \sum_{i \neq j} b \vec{S}_i \vec{S}_j. \quad (4)$$

Our assumption drastically simplifies the problem. For example, when calculating TCF (1) for spin  $1/2$ , the term  $H_{\text{ex}}$  drops out of consideration because the terms  $H_{zz}$  and  $H_{\text{ex}}$  now commute, and  $H_{\text{ex}}$  also commutes with  $S_x$ . It is worth mentioning here that the problem complexity also forced the authors of [6], [7] to use the equal-interaction approximation when calculating the coefficients for modeling the diffusion in the Liouville space. In the present paper (in contrast to [6], [7]), we consider the exact dynamics of multispin multiquantum coherences in the framework of the above model. Moreover, we mention that in the regular solids in which every spin is surrounded by a large number of equivalent neighbors, the TCF form is practically independent of the value of the spin  $S$ , which determines the time scale [16].

When calculating TCF (1) for  $S = 1/2$ , we therefore replace Hamiltonian (4) with the expression

$$H_d^0 = H = B S_z^2 - \frac{N}{4}, \quad B = \frac{3}{2} b, \quad (5)$$

where  $N$  is the number of spins in the sample. Because of this, we have

$$\exp(iHt) S^+ \exp(-iHt) = \exp[itB(S_z^2 - (S_z - 1)^2)] S^+ = \exp\left[2itB\left(S_z - \frac{1}{2}\right)\right] S^+. \quad (6)$$

The term  $-1/2$  in evolution operator (6) appears because the spin itself is excluded from the local field acting on this spin. This term can obviously be neglected for large  $N$ . Moreover, in this approximation,  $S_z$ ,  $S_x$ , and  $S_y$  are numbers (not operators), each of which is normally distributed with the second moment

$$\langle S_\alpha^2 \rangle = \sum_i S_{\alpha i}^2 = \frac{N}{4}, \quad (7)$$

$$P_\alpha(S_\alpha) = \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{2S_\alpha^2}{N}\right), \quad \alpha = x, y, z. \quad (8)$$

Calculating the trace in formula (1) means averaging the projections w.r.t. distribution measure (8).

We can therefore easily obtain

$$\Gamma(t) = \exp\left(-\frac{M_2 t^2}{2}\right), \quad M_2 = \frac{B^2}{N}. \quad (9)$$

As mentioned, the following action scheme is customary when experimentally forming and observing multispin and multiquantum coherences: at the first stage, the evolution of a system with the dipole Hamiltonian (Hamiltonians (4) or (5) for the system under consideration) is provoked on the time interval

$t$  with the appearing multispin coherences subsequently segregated into classes according to the number of (adsorbed) quanta and labeled. The latter is realized by rotating through some angle  $\varphi$  about the RFS axis  $x$ . At the last stage, the evolution of the system with the Hamiltonian  $-H$  is forced on the time interval  $\tau$ . The desired TCF can therefore be written in the form

$$\Gamma_\varphi(t, \tau) = \frac{\text{Sp}[U^+(\tau)U_\varphi U(t)S_x U^+(t)U_\varphi^+ U(\tau)S_x]}{\text{Sp} S_x^2}. \quad (10)$$

Strictly speaking, the experiment described in [4] was performed with an effective Hamiltonian slightly differing from our Hamiltonian (see formula (39) and the discussion that follows it). Nevertheless, these differences are inessential for analyzing the appearing multiparticle correlation dynamics. This is also indicated by the results in [7], [8].

As we show below, describing the evolution of multiquantum TCF (10) even for the model Hamiltonian is a much more cumbersome problem than calculating free precession signal (9).

### 3. Expansion over orthogonal operators

To explicitly segregate multiparticle coherences appearing in evolution operator (6), we expand this operator in a series in orthogonal operators. In accordance with the methods in [11], [17], we construct the orthogonal basis using the commutators with Hamiltonian (5)

$$Q_1 = [H_d^0, S_0^+] = 2B \sum_i S_{zi} S_0^+, \quad (11)$$

$$Q_2 = [H_d^0, [H_d^0, S_0^+]] = (2B)^2 \sum_{j \neq i} S_{zj} S_{zi} S_0^+ + (2B)^2 \frac{N}{4} S_0^+. \quad (12)$$

The spin subscript 0 indicates a (any) selected spin in the lattice. Only the first term in operator (12) is orthogonal to the operator  $S_0^-$ . Absolutely analogously, the part of the  $n$ -fold commutator

$$Q_n = [H_d^0, [H_d^0, \dots, [H_d^0, S_0^+] \dots]] \quad (13)$$

that is orthogonal to all the previous operators is

$$Q_n^{(\text{ort})} = (2B)^n \left(\frac{N}{4}\right)^{n/2} O_n^+,$$

where

$$O_n^+ = \sum_{i \neq j \neq j \neq \dots \neq q} S_{zi} S_{zj} \dots S_{zq} S_0^+ \left(\frac{4}{N}\right)^{n/2}. \quad (14)$$

