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Reversible and Irreversible Propagation of Quantum Information and Its Manifestation in Multiple-Quantum NMR Spectra in Solids

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Received January 22, 2020; revised February 5, 2020; accepted February 6, 2020

Abstract—On the basis of the earlier developed statistical theory of the growth of the effective size of correlated clusters (the number of correlated spins), an expression for the shape of the multiple-quantum (MQ) NMR spectrum is obtained that takes into account the loss of coherence in a spin system due, for example, to the controlled intervention of the experimenter. It is shown that the scrambling and decoherence processes in the MQ spectrum of the multiparticle system of a solid are not separated, unlike the corresponding spectra of some large isolated molecules [27] in a solution. The relations obtained allow one to extract the necessary information about the above processes (scrambling and decoherence) from the dependence of the MQ spectra on experimental parameters.

DOI: 10.1134/S1063776120060096

1. INTRODUCTION

The dynamic behavior of multispin multiple-quantum (MQ) coherences arising upon exposure of the nuclear spin subsystem of a substance in the condensed phase to a sequence of rf pulses underlies MQ NMR spectroscopy [1].

On the one hand, MQ NMR is a powerful and often indispensable tool for studying clusters and local structures arranged, for example, on surfaces [2], in liquid crystals [3], nanosized cavities [4], etc. On the other hand, the improvement of MQ spectroscopy methods made it possible to study experimentally the time evolution of multispin correlations through the observation of emerging coherent states with the use of MQ NMR methods [5–10]. The development and propagation of multiparticle correlations is of fundamental interest for the statistical mechanics of irreversible processes [11]. In addition, multiparticle spin correlations may serve as a “quantum register” (see, for example, [5–9]) for quantum computations.

Coherent states prepared in a nuclear spin system can be controlled by sequences of rf pulses by initiating various processes, for example, the processing of quantum information when implementing quantum algorithms.

In MQ spectroscopy, initially localized quantum information is redistributed over a multiparticle system, involving (generally speaking) all particles, and is accompanied by the appearance of various, in particular, nonlocal correlations. Thus, using the above cor-

relations, one can create a register of a quantum computer. The process of reversible redistribution of quantum information (scrambling) over multiparticle correlations is usually accompanied by irreversible (although, as a rule, partial) disturbances in the transmission process. These disturbances are called loss of coherence (decoherence), and they can be caused by various factors. In particular, decoherence can be caused by imperfections of the measurement equipment. Thus, actually, two processes compete in the dynamics of MQ coherences: the development of complex time correlation functions (TCFs) that reflect the development of the above coherences, and their damage (or total decay) due to decoherence processes.

To study scrambling and to determine its rate, etc., four-particle out-of-time-ordered correlation (OTOC) TCFs are used [12–15]. These TCFs, associated with information entropy, contain specific information about the most intimate processes in a multiparticle system, for example, about multiparticle entanglement, localization in a many-body system, development of chaos, and so on, up to some aspects of black hole physics (see, for example, [14]).

Since both of these processes are very important for modern condensed matter physics and quantum informatics, it is not at all surprising that the most serious efforts have been made to study them both theoretically and experimentally in various multiparticle systems. The possibilities of separating the effects of

these processes on a system have also been investigated.

It should be noted that the experimental study of MQ NMR in multispin systems has a number of notable advantages over other multiparticle systems, such as, for example, ultracold neutral atoms [16] or trapped ions [17]. The point is that the (naturally arising) TCFs used in MQ spectroscopy belong to the class of OTOCs. These are four-particle TCFs that contain (by definition) a time-reversed stage of evolution. It is worth noting that, among the set of different four-particle TCFs, the second moment of the MQ NMR spectrum plays a very significant role [10, 18], which is due to two circumstances. The value of this moment determines the lower bound [19, 20] of the Fisher criterion for quantum information, which represents a measure of entanglement. In addition, the second moment of the MQ spectrum is a quantity that is directly measured in the experiment and therefore allows one to experimentally determine the corresponding OTOC TCF [15]. These properties of the second moment hold only when recording an undistorted MQ spectrum. Processes causing loss of coherence distort the shape of the MQ spectrum; therefore, the study of these processes is very important for a corresponding method for measuring the propagation of quantum information.

