Solid-state multiple quantum NMR in quantum information processing: exactly solvable models

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Multiple quantum (MQ) NMR is an effective tool for the generation of a large cluster of correlated particles, which, in turn, represent a basis for quantum information processing devices. Studying the available exactly solvable models clarifies many aspects of the quantum information. In this study, we consider two exactly solvable models in the MQ NMR experiment: (i) the isolated system of two spin-1/2 particles (dimers) and (ii) the large system of equivalent spin-1/2 particles in a nanopore. The former model is used to describe the quantum correlations and their relations with the MQ NMR coherences, whereas the latter helps one to model the creation and decay of large clusters of correlated particles.

Keywords: multiple quantum NMR; quantum entanglement; quantum discord; dimers; nanopore; multiple quantum NMR coherence

1. Introduction

At present, the perspectives of technological development are incredible without combining classical and quantum devices, i.e. devices whose operation is based on the principles of quantum mechanics. The development of quantum information technology stimulates an in-depth study of the properties of quantum correlations inherent in a quantum system. In particular, there is a problem of identification of those quantum correlations that are responsible for the advantages of quantum computations in comparison with classical counterparts. Entanglement [1–5], which was originally taken as a measure of such correlations, seemed to not cover all of them. As a consequence, there are quantum systems without entanglement, which, nevertheless, reveal either a quantum non-locality [6–8] or speed up certain calculations in comparison with the classical analogues [9–13]. Such observations cause a new stimulus for studying those quantum correlations that are not captured by entanglement. Thus, the concept of quantum discord has been intensively developed during past years [14–16]. Originally, the quantum

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discord was introduced to characterize the impact of classical measurements on a quantum system with the purpose to get the maximal information about this system with the minimal influence on it [17]. At first glance, the quantum discord seems to cover all quantum correlations. However, it was shown that the quantum discord may be either bigger or smaller than the entanglement [15,18,19]. Thus, we may state that the quantum discord involves different quantum correlations than entanglement does, in general, which causes doubts whether the discord captures all correlations. Moreover, the discord is not symmetrical with respect to the subsystem chosen for the projective measurements [14], which stimulates further study of this ambiguity [20] and suggests introducing the discord under two-side projective measurements [21] (a symmetrical discord).

Quantum cryptography [22,23], teleportation [24–28] and metrology [29–31] seem to be most progressive by way of application of quantum systems. Another promising advantage of quantumness, which still is not realized, is the quantum computation. The first result in this direction was demonstrated in Knill et al. [31], where ensemble quantum computing with liquid state nuclear magnetic resonance (NMR) offers the seven-qubit quantum register. However, perspectives of quantum information processing (QIP) based on liquid state NMR cause doubts because of two basic reasons: (i) the number of correlated qubits is very restricted (about 10) [32] and (ii) the quantum correlations in liquid qubit system are not strong. In particular, the entanglement is almost absent [33]. However, quantum correlations are believed to be the main resource of quantum devices allowing, in particular, the speeding up of quantum processes in comparison with their classical analogues.

For this reason, development of QIP based on NMR in solids seems to be much more promising, because (i) the number of correlated qubits may be much bigger than in liquids and (ii) there are entangled states in solid quantum systems that must provide advantages for such QIP.

The magnetic resonance force microscopy work of Yamamoto et al. [34–37] has inspired us to ask ‘Could we design a solid-state NMR QIP device with quasi-one-dimensional hydroxyapatite or one of its modified derivatives?’ [38,39]. Our efforts to answer this question have been strongly influenced by NMR work on this material from the 1960s to today [37,40–42]. While we realize that other solid-state NMR QIP device proposals exist with modest numbers of qubits [34–37], the unique combination of circumstances suggests that in a macroscopic sample of hydroxyapatite, the ultimate physical limit of 100 qubits could be achievable, in principle, with bulk NMR methods. Physical estimations with current technology indicate that hundreds to thousands of qubits should be within reach.

As an example [39], we consider a crystalline sample of calcium hydroxyapatite, Ca$_5$(PO$_4$)$_3$OH ($3.5 \times 9.5 \times 9.5$ cm) that contains approximately 1024 hydrogens. The microscopic structure of such a sample consists of one-dimensional chains of hydrogens, from hydroxyl groups, with a lattice spacing of 3.44 Å, and with each chain surrounded by six nearest-neighbour (NN) parallel chains at a distance of 9.42 Å; calcium and phosphate ions are interspersed among the chains [38]. When the hydrogen chains are parallel to a strong Zeeman magnetic field along the $z$-direction, the sample has $10^8$ planes oriented perpendicularly to the field, with $10^{16}$ hydrogen nuclear spins in each plane. Thus, by adding a static magnetic
field gradient along the $z$-direction, each plane of spins would be identified with a different resonant Zeeman frequency. These individual planes would be the working qubits.