We calculate the scalar product in accordance with the rule

$$\langle O_n^+ | O_m^- \rangle = \delta_{nm} \text{Sp}(S_0^+ S_0^-) n!. \quad (15)$$

We now expand the evolving transverse component of the spin in the series in orthogonal operators

$$U(t)S_0^+U^+(t) = \sum_{n=0} i^n A_n(t)O_n^+. \quad (16)$$

The TCF  $A_n(t)$  are multiparticle coherences. Multiplying (16) by  $O_n^-$  and calculating the scalar product, we obtain

$$\begin{aligned} \text{Sp}[S_0^+(t)O_n^-] &= \text{Sp}\left[\exp(2iBS_z t)S_0^+ \sum_{i \neq j \neq \dots \neq 0} S_{zi}S_{zj} \dots S_{zn}S_0^-\right] \left(\frac{4}{N}\right)^{n/2} = \\ &= i^n A_n(t)n! \text{Sp}(S_0^+ S_0^-). \end{aligned} \quad (17)$$

We now expand the exponent in formula (17) in the series

$$\exp(2iBS_z t) = \sum_m \frac{(2iBt)^m}{m!} \left(\sum_i S_{zi}\right)^m \quad (18)$$

and calculate the trace. This trace vanishes for  $m < n$ . At  $m = n$ , we can pair the operators  $S_{zj}$  from  $O_n^-$  with the operators  $S_{zi}$  arising in the exponent expansion  $n!$  ways. At  $m = n$ , we therefore obtain

$$(2iBt)^n \text{Sp}(S_0^+ S_0^-) \left(\frac{n!}{n!}\right) \left(\frac{N}{4}\right)^n \left(\frac{4}{N}\right)^{n/2}. \quad (19)$$

For  $m > n$ , we can choose from  $(S_z)^m$  operators for pairing with the operators  $S_{zj}$  from  $O_n^-$   $m(m-1) \dots (m-n-1) = m!/(m-n)!$  ways. Hence, for the whole series, we have

$$\begin{aligned} \text{Sp}(S_0^+ S_0^-) (2iBt)^n \left\langle \sum_{m \geq n} \frac{(2iBtS_z)^{n-m}}{(m-n)!} \right\rangle \left(\frac{N}{4}\right)^n \left(\frac{4}{N}\right)^{n/2} = \\ = \text{Sp}(S_0^+ S_0^-) (2iBt)^n \left(\frac{N}{4}\right)^{n/2} \exp\left(-\frac{B^2 t^2 N}{2}\right). \end{aligned} \quad (20)$$

Substituting expression (20) in (16), we find the explicit expression for the multispin coherence in the model under consideration:

$$A_n(t) = (2Bt)^n \left(\frac{N}{4}\right)^{n/2} \exp\left(-\frac{B^2 t^2 N}{2}\right) = (\sqrt{M_2} t)^n \frac{\exp(-M_2 t^2/2)}{n!}. \quad (21)$$

#### 4. Calculating intensities of multiparticle coherences

To describe multispin multiquantum coherences, we express the operators  $S_x$  in relation (10) through the operators  $S^+$  and  $S^-$ . Then

$$\Gamma_\varphi(t, \tau) = \frac{1}{2} (\Gamma_\varphi^{+-}(t, \tau) + \Gamma_\varphi^{++}(t, \tau) + \Gamma_\varphi^{-+}(t, \tau) + \Gamma_\varphi^{--}(t, \tau)). \quad (22)$$

We now consider the first term in the r.h.s. of (22). Performing the cyclical permutation under the trace sign, we obtain

$$\Gamma_\varphi^{+-}(t, \tau) = \frac{\text{Sp}[U_\varphi U(t)S^+U^+(t)U_\varphi^+U^+(\tau)S^-U(\tau)]}{\text{Sp}(S^+S^-)}. \quad (23)$$

Substituting expansion (16) in (23), we have

$$\Gamma_\varphi^{+-}(t, \tau) = \frac{\text{Sp}[U_\varphi (\sum_n i^n A_n(t) (\sum_0 O_n^+)) U_\varphi^+ (\sum_m (-i)^m A_m(\tau) (\sum_{0'} O_m^-))]}{\text{Sp}(S^+S^-)}. \quad (24)$$

We must sum the orthogonal operators over all possible positions of the selected spin “0” (“0'”) in relation (24); otherwise, the function  $\Gamma_{\varphi}^{+-}(t, \tau)$  would reduce to its autocorrelation part, which is incorrect in the framework of our model.