To study the processes of decoherence, in [8], the authors significantly modified for the first time the standard MQ NMR technique [21]. The declared purpose of the modification was to investigate the question, “How far can quantum information be transmitted in the presence of gates of finite (and controlled by the experimenter) precision?” In other words, the authors investigated the question of how large can a cluster of correlated spins grow under such conditions. In this regard, the authors of [8, 22] observed the growth of clusters of correlated spins by introducing a controlled perturbation into the Hamiltonian creating these clusters. As suggested in [8, 22], the maximum cluster size in such a situation is limited, and the maximum-size clusters are in dynamic equilibrium with the environment. If the initial cluster size is larger than its equilibrium value, it decreases under the action of the perturbing Hamiltonian, while the unperturbed Hamiltonian only leads to unbounded growth of the cluster size. The equilibrium cluster size, according to the authors, decreases with increasing perturbation intensity. According to the conception of the articles [8, 22], all the above means the process of Anderson localization [23].

However, in [24, 25], based on the previously developed theory of the growth of correlated clusters under ideal conditions [10] and the theory of relaxation of MQ coherences [26], we explained the change in the intensity profile of MQ coherences observed in [8] and showed that the stabilization of the latter with increasing time is not related to the stabilization of the

cluster size. On the contrary, a cluster of correlated spins grows monotonically, while the observed changes in the intensity profile (of the MQ spectrum) and its stabilization are due to the dependence of the decay rate of MQ coherence on its order (its position in the MQ spectrum).

Recently, in [27], the authors proposed a scheme of experiment that would allow, according to them, separation of the decoherence and scrambling processes. The operation of the scheme was demonstrated in an NMR experiment on specific star-shaped molecules of $P(OCH_2CF_3)_3$ (complete ester of phosphorous acid and 2,2,2-trifluoroethanol). The system contains one spin of phosphorus ^{31}P , six protons 1H , and nine ^{19}F spins. The phosphorus nucleus is the central spin (qubit), and the nuclei of hydrogen and fluorine form, respectively, the second and the third layers, due to which (when they are coupled to phosphorus by pulse sequences) scrambling and decoherence processes occur. Each of the three branches of the system contains two protons and three fluorine nuclei. This “structure” was placed in a deuterated solution. The role of the dipole–dipole interaction was played by the scalar exchange (through electron shells) interaction.

The presence of three types of nuclei necessitates the exposure of the sample to a rather specific sequence of rf pulses at different frequencies (see Fig. 4 in [27]). Nonetheless, actually the experiment can be described as follows. While the loss of coherence occurs during the entire fixed mixing time T , the scrambling interval t was regulated in the preparatory period by setting the duration of the intervals of forward and backward evolution (by the direct evolution of the system and its reconstruction during time reversal): $(T + t)/2$ and $(T - t)/2$, respectively.

The loss of coherence in the new experimental scheme proposed in [27] has not been previously considered in solid state NMR. The analysis of this process, which is important for studying the dynamics of quantum information by the MQ NMR method, is the goal of the present work.

2. DYNAMICS OF MQ COHERENCES IN SOLIDS

As is known [28], the main factor responsible for the broadening of NMR lines in nonmetallic diamagnetic solids is the secular part of the internuclear dipole–dipole interactions, which completely determines the dynamics of the nuclear spin system:

$$H_d = \sum_{i \neq j} b_{ij} S_{zi} S_{zj} \quad (1)$$

$$-\frac{1}{4} \sum_{i \neq j} b_{ij} (S_{+i} S_{-j} + S_{-i} S_{+j}) = H_{zz}^0 + H_{ff},$$

where

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

\mathbf{r}_{ij} is the vector connecting the spins i and j , θ_{ij} is the angle formed by the vector \mathbf{r}_{ij} with the external static magnetic field, γ is the gyromagnetic ratio, and $S_{\alpha i}$ is the α -component ($\alpha = z, +, -$) of the vector spin operator at site i . Henceforth, energy is expressed in frequency units.