Multiple quantum (MQ) NMR spectroscopy provides some insights into the space-filling properties of condensed matter on microscopic and possibly mesoscopic length scales [43]. The interplay of MQ NMR spin dynamics and the dimensionality of the space embedding the spins has been probed in materials with quasi-one-dimensional distributions of spins $\frac{1}{2}$ by Yesinowsksi et al. [40,44,45]. Efforts to understand these experimental results were limited to arguments involving less than typically 10 spins. An exact solution for MQ NMR spin dynamics in an infinite one-dimensional quantum spin chain with NN dipolar interactions has been obtained in the high-temperature approximation [46] as well as in the low-temperature case [47]. This model is the first exactly solvable model in MQ NMR for a system with a macroscopic number of coupled spins. Numerous reasons exist to study simplified and tractable one-dimensional models [48]. Our motivations and justifications include the following: (i) the hope to gain insights, understanding and predictions of some features of MQ NMR in materials with quasi-one-dimensional distributions of spins [40,44,45], (ii) in many cases, consideration of only NN dipolar interactions in a one-dimensional chain is a reasonable approximation because 83 per cent of the average of the distribution of the dipolar coupling constants in a one-dimensional chain is determined by NN interactions [49], (iii) the results can serve as a basis for elaborating a perturbation theory in order to take into account the interactions with remote spins [41] and also extrapolations to higher dimensions, and (iv) the results provide an opportunity to test the validity of other approximation methods in MQ NMR such as the commutator series expansion for the equations of motion of the spin density operator [46]. Numerical [9,50,51] and theoretical [46,52] investigations of one-dimensional spin chains have also been performed. Simplified and tractable one-dimensional models [48] yield physical insights into the complexities of many-body spin dynamics [46,52]. In some cases, the application of MQ NMR to problems of QIP is simplified by using pseudo-pure spin states [53,54]. Methods of producing these states in large spin clusters are developed in recent studies [55,56].

Although MQ NMR was successful in a lot of applications, and experimental methods of MQ NMR have been developed adequately, the theoretical interpretation of many-spin MQ NMR dynamics is restricted by the phenomenological approach [57]. A systematic quantum-mechanical approach was developed [41,58,59] only for one-dimensional systems in the approximation of NN dipolar interactions. Usually, the thermodynamic equilibrium density matrix in a strong external magnetic field has been considered as the initial condition for these experiments and theoretical interpretations. In addition, it has been suggested [60] to consider the dipolar-ordered initial state for such experiments. It is well known that the dipolar-ordered state can be prepared using the method of adiabatic demagnetization in a rotating frame [61,62] or with the Jeener–Broekaert (JB) two-pulse sequence [61,63]. It has been shown that the spin system contains MQ coherences immediately following the second pulse of the JB pulse sequence [64]. By encoding the coherence numbers in an orthogonal basis (the $x$-basis), it was shown that
the dipolar-ordered state is a two-spin-correlated one [65]. As a result of using the dipolar-ordered initial condition, many-spin clusters and correlations appear faster than in the ordinary MQ NMR experiments in solids [57], and some peculiarities of MQ dynamics can be investigated with these experiments. Of course, it is necessary to make some changes in the scheme of the standard experiment in order to obtain non-zero signals of MQ coherences.

MQ NMR has been used [66,67] to investigate the size of spin clusters when the growth of MQ clusters occurs in the process of the irradiation of the spin system on the preparation period of the MQ NMR experiment [57]. The unique possibilities of MQ NMR to study dynamics of many-spin clusters have been used [68,69] for a measurement of the decoherence rate for highly correlated spin states. The scaling of the decoherence rate with the number of correlated spins has also been presented [68]. The theoretical description of MQ NMR dynamics is a very difficult task because this is a many-spin and MQ problem. Although the first phenomenological approach was developed together with the experimental realization of MQ NMR [57], a consistent quantum-mechanical theory has not been developed up to now except for one-dimensional systems. In particular, the one-dimensional homogeneous spin chain with the NN double quantum Hamiltonian [57] is exactly solvable and it has been shown that, starting with a thermodynamic equilibrium state, only zero and double quantum coherences are produced [41,46,58]. This conclusion has been confirmed experimentally for relatively small excitation times [70,71]. However, next-nearest couplings and other distant interactions lead to higher-order coherences in MQ NMR spectra. These interactions are beyond the exact solvable models [41,46,58]. Thus, one should apply numerical methods in order to take into account distant spin–spin couplings. However, even supercomputer calculations allow us to study the MQ NMR dynamics of a spin chain consisting of not more than 20 spins [72], which is insufficient to solve some subtle problems of the MQ NMR dynamics. In particular, the dependence of the MQ coherence intensities on their orders (the profile of MQ NMR coherences [66]) cannot be found. Some progress in the study of larger systems (up to 40 spins) has been achieved owing to special techniques based on the Chebyshev polynomial expansion [73,74] and on the phenomenon of quantum parallelism [75]. Meanwhile, a large spin system whose dynamics allows a theoretical description would be of great interest in helping one to foresee the general properties of spin dynamics in large systems. A system of spin-carrying particles in a nanopore seemed to be an example of such systems. In fact, it was demonstrated [76] that the spin dynamics of a system of hundreds of particles may be numerically simulated owing to the special symmetry inherent in such systems. Results of simulations demonstrate, in particular, that the profile of MQ NMR coherences can be approximated by the exponential curve [77,78]. This conclusion contradicts the traditional phenomenological standpoint that the profile of MQ NMR coherences is approximated by the Gaussian distribution function [57].