We set the angle  $\varphi = 0$  in formula (22). The terms  $\Gamma_{\varphi}^{++}(t, \tau)$  and  $\Gamma_{\varphi}^{--}(t, \tau)$  then vanish, and we must set  $n = m$  and  $0 = 0'$  for the orthogonal operators in expression (22). Then

$$\Gamma_{\varphi=0}^{+-}(t, \tau) = \sum_n A_n(t) A_n(\tau) i^n (-i)^n n!. \quad (25)$$

Substituting (21) in (25), we have

$$\Gamma_{\varphi=0}^{+-}(t, \tau) = \sum_n (M_2 t \tau)^n \frac{\exp[-M_2(t^2 + \tau^2)/2]}{n!} = \exp\left[\frac{-M_2(t - \tau)^2}{2}\right]. \quad (26)$$

As expected, we then obtain  $\Gamma_{\varphi=0}^{+-}(\tau, \tau) = 1$  at  $t = \tau$ , i.e., we obtain the complete “time reversal.” Now acting with the rotation operator  $U_{\varphi} = \exp(i\varphi S_x)$  on the operator  $O_n^+$  in (11), we obtain

$$\begin{aligned} O_n^+(\varphi) &= \left(\frac{4}{N}\right)^{n/2} \sum_{i \neq j \neq \dots \neq q \neq 0} (S_{zi} \cos \varphi - S_{yi} \sin \varphi) \cdots (S_{zq} \cos \varphi - S_{yq} \sin \varphi) \times \\ &\times (S_0^x + iS_{y0} \cos \varphi + iS_{z0} \sin \varphi). \end{aligned} \quad (27)$$

The last multiplier under the summation sign in formula (27) can be rewritten as

$$iS_{z0} \sin \varphi + \frac{1}{2} S_0^+(1 + \cos \varphi) + \frac{1}{2} S_0^-(1 - \cos \varphi). \quad (28)$$

We obtain the autocorrelation contribution in (24) at coinciding subscripts “0” and “0'” and upon pairing the operators  $S_{zi} \cdots S_{zq}$  from the first  $n$  brackets with the operators  $S_{zl}$  from the analogous set. The operator  $S_0^+$  is then paired with the operator  $S_0^-$ , and we obtain

$$\begin{aligned} \Gamma_{\varphi \text{ auto}}^{+-}(t, \tau) &= \sum_n \frac{1}{2} (M_2 t \tau)^n \exp\left[-\frac{M_2(t^2 + \tau^2)}{2}\right] (\cos \varphi)^n \frac{(1 + \cos \varphi)}{n!} = \\ &= \frac{1}{2} (1 + \cos \varphi) \exp\left[-\frac{M_2(t^2 + \tau^2)}{2} + M_2 t \tau \cos \varphi\right]. \end{aligned} \quad (29)$$

The cross contribution to (24) results from the term in which the subscript “0'” of the operators  $O_m^-$  coincides with one of the subscripts of the operators  $S_{yi}$  in product (27) and the subscript “0” of the operator  $S_{z0}$  coincides (see (28)) with one of the subscripts of the operators  $S_{zl}$  in  $O_m^-$ :

$$\begin{aligned} \Gamma_{\varphi \text{ cross}}^{+-}(t, \tau) &= -\frac{1}{2} \sum_n (M_2 t \tau)^n (\cos \varphi)^{n-1} \sin^2 \varphi \frac{\exp[-M_2(t^2 + \tau^2)/2] n}{n!} = \\ &= -\frac{1}{2} \sin^2 \varphi (M_2 t \tau) \exp[M_2 t \tau \cos \varphi] \exp\left[-\frac{M_2(t^2 + \tau^2)}{2}\right]. \end{aligned} \quad (30)$$

Adding (29) and (30), we obtain

$$\Gamma_{\varphi}^{+-}(t, \tau) = \frac{1}{2} (1 + \cos \varphi - M_2 t \tau \sin^2 \varphi) \exp\left[-\frac{M_2(t^2 + \tau^2)}{2} + M_2 t \tau \cos \varphi\right]. \quad (31)$$

We now consider the second term in (22):

$$\Gamma_{\varphi}^{++}(t, \tau) = \frac{\text{Sp}[U_{\varphi}(\sum_n A_n(t)(\sum_0 i^n O_n^+))U_{\varphi}^+(\sum_m A_m(\tau)(\sum_0 i^m O_m^+))]}{\text{Sp}(S^+S^-)}. \quad (32)$$