Usually, when using pulsed NMR methods in a solid, the basic Hamiltonian (1) is transformed by spin alchemy (various sequences of rf pulses) into other Hamiltonians that are of interest to the researcher [29]. For example, in traditional MQ NMR spectroscopy, the original Hamiltonian is transformed into a two-spin/two-quantum effective Hamiltonian [21, 30]:

$$H_{\text{eff}} = H_{DQ} = (-1/4) \sum_{i \neq j} b_{ij} (S_{+i} S_{+j} + S_{-i} S_{-j}), \quad (2)$$

which is nonsecular with respect to a strong external magnetic field. Under this Hamiltonian, during the so-called preparatory period of length t , the original magnetization is transformed into various TCFs of a rather complex structure that depend on the product of different numbers of spin operators Q , called clusters. In other words, the equilibrium high-temperature density matrix in a strong static magnetic field of the form [28]

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

(here k is the Boltzmann constant, T temperature, and N is the total number of spins in the sample) turns into a nonequilibrium density matrix, which can be conveniently represented as the sum of off-diagonal elements ρ_M with a certain difference M of magnetic quantum numbers, called multiple-quantum coherences (M being the coherence order):

$$\rho(t) = \exp\{-iH_{\text{eff}}t\} \rho_{\text{eq}} \exp\{iH_{\text{eff}}t\} = \sum_M \rho_M(t), \quad (3)$$

$$\rho_M(t) = \sum_{Q=M}^{Q=N} \sum_{\{i\}} \sum_p g_{QMp\{i\}}(t) |QMp\{i\}\rangle,$$

where $|QMp\{i\}\rangle$ is the basis operator in which Q single-spin operators form a product that couples Zeeman states differing by M units and $\{i\}$ are the numbers of crystal lattice sites occupied by this cluster. Thus, $\{i\}$ is actually a multi-index. Summation over $\{i\}$ implies summation both over a set of clusters and over a set of spins within each cluster. The expression under summation depends only on the differences of the coordinates specified by it. Thus, the dependence on one of the coordinates is missing. Setting this coordinate to be arbitrary, we find that the summed expression decays fast enough with respect to other coordinates. Here a cluster is given by a group of spins for which the summed expression is not negligible. The index p

numbers different basis states with the same values of Q and M , and N is the total number of spins in the system. The coherences arising during the preparation time t are labeled by the phase shift φ [21, 30]. The resulting phase shift is proportional to $M\varphi$, where M is an integer. Thus, Q -spin correlations are also distinguished by the number of quanta ($M \leq Q$) [1, 21, 30]. Further, in many experiments of interest, these coherences relax over a time period t_d under the secular dipole–dipole Hamiltonian (1). The free evolution period is followed by a mixing period, during which a new pulse sequence is applied to the system, which reverses the sign of the effective Hamiltonian (2); thus, a time reversal is performed [21, 30], owing to which the order is again returned to the observable—the single-quantum longitudinal magnetization. This magnetization can be measured with the use of a $\pi/2$ pulse, which turns the magnetization into a plane perpendicular to the external magnetic field. The amplitude of the partial (for a given value of M) magnetization is extracted using the Fourier transformation with respect to the variable φ . To determine the relaxation rate, one should repeat the experiment many times for different values of t_d [5–7].

It should be specially noted that the observation of MQ coherence signals is possible only under certain conditions, due to which all contributions to the coherence of a given order appear (after a recovery (mixing) period) with the same phase [21]. In view of the fundamental importance of this circumstance, we discuss this aspect of MQ spectroscopy in detail.

The amplitude and phase of partial magnetization is completely determined by the history of the development of the spin system. Thus, if, during the preparatory period, the development of the system occurs under the Hamiltonian (2) (the corresponding propagator is $U(t) = \exp(-iH_{\text{eff}}t)$), while, during the mixing period, the development occurs under a certain, generally speaking, different Hamiltonian H'_{eff} (the corresponding propagator is $V(\tau) = \exp(-iH'_{\text{eff}}\tau)$), then the total magnetization amplitude is described by the expression [21]

$$\Gamma_0(t, t_d, \tau) \propto \text{Sp}\{S_z \rho(t, t_d, \tau)\} \propto \text{Sp}\{S_z V^+(\tau) \times \exp(-iH_d t_d) U^+(t) S_z U(t) \exp(iH_d t_d) V(\tau)\}.$$

Here S_z is the z component the vector operator of the total spin of the system.