Although the theoretical study of the MQ NMR spin dynamics reduces to the cumbersome computational problem, which, in general, may be solved only for a restricted number of spins, there are some models allowing either analytical or numerical description. Two of them are considered in this study. Namely, the system of isolated pairs of spin-\(\frac{1}{2}\) particles (dimers) and the system of equivalent spin-\(\frac{1}{2}\) particles in a nanopore.
We organize the paper as follows. The general scheme of the MQ NMR experiment is given in §2. Entanglement, discord and their relation with the intensity of the second-order MQ NMR coherence in dimers are obtained in §3. The features of the spin dynamics in nanopores and the formation of the coherence clusters therein are considered in §4. Conclusions are given in §5.

2. General scheme of MQ NMR experiment

The MQ NMR experiment consists of four distinct periods of time (figure 1): preparation ($\tau$), evolution ($t$), mixing ($\tau$) and detection.

(a) Preparation period

The spin system is irradiated by the proper multi-pulse sequence on the preparation period. As a result, the anisotropic dipole–dipole interaction (DDI) of nuclear spins in the external magnetic field $B$ (directed along the $z$-axis) oscillates rapidly. In the rotating reference frame (RRF) [61], the dynamics of the spin system is described by the Hamiltonian, $H_{\text{MQ}}$ [57,79]:

$$H_{\text{MQ}} = H^{(+2)} + H^{(-2)}, \quad H^{(\pm 2)} = -\frac{1}{2} \sum_{j<k} D_{jk} I_j^{\pm} I_k^{\pm}. \quad (2.1)$$

Here, $D_{jk} = \gamma^2 \hbar (1 - 3 \cos^2 \theta_{jk})/2r_{jk}^3$ is the coupling constant between spins $j$ and $k$, $\gamma$ is the gyromagnetic ratio, $r_{jk}$ is the distance between spins $j$ and $k$, $\theta_{jk}$ is the angle between the vectors $r_{jk}$ and $B$, and $I_j^{\pm} = I_{jx} \pm iI_{jy}$ are the raising and lowering operators of spin $j$, where $I_{j\alpha}$ ($\alpha = x, y, z$) are the $j$th spin momentum projections on the axis $\alpha$. Let the preparation period consist of $K$ (a big number) cycles of duration $\tau_c$, so that one can introduce the parameter $\tau = K\tau_c$.

(b) Evolution period

Let the spin system be governed by the following Hamiltonian ($H_{\text{ev}}$) on the evolution period:

$$H_{\text{ev}} = H_{dz} + \Delta I_z \quad (2.2)$$
and

\[ H_{dz} = \sum_{j<k} D_{jk} (2I_{jz}I_{kz} - I_{jx}I_{kx} - I_{jy}I_{ky}). \]  

(2.3)

The offset \( \Delta \) encodes the MQ NMR coherences of different orders (see equation (2.11) and Baum et al. [57]). The Hamiltonian \( H_{dz} \) describes the secular (with respect to the \( z \)-axis) DDIs. This Hamiltonian is responsible for the relaxation of the MQ NMR coherences, which is considered in §4.

(c) Mixing period

The spin system on the mixing period is governed by the Hamiltonian \(-H_{MQ}\) in all experiments considered in this study.