In the calculation of the autocorrelation part of (32), the difference (compared to calculations when deriving expression (31)) is that we change the sign of the term  $\cos \varphi$  because the sign of  $i^m$  changes and we pass from the second to the last term in formula (28). We perform the analogous change when calculating the cross contribution as well. We then obtain

$$\Gamma_{\varphi}^{++}(t, \tau) = \frac{1}{2}(1 - \cos \varphi - M_2 t \tau \sin^2 \varphi) \exp\left[-\frac{M_2(t^2 + \tau^2)}{2} - M_2 t \tau \cos \varphi\right]. \quad (33)$$

The two remaining terms in expression (22) are complex conjugate to the expressions already presented (i.e., they coincide in the case under consideration). Eventually, we obtain

$$\begin{aligned} \Gamma_{\varphi}(t, \tau) &= \frac{1}{2}(1 + \cos \varphi - M_2 t \tau \sin^2 \varphi) \exp\left[-\frac{M_2(t^2 + \tau^2)}{2} + M_2 t \tau \cos \varphi\right] + \\ &+ \frac{1}{2}(1 - \cos \varphi - M_2 t \tau \sin^2 \varphi) \exp\left[-\frac{M_2(t^2 + \tau^2)}{2} - M_2 t \tau \cos \varphi\right]. \end{aligned} \quad (34)$$

The desired amplitude of the  $n$ th harmonic, which can be experimentally observed, is the Fourier transform of (34):

$$g_n(t, \tau) = (2\pi)^{-1} \int_{-\pi}^{\pi} d\varphi \exp(in\varphi) \Gamma_{\varphi}(t, \tau). \quad (35)$$

We can further use the Euler formulas and the definition of the Bessel function

$$I_n(x) = \pi^{-1} \int_0^{\pi} dt \exp(x \cos t) \cos nt. \quad (36)$$

Changing the sign of  $\cos \varphi$  in the exponential in (34) results in changing the sign of the Bessel function at odd  $n$  and retaining this sign at even  $n$ . The two terms in (34) therefore mutually cancel at odd  $n$  and are added at even  $n$ . The calculations in the framework of our model therefore only result in the appearance of coherences of even orders, as in the experiments [4]. We eventually find

$$\begin{aligned} g_{2n}(t, \tau) &= \exp\left[-\frac{M_2(t^2 + \tau^2)}{2}\right] \left[ I_{2n}(M_2 t \tau) \left(1 - \frac{M_2 t \tau}{2}\right) + \frac{1}{2} I_{2n+1}(M_2 t \tau) + \right. \\ &\left. + \frac{1}{2} I_{2n-1}(M_2 t \tau) + \frac{1}{4} M_2 t \tau (I_{2n+2}(M_2 t \tau) + I_{2n-2}(M_2 t \tau)) \right]. \end{aligned} \quad (37)$$

Further, using the recursive relations for the Bessel functions [18], we obtain

$$g_n(t, \tau) = I_n(M_2 t \tau) \left(1 + \frac{n^2}{M_2 t \tau}\right) \exp\left[-\frac{M_2(t^2 + \tau^2)}{2}\right]. \quad (38)$$

We note that we obtain expression (38) by assuming an infinite number  $N$  of spins in the system. At the same time, it is a common practice in molecular solids to use a deuteration method to create groups of isolated spins belonging, as a rule, to a single molecule (or to its fragment) with a high symmetry. As a rule, the intermolecular contribution of the dipole–dipole interaction to the spectrum widening in such systems can be almost completely eliminated, and the intramolecular contribution can then be adequately described by model Hamiltonian (4), (5) above. But we must then take into account that the number  $N$  is finite [19]. The corresponding calculations are in Appendix 1.

## 5. Discussing the results

In Fig. 1, we draw the dependences  $g_n(t)$  for hexamethylbenzol constructed using formula (38). Such dependences were first observed experimentally by the authors of [4], where the dynamics of the nuclear spin system was governed by the Hamiltonian

$$H_{\text{eff}} = \frac{1}{3}(H_{xx} - H_{yy}) = \frac{1}{2} \sum_{i \neq j} b_{ij}(S_{xi}S_{xj} - S_{yi}S_{yj}). \quad (39)$$

The observed TCF was proportional to  $\text{Sp}(S_z(t)S_z)$  there. We can pass from the correlation function for the  $z$  component to the correlation function for the  $x$  component of the spin using the cyclic permutation  $x \rightarrow y \rightarrow z$  of the RFS coordinate axes.