Let us calculate the trace of this expression in the basis of eigenfunctions of the secular dipole–dipole Hamiltonian (1), denoting them by $|i\rangle$ and $|j\rangle$. Writing the complex matrix elements in the form

$$P_{ij}(t) = \langle i | U^+(t) S_z U(t) | j \rangle,$$

$$Q_{ij}(\tau) = \langle i | V^+(\tau) S_z V(\tau) | j \rangle,$$

we obtain

$$\Gamma_0(t, t_d, \tau) \propto \sum_{i,j} P_{ij}(t) Q_{ji}(\tau) \exp\{-i(\omega_i - \omega_j)t_d\}.$$

Here ω_i and ω_j are the eigenvalues (in frequency units) of the Hamiltonian (1). It follows from the above that if the Hamiltonians controlling the evolution of the spin system during the preparatory period and the mixing period are different, then the MQ coherences created in the preparatory period will undergo only an additional transformation during the mixing period. If the operator controlling the evolution of the system during the mixing period is constructed so that $V^+(\tau) = U(t)$, or it differs from $U(t)$ only by a phase factor φ , i.e.,

$$V^+ = \exp(-i\varphi S_z) U \exp(i\varphi S_z),$$

(it is this situation that is realized by time reversal), the observed signal takes the form of a Fourier series with respect to coherences of different orders [21]:

$$\Gamma_0(t, t_d, t) \propto \sum_M \sum_{i,j} |P_{ij}|^2 \exp(iM\varphi) \exp\{-i(\omega_i - \omega_j)t_d\}.$$

Thus, in the above-described evolution of events, each partial coherence includes contributions from all coherences of a given order, differing in phase by $\pm\varphi$ from the neighboring ones.

Following the simplest statistical model [21, 30], in the experiment one usually uses a Gaussian form for the distribution of coherences of various (small) orders in the MQ spectrum:

$$g_M(t) = \frac{2}{\sqrt{\pi K(t)}} \exp\left\{-\frac{M^2}{K(t)}\right\}. \quad (4)$$

Notice that, as shown in [31], for large values of the order M , the distribution in formula (4) becomes exponential. The variance of the distribution in the statistical model ($K(t)/2$) is determined by the average number of spins $K(t)$ between which a dynamic correlation was established due to the interaction (2) during the preparation time t . This number, called the number of correlated spins, or the effective cluster size, increases with increasing preparation time t .

In the traditional scheme of MQ NMR, one observes the TCF

$$\Gamma_\varphi(t, \tau) = \text{Sp}\{U^+(\tau) U_\varphi U(t) S_z U^+(t) U_\varphi^+ U(\tau) S_z\} / \text{Sp}\{S_z^2\}, \quad (5)$$

where $U(t)$ is the evolution operator with the Hamiltonian $H_{\text{eff}} = H_{DQ}$ from (2) and $U_\varphi = \exp(i\varphi S_z)$ is the operator of rotation through angle φ about the z axis. We introduced a notation τ for the evolution with “reversed time” (with the Hamiltonian H_{DQ}). Under experimental conditions, $\tau = t$. Rotation about the corresponding axis through angle φ marks and distinguishes TCFs corresponding to coherences of different orders M , which are determined by the difference of magnetic quantum numbers. The full spectrum of MQ

NMR can be obtained by the Fourier transformation of TCF (5) with respect to the variable φ .

In the new scheme of experiment proposed in [27], the evolution operator in the preparatory period is realized by replacing the unitary operator $U(t)$ by a composite operator, which corresponds in the experiment to the reversal of evolution in the time interval $[(T+t)/2, T]$:

$$U_T(t) = U\left(\frac{T+t}{2}\right) U^+\left(\frac{T-t}{2}\right). \quad (6)$$

Note that such a scheme was used in the fundamental work on MQ NMR [21] to experimentally illustrate the changes in MQ coherences and the decrease in the number of correlated spins during time reversal. Without decoherence, $U_T(t) = U(t)$, and one observes the same MQ spectrum.

To correlate the methods of [8] and [27], we rewrite the evolution operator with controlled loss of coherence from [8], taking into account formula (6). To control the loss of coherence in [8] in the preparatory period $[0, t]$, the authors created the effective Hamiltonian

$$H_{\text{eff}} = (1-p)H_{DQ} + pH_d, \quad (7)$$

where p is a small parameter, which controls decoherence. To explicitly take into account the loss of coherence, we set

$$U_T(t) = \exp\left\{-i\frac{T+t}{2}[(1-p)H_{DQ} + pH_d]\right\} \times \exp\left\{+i\frac{T-t}{2}[(1-p)H_{DQ} - pH_d]\right\}, \quad (8)$$

with $p \neq 0$ and $U_T(t) \neq U(t)$. Thus, we transform the experimental scheme of [27] so that it can be applied to simpler and traditional spin systems, such as, for example, adamantane, which was used in [8, 22].

3. LOSS OF COHERENCE IN THE SYSTEM AND ITS EFFECT ON THE MQ SPECTRUM

To assess the effect of decoherence, we consider the dynamics of the system when it is acted upon by the unitary operator from formula (8). Due to the interaction H_{DQ} , the cluster size K of the correlated spins (the number of spins in the cluster) first increases in the interval $[0, (T+t)/2]$ and then, in the interval $[(T+t)/2, T]$, decreases, as shown schematically in the Fig. 1.

Before analyzing the general case corresponding to the figure, we consider a simpler situation, which was investigated earlier, and briefly outline the main features. Suppose that a cluster of K spin operators with coherence order M is formed, and let K and M remain unchanged in what follows, while the dynamics of the system is determined by the Hamiltonian pH_d . This case was investigated experimentally (for $p = 1$) in [5–7] and theoretically in [26]. In [26], the authors

obtained the following expression for the decay of this coherent state:

$$\begin{aligned} \Gamma_{KM}(t_d) &= \exp(-KB^2 t_d^2/2) \exp(-A^2 M^2 t_d^2) \\ &= F_K(t_d) F_M(t_d), \end{aligned} \quad (9)$$

where $A^2 = p^2 A_d^2$, $B^2 = p^2 B_d^2$, and A_d^2 and B_d^2 are some constants determined by the field arising due to the dipole–dipole interaction of the spins surrounding the cluster in the lattice with the spins of the cluster. These constants are directly related to the lattice sums of the coefficients b_{ij} of Hamiltonian (1). In this case, the parameter B^2 characterizes the uncorrelated contribution to the local field on each of the spins, independent of the contributions on other spins. The parameter A^2 characterizes the average field that acts in a correlated manner on all spins of the cluster [24, 26]. Note that the formula can be generalized to the case when the spins of the cluster are acted upon by an additional inhomogeneous (for example, external, created by the apparatus) magnetic field having two different, local and nonlocal, components. If the contributions to this field are described by Gaussian distributions with variances W_{loc} and W_{av} , then the corresponding contributions can be added to the constants: $A^2 = p^2 A_d^2 + W_{\text{av}}^2$, $B^2 = p^2 B_d^2 + W_{\text{loc}}^2$.

Let us return to the general case shown in Fig. 1. As the current time t' increases, the number $K(t')$ of spin operators in the cluster changes. The operators associated with the cluster on each interval $[t' - \Delta t, t' + \Delta t/2]$ will relax with their own time t_d in formula (9), which depends on t' . The number of such operators is $\Delta t dK/dt'$. Summing up the contributions from different intervals and letting Δt go to zero, we obtain the following expression for the first factor in formula (9):

$$F_K(T, t) = \exp \left\{ -\frac{B^2}{2} \int_0^{(T+t)/2} \frac{dK(t')}{dt'} [t_d(t')]^2 dt' \right\}. \quad (10)$$

The spins that appear in the cluster in the interval $[0, t]$ (they correspond to certain operators in TCFs) will relax until time T . Therefore, $t_d(t') = (T - t')$ in this interval. The spins that appear in the interval $[t, (T + t)/2]$ will relax only until they disappear. For these spins, $t_d(t') = 2[(T + t)/2 - t']$. Separating these two intervals in formula (10), we obtain

$$\begin{aligned} F_K(T, t) &= \exp \left\{ -\frac{B^2}{2} \int_0^t \frac{dK(t')}{dt'} [T - t']^2 dt' \right. \\ &\quad \left. - \frac{B^2}{2} \int_t^{(T+t)/2} \frac{dK(t')}{dt'} [T + t - 2t']^2 dt' \right\}. \end{aligned} \quad (11)$$

To complete the calculations, we should specify the dependence of the average size of the cluster of correlated spins on the preparation time in formula (11). This dependence is determined by the properties of