The second moment of the spectrum determined by Hamiltonian (39) is related to the second moment of the NMR absorption spectrum by

$$M_{2\text{eff}} = \frac{2}{3}M_{2\text{NMR}}. \quad (40)$$

The temperature dependence for the quantity  $M_{2\text{NMR}}$  was measured in [20].

Hexamethylbenzol is a molecular crystal containing benzol rings to which methyl groups are attached. Four, six, and more quantum coherences cannot appear inside a single methyl group, and the intergroup dipole-dipole interaction therefore plays the determining role in forming these coherences. This relatively weak interaction determines the time scale for the appearance of higher-order correlations.

At a room temperature corresponding to the experimental conditions described in [4],  $M_{2\text{NMR}} = 2.5 \text{Oe}^2$ , which corresponds to a time scale of the order of  $33 \mu\text{sec}$ . At low temperatures when both the methyl groups and the benzol rings are at rest, the contribution to the second NMR moment from the protons of the same methyl group is  $1/6$  of the contribution from protons of other methyl groups. The ratio between these contributions is unknown at room temperature, when both the methyl groups and the benzol rings rotate rapidly about their symmetry axes. When calculating the dependences in Fig. 1, we nevertheless assume that this ratio between contributions to the second moment remains approximately the same as at low temperatures.

The experiments described in [4] were conducted for polycrystal samples; therefore, their correct description, rigorously speaking, requires averaging formula (38) over powder, which seems rather difficult. We therefore choose the second moment (and hence the time scale) to correspond to a polycrystal, which, taking the above into account, results in the value  $T^* \approx 90 \mu\text{sec}$ . The obtained results completely agree qualitatively and agree well quantitatively with the results of the experiment described in [4].

The expression

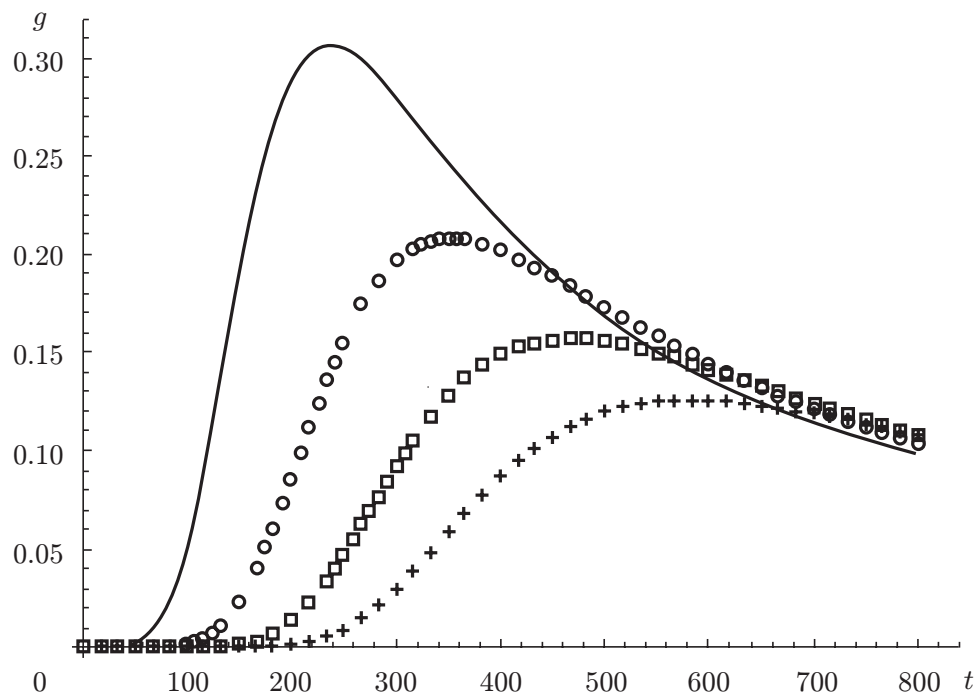
$$g_n = \left[ I_n(M_2\tau^2) + \frac{1}{2}(I_{n+1}(M_2\tau^2) + I_{n-1}(M_2\tau^2)) \right] \exp(-M_2\tau^2) \quad (41)$$

was obtained in [8] to describe the results of the experiment in [4].

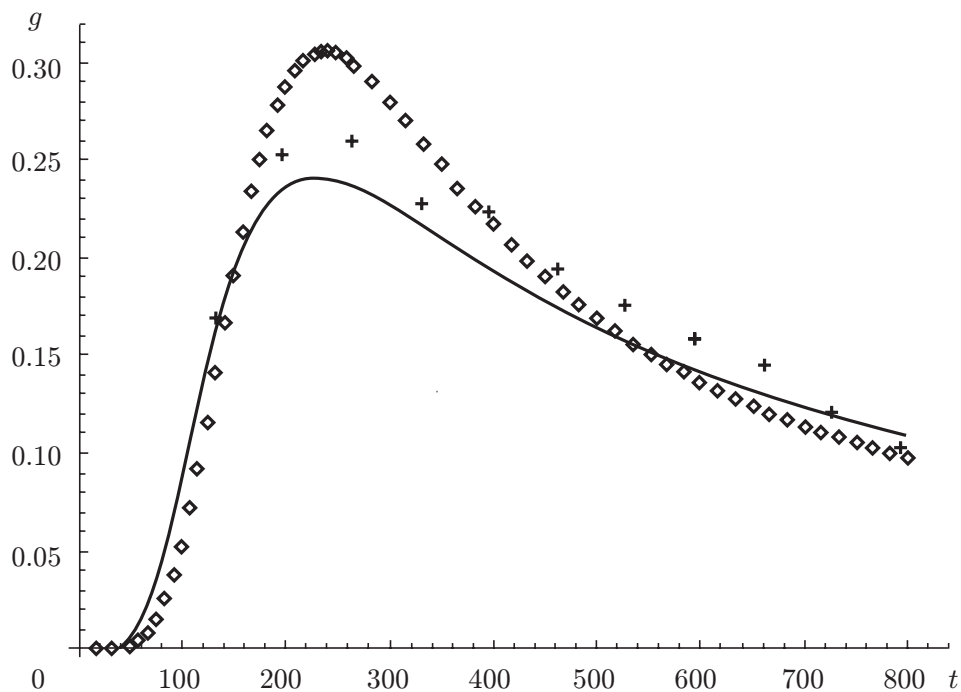
The power-averaging over the powder was performed neither there nor in the present paper, and the time scale, without comments, was set to be  $T^* = 57 \mu\text{sec}$ , which nevertheless resulted in a good agreement between the theory and experiment. We note that formula (41) was obtained for a model different from our model. Finally, the difference between formulas (41) and (38) reduces to neglecting the contribution from cross term (30) in (41).

In Fig. 2, we compare the results of calculations following formulas (38) and (41) with the experimental data [4]. We use the time scale values above.





**Fig. 1.** The time dependence for the doubled amplitudes of multispin multiquantum correlation functions of hexamethylbenzol:  $n = 4$  is denoted by solid curve,  $n = 6$  by  $\circ$ ,  $n = 8$  by  $\square$ , and  $n = 10$  by  $+$ .



**Fig. 2.** The time dependence for the doubled amplitudes of multispin multiquantum correlation functions of hexamethylbenzol for  $n = 4$ . The solid curve corresponds to our theory,  $+$  to calculations according to formula (41), and  $\square$  to the experimental data [7].

## 6. Conclusion

It is a commonly accepted fact stated long ago in the statistical mechanics of nonequilibrium systems that the dynamical evolution of systems of many interacting particles is accompanied by the appearance of multiparticle correlation functions (see, e.g., [21]). Nuclear spin systems are by no means an exception [17]. At the same time, obviously arising problems make calculating any complex multiparticle TCF for actual systems impossible. The exactly solvable model considered in the present paper makes it possible. We have obtained the complete set of orthogonal multispin operators explicitly and found the time dependence for the amplitudes of multiparticle TCF, which are important for the contemporary physics of magnetic resonance.

Our model describes the behavior of multiparticle correlation functions well, at least for small  $n$ . At the same time, correlation functions may start to deviate for large numbers of particles because a more rapid growth of moments as this number increases is observed for systems with Hamiltonian (39) (see Appendix 2) than with the Gaussian function. This probably explains the very rapid growth of the mean number of particles with correlated motion observed in adamantane [4]. These effects will be considered elsewhere.

## Appendix 1

We find the expressions for the desired TCF determined on a lattice containing a finite number  $N$  of spins. The evolution operator is

$$\exp(iHt)S_0^+ \exp(-iHt) = \prod_{j \neq 0}^{N-1} (\cos Bt + 2iS_{zj} \sin Bt)S_0^+. \quad (1.1)$$

Here we use the known properties of exponential operators for the spin 1/2. For the orthogonal operators, we obtain

$$O_n^+ = \left(\frac{4}{N-1}\right)^{n/2} \sum_{i \neq j \neq \dots \neq q \neq 0} \overbrace{S_{zi} S_{zj} \dots S_{zq}}^n S_0^+, \quad n < N, \quad (1.2)$$

$$\text{Sp}(O_n^+ O_m^-) = \frac{1}{(N-1)^n} \delta_{nm} \frac{n!(N-1)!}{(N-1-n)!} \text{Sp}(S_0^+ S_0^-).$$