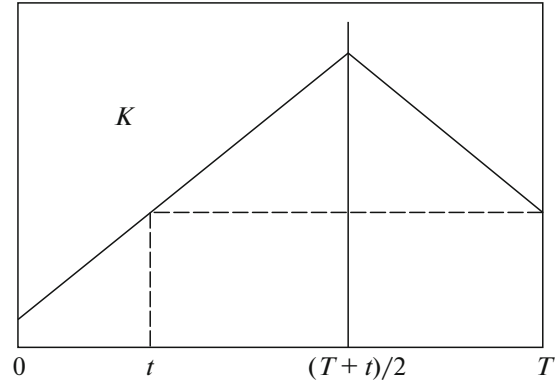


Fig. 1. Schematic dependence of the average size $K(t')$ of a cluster of correlated spins on current time t' in the preparatory period with composite evolution operator (6). The dashed line marks the evolution interval $[0, t]$ corresponding to the standard operator $U(t)$.

the spin system and, in particular, depends on the dimension of the space. In accordance with the earlier developed theory [10], in three-dimensional lattices, one should expect an exponential time dependence, while, in one-dimensional lattices, a linear dependence. Indeed, a linear dependence was observed in the quasi-one-dimensional system of fluorapatite [32], while, in three-dimensional adamantane, a significantly faster growth was observed [5, 8, 22], which is well described by an exponential function [10, 24, 25, 33].

For the exponential growth of the average number of correlated spins, $K(t') = \exp(at')$, the integration in (11) yields

$$\begin{aligned} F_K(T, t) &= \exp \left\{ -\frac{B^2}{2a^2} [8e^{a(T+t)/2} \right. \\ &\quad \left. - e^{at} (2a(T-t) + 6) - a^2 T^2 - 2aT - 2] \right\}. \end{aligned} \quad (12)$$

In the two limiting cases, we obtain

$$F_K(T, t) = \exp \left\{ -\frac{B^2 a}{6} [T^3 - (T-t)^3/2] \right\} \quad (13)$$

for $aT \ll 1$ and

$$\begin{aligned} F_K(T, t) &= \exp \left\{ -\frac{4B^2}{a^2} e^{a(T+t)/2} + \frac{B^2}{a^2} e^{at} [a(T-t) + 3] \right\} \end{aligned} \quad (14)$$

for $aT \gg 1$.

The second factor in (9) determines the dependence of the relaxation time on the coherence order M . It is the clusters with order M at the end of the preparatory period (at time T), marked by the phase factor $\exp(iM\phi)$, that contribute to the corresponding component of the MQ spectrum. The change of the cluster size in the preparatory period is accompanied

by a change in the order of coherence with time, $M(t')$. In the ideal case of $p = 0$, this change does not affect the final result. In the general case shown in Fig. 1, we write the second factor in the form that follows from the theory of [26]:

$$F_M(T, t) = \exp \left\{ -A^2 \left[\int_0^T M(t') dt' \right]^2 \right\}. \quad (15)$$

This expression should be averaged over all possible trajectories of change in $M(t')$ with a given value of M at time T . It is clear that $M(t')$ will grow in the interval $[0, (T + t)/2]$, while, in the interval $[(T + t)/2, T]$, it

will decrease or keep the value of M . In [24], we proposed a simple technique for an adequate estimate. Assuming that a coherence of given order M in a growing cluster appears at a random time t' and does not change further, we obtain

$$F_M(T, t) \approx \exp(-A^2 M^2 \langle (T - t')^2 \rangle), \quad (16)$$

where $\langle (T - t')^2 \rangle$ is the average over the occurrence time t' of coherence in the interval $[0, (T + t)/2]$, which is characterized by the probability density $R(t')$:

$$R(t') = a \exp(at') / [\exp\{a(T + t)/2\} - 1]. \quad (17)$$

After averaging, we find

$$\langle (T - t')^2 \rangle = \frac{a^2(T - t)^2/4 + (T - t)a + 2 - e^{-a(T+t)/2}(T^2 a^2 + 2Ta + 2)}{a^2(1 - e^{-a(T+t)/2})}. \quad (18)$$

In particular, if $aT \gg 1$, then

$$\langle (T - t')^2 \rangle \approx \frac{(T - t)^2}{4} + \frac{T - t}{a} + \frac{2}{a^2}. \quad (19)$$

After substituting (18) into (16), we obtain the sought expression for $F_M(T, t)$.