Expanding the evolution operator in a series in the orthogonal operators, we find

$$\exp(iHt)S_0^+ \exp(-iHt) = i^n \sum_{n=0}^{N-1} A_n(t) O_n^+, \quad (1.3)$$

where

$$A_n(t) = \frac{1}{n!} (N-1)^{n/2} (\sin Bt)^n (\cos Bt)^{N-n-1}.$$

The desired TCF can therefore be represented in the form

$$\Gamma_\varphi^{+-}(t, \tau) = \frac{\text{Sp}[U_\varphi(\sum_{n=0}^{N-1} (i)^n A_n(t) \sum_0 O_n^+) U_\varphi^+(\sum_{m=0}^{N-1} (-i)^m A_m(\tau) \sum_{0'} O_m^+)]}{\text{Sp}(S^+ S^-)}. \quad (1.4)$$

We have

$$\begin{aligned} \Gamma_{\varphi_{\text{auto}}}^{+-}(t, \tau) &= (1 + \cos \varphi) \sum_n \frac{1}{2(N-1)^n} \frac{n!(N-1)!}{(N-1-n)!} A_n(t) A_n(\tau) \cos^n \varphi = \\ &= \frac{1}{2} (1 + \cos \varphi) (\cos Bt \cos B\tau + \cos \varphi \sin Bt \sin B\tau)^{N-1} \end{aligned} \quad (1.5)$$

for the autocorrelation part and

$$\begin{aligned}\Gamma_{\varphi^{\text{cross}}}^{+-}(t, \tau) &= -\frac{1}{2} \sin^2 \varphi \sum_n^{N-1} \frac{(N-1)!}{(N-n-1)!(n-1)!} \cos^{n-1} \varphi (\cos Bt \cos B\tau)^{N-n-1} (\sin Bt \sin B\tau)^n = \\ &= -\frac{1}{2} (N-1) \sin^2 \varphi \sin Bt \sin B\tau (\cos Bt \cos B\tau + \cos \varphi \sin Bt \sin B\tau)^{N-2}\end{aligned}$$

for the cross part.

As above, the expression for  $\Gamma_{\varphi}^{++}(t, \tau)$  can be obtained by changing the sign of  $\cos \varphi$ , which results in the sum containing only even powers of  $\cos \varphi$ . We eventually obtain

$$\begin{aligned}\Gamma_{\varphi}(t, \tau) &= \frac{1}{2} (1 + \cos \varphi) (\cos Bt \cos B\tau + \cos \varphi \sin Bt \sin B\tau)^{N-1} - \\ &\quad - \frac{1}{2} (N-1) \sin Bt \sin B\tau (\cos Bt \cos B\tau + \cos \varphi \sin Bt \sin B\tau)^{N-2} + \\ &\quad + \frac{1}{2} (1 - \cos \varphi) (\cos Bt \cos B\tau - \cos \varphi \sin Bt \sin B\tau)^{N-1} - \\ &\quad - \frac{1}{2} (N-1) \sin Bt \sin B\tau (\cos Bt \cos B\tau - \cos \varphi \sin Bt \sin B\tau)^{N-2}.\end{aligned}$$

## Appendix 2

After performing the cyclical permutation of the variables  $S_x$ ,  $S_y$ , and  $S_z$  in the model with infinite-range interaction, we can write Hamiltonian (39) in the form

$$H = \frac{1}{2} b (S_z^2 - S_y^2).$$

In what follows, we set  $b = 1$ , which corresponds to an obvious choice of the time scale. For the equations of motion

$$\dot{S}_x(t) = -2S_z S_y, \quad \dot{S}_y(t) = S_z S_x, \quad \dot{S}_z(t) = S_y S_x, \quad (2.1)$$

we have two integrals of motion:

$$S_x^2 + S_y^2 + S_z^2 = S^2, \quad \frac{1}{2} (S_z^2 - S_y^2) = E. \quad (2.2)$$

Analogous equations were obtained in [14] for a system of classical magnetic moments. The explanation why the dynamical properties of systems containing quantum and classical magnetic moments coincide in the limit of an infinite number of nearest neighbors was previously given in [16]. Hence, the corresponding results in [14] are applicable to our spin system.