For the linear growth of the average cluster size, $K(t') = mt'$, in the same way we find

$$F_K(T, t) = \exp \left\{ -\frac{B^2 m}{12} [2T^3 - (T - t)^3] \right\}, \quad (20)$$

$$\langle (T - t')^2 \rangle = \frac{8T^3 - (T - t)^3}{12(T + t)}. \quad (21)$$

Finally, taking into account decoherence, for the MQ NMR spectrum we find

$$g_M(T, t) = \frac{2}{\sqrt{\pi K(t)}} \exp \left\{ -\frac{M^2}{K(t)} \right\} F_K(T, t) F_M(T, t). \quad (22)$$

Here, $F_K(T, t)$ defines a decrease in the total intensity of the MQ spectrum, and $F_M(T, t)$ defines a change in the shape of the MQ spectrum due to the loss of coherence. Both $F_K(T, t)$ and $F_M(T, t)$ depend on the available time parameters T and t in a rather complicated way; hence, the two processes, scrambling and decoherence, are not separated, as observed for a large isolated molecule under the conditions of [27].

The final formula (22) is obtained for the conditions of the MQ experiments of [8], when the interval of free evolution between the preparatory period and the mixing period is minimal. If this interval t_d increases [5–7], an additional loss of coherence occurs under the secular dipole–dipole interaction. To take this loss into account, according to the results of [26], we should additionally multiply the right-hand side of formula (22) by two factors given in formula (9), which, however, should be taken with coefficients A_1 and B_1 (that is, for $p = 1$).

Since decoherence has changed the shape of the MQ spectrum, the value of its second moment is also changed. From formula (22) we obtain the following expression for the effective average cluster size associated with this moment:

$$K_{\text{eff}}(T, t) = [(K(t))^{-1} + A^2 \langle (T - t')^2 \rangle + A_1^2 t_d^2]^{-1}.$$

These changes should be taken into account in the method, proposed in [15], for measuring OTOC functions through the second moment of the MQ spectrum.

Finally, note that, in a number of works, the authors present arguments in favor of the exponential (rather than Gaussian) profile of MQ coherences (see, for example, [4, 31]). For this shape of the spectrum, the exponent in (22) is described by the expression $|M|/K(t)$; however, the description of the effect of decoherence is not qualitatively changed in this case. A quantitative result for the effective average cluster size can be obtained numerically, by the e -fold relaxation of the MQ spectrum [24, 25]. Our calculations of the change in the spectrum, performed in [25], when the Gaussian profile was changed to the exponential under the conditions of the MQ experiments of [8], demonstrated that the effect of this modification is negligible.

4. CONCLUSIONS

As a rule, in the literature devoted to the theoretical studies of four-particle OTOC TCFs, the authors use numerical calculations for some sufficiently simple model Hamiltonians, which, of course, is caused by the complexity of the general problem of calculating the corresponding TCF:

$$C(t) = \langle W^+(t) V^+(0) W(t) V(0) \rangle_\beta. \quad (23)$$

Here $V(0)$ and $W(0)$ are two commuting operators, and the time dependence is determined by a unitary

operator with the system Hamiltonian in the exponent. The angle brackets $\langle \dots \rangle_{\beta}$ denote the statistical mean (see, for example, [19]).

In [10], we analytically demonstrated that, for three-dimensional nuclear spin systems with secular dipole-dipole interaction (1) (or with effective two-quantum interaction (2)) at high temperatures, the OTOC TCF, which in this case represents the second moment of MQ NMR and determines the number of correlated spins, grows exponentially with time. The latter means that all nuclear spins of the sample would be instantly correlated if there were no destructive decoherence processes. In the present work, on the basis of the previously developed statistical theory of MQ NMR spectra [24–26], we have obtained expressions for the MQ NMR spectrum of a multispin system with regard to decoherence processes. We have shown that the scrambling and decoherence processes are not separated, at least in a multispin system, due to their entangled time dependence (see formula (22)). Nevertheless, the relations obtained allow the extraction of the necessary information about these processes from the experimental dependence on the corresponding time parameters T and t .

FUNDING

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the State Task 0082-2019-0001 (State Registration Number AAAA-A19-119012890064-7).

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Translated by I. Nikitin