System of equations (2.1) is solved [14] by the Jacobi elliptic functions

$$\begin{aligned}S_x(t) &= a_x \operatorname{sn}(\Omega t + \varphi_0 k), \\ S_y(t) &= a_y \operatorname{dn}(\Omega t + \varphi_0 k), \\ S_z(t) &= a_z \operatorname{cn}(\Omega t + \varphi_0 k),\end{aligned} \quad (2.3)$$

where

$$\begin{aligned}a_x^2 &= S^2 - 2\varepsilon, & a_y^2 &= \frac{1}{2}(S^2 + 2\varepsilon), & a_z^2 &= \frac{1}{2}(S^2 - 2\varepsilon), \\ \Omega^2 &= 2\varepsilon + S^2, & K^2 &= \frac{S^2 - 2\varepsilon}{2\varepsilon + S^2}, & \varepsilon &= |E|.\end{aligned}$$

These parameters together with the phase  $\varphi_0$  are determined by the values of the spin projections at  $t = 0$ . The trajectories  $S_x(t)$ ,  $S_y(t)$ , and  $S_z(t)$  obtained from (2.3) must be averaged over all possible initial values, i.e., over all distributions with the Gaussian density functions.

A solution of Eqs. (2.1) can also be sought in the form of the time series

$$S_x(t) = \sum_{n=0}^{\infty} X_n t^n, \quad S_y(t) = \sum_{n=0}^{\infty} Y_n t^n, \quad S_z(t) = \sum_{n=0}^{\infty} Z_n t^n. \quad (2.4)$$

Substituting (2.4) in (2.1) and equating the coefficients of equal powers of time, we obtain the system of recursive equations

$$\begin{aligned} (n+1)X_{n+1} &= -2 \sum_{m=0}^n Y_{n-m} Z_m, \\ (n+1)Y_{n+1} &= \sum_{m=0}^n Z_{n-m} X_m, \\ (n+1)Z_{n+1} &= \sum_{m=0}^n X_{n-m} Y_m \end{aligned} \quad (2.5)$$

with the initial conditions  $X_0 = S_x(0)$ ,  $Y_0 = S_y(0)$ , and  $Z_0 = S_z(0)$ . The coefficients  $X_n$  can then be obtained as the sums

$$X_n = \sum_{m,q,k}^{m+q+k=n+1} C_{mqk}^n S_x^m S_y^q S_z^k. \quad (2.6)$$

The expressions for  $Y_n$  and  $Z_n$  are analogous.

We give the nonzero coefficients  $C_{mqk}^{(n)}$  in the first four orders:

$$\begin{aligned} C_{11}^{(1)} &= -2, & C_{102}^{(2)} &= C_{120}^{(2)} = -1, & C_{013}^{(3)} &= C_{031}^{(3)} = \frac{4}{3!}, & C_{211}^{(3)} &= -\frac{8}{3!}, \\ C_{122}^{(4)} &= 7 \cdot \frac{8}{4!}, & C_{104}^{(4)} &= C_{140}^{(4)} = \frac{4}{4!}, & C_{302}^{(4)} &= C_{320}^{(4)} = -\frac{8}{4!}. \end{aligned} \quad (2.7)$$

Using relation (6), we can find the moments of the correlation function:

$$M_{2n} = (-1)^n \langle S_x^2 \rangle^{-1} \left. \frac{d^{2n} \langle S_x(t) S_x \rangle}{dt^{2n}} \right|_{t=0} = (-1)^n \left\langle \left. \frac{d^{2n} S_x(t)}{dt^{2n}} \right|_{t=0} S_x \right\rangle \langle S_x^2 \rangle^{-1}. \quad (2.8)$$

As in formula (7), we let  $\langle \cdot \rangle$  denote averaging over the initial data with the Gaussian distribution function. Because

$$\left. \frac{d^n S_x(t)}{dt^n} \right|_{t=0} = X_n n!, \quad (2.9)$$

substituting (2.9) in (2.8) and averaging over independent Gaussian random variables  $S_x$ ,  $S_y$ , and  $S_z$ , we obtain

$$M_2 = 4 \langle S_x^2 \rangle, \quad M_4 = 2(M_2)^2, \quad M_6 = 9(M_2)^3, \quad M_8 = 117(M_2)^4.$$

We note that for the Gaussian distribution  $\varphi(x) = (1/M_2(2\pi^{1/2})) \exp(-0.5x^2/M_2^2)$ , the moments are  $\mu_{2k} = 1 \cdot 3 \cdot \dots \cdot (2k-1)M_2^k$ , where  $k = 1, 2, \dots$ .

Using (2.6), we can determine not only the moments but also the orthogonal operators in full analogy with what was done in the body of the paper. For this, we must substitute  $S_\alpha = \sum_i S_{\alpha i}$ ,  $\alpha = x, y, z$ , in (2.6) preserving only operators corresponding to spins located at different sites in the sums.

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