In order to investigate the MQ NMR dynamics of the system, one has to find the density matrix \( \rho \) by solving the Liouville evolution equation [61]

\[
\frac{d\rho}{d\tilde{\tau}} = [H, \rho(\tilde{\tau})], \quad H = \begin{cases} 
H_{MQ}, & 0 \leq \tilde{\tau} \leq \tau, \\
H_{ev}, & \tau < \tilde{\tau} \leq \tau + t, \\
-H_{MQ}, & \tau + t < \tilde{\tau} \leq 2\tau + t
\end{cases}
\]  

(2.4)

with the initial density matrix \( \rho(0) = \rho_0 \). The solution to this equation at the end of the mixing period may be conveniently written in the following form:

\[
\rho(2\tau + t) = e^{iH_{MQ}t} e^{-iH_{ev}t} \rho(\tau) e^{iH_{ev}t} e^{-iH_{MQ}t},
\]  

(2.5)

where \( \rho(\tau) \) is the density matrix in the end of the preparation period:

\[
\rho(\tau) = e^{-iH_{MQ}t} \rho_0 e^{iH_{MQ}t}.
\]  

(2.6)

Taking into account the pointed information about the Hamiltonians on the different periods of the MQ NMR experiment, one can write the expression for the longitudinal polarization \( \langle I_z \rangle(2\tau + t) \) after the mixing period of the MQ NMR experiment (figure 1) as follows [57]:

\[
\langle I_z \rangle(2\tau + t) = \text{Tr} \{ e^{-iH_{ev}t} \rho(\tau) e^{iH_{ev}t} \rho^{ht}(\tau) \},
\]  

(2.7)

where

\[
\rho^{ht}(\tau) = e^{-iH_{MQ}t} I_z e^{iH_{MQ}t}.
\]  

(2.8)

It is convenient to expand the spin density matrices \( \rho \) and \( \rho^{ht} \) in the series as

\[
\rho(\tau) = \sum_k \rho_k(\tau), \quad \rho^{ht}(\tau) = \sum_k \rho^{ht}_k(\tau),
\]  

(2.9)

where \( \rho_k(\tau) \) (or \( \rho^{ht}_k(\tau) \)) is the contribution to \( \rho(\tau) \) (or \( \rho^{ht}(\tau) \)) from the MQ coherence of the \( k \)-th order and satisfy the following relations [41]:

\[
e^{-i\Delta t} \rho_k e^{i\Delta t} = e^{-ik\Delta t} \rho_k, \quad e^{-i\Delta t} \rho^{ht}_k e^{i\Delta t} = e^{-ik\Delta t} \rho^{ht}_k.
\]  

(2.10)
Then, equation (2.7) may be written as

\[
\langle I_z \rangle (2t + t) = \sum_{k=-N}^{N} e^{-ik \Delta t} J_k(t, t), \quad J_k(t, t) = \text{Tr}\{e^{-iH_{\text{MQ}}t}\rho_k(\tau) e^{iH_{\text{MQ}}t}\rho_{-k}(\tau)\},
\]

(2.11)

where \( J_k(t, t) \) is the intensity of the \( k \)th order MQ NMR coherence, which is an observable in the MQ NMR experiment [57]. The Hamiltonian \( H_{\text{MQ}} \) leads to the emergence of MQ coherences of even orders only, and the coherence order cannot exceed the number of spins \( N \) [57].

3. Entanglement and quantum discord in MQ NMR experiments with dimers

As the first theoretically solvable model, we consider a system of two spin-\( \frac{1}{2} \) particles (dimers) in a strong external magnetic field \( H_0 \). This model allows us the analytical study of both measures of quantum correlations: entanglement and discord. The initial state is the thermodynamic equilibrium density matrix, \( \rho_0 \), of the system:

\[
\rho_0 = \frac{\exp(\beta I_z)}{\text{Tr}(\exp(\beta I_z))} \quad \text{and} \quad \beta = \frac{\hbar \omega_0}{k_B T},
\]

(3.1)

where \( \omega_0 = \gamma H_0 \) (\( \gamma \) is the gyromagnetic ratio), \( T \) is the temperature and \( k_B \) is the Boltzmann constant. Consider the evolution period neglecting the DDIs. Then, equation (2.2) reduces to \( H_{\text{ev}} = \Delta I_z \). The Hamiltonian (2.1) reads in this case

\[
H_{\text{MQ}} = -\frac{D}{2}(I_1^+ I_2^- + I_1^- I_2^+).
\]

(3.2)

The density matrix \( \rho(\tau) \) (2.6) at the end of the preparation period is

\[
\rho(\tau) = e^{-iH_{\text{MQ}}\tau}\rho_0 e^{iH_{\text{MQ}}\tau} = \frac{1}{2(1 + \cosh \beta)} \times \begin{pmatrix}
\cosh \beta + \cos(D\tau) \sinh \beta & 0 & 0 & -i \sin(D\tau) \sinh \beta \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
i \sin(D\tau) \sinh \beta & 0 & 0 & \cosh \beta - \cos(D\tau) \sinh \beta
\end{pmatrix}.
\]

(3.3)

Hereafter, we describe the entanglement in terms of concurrence.

(a) Entanglement in MQ NMR experiment

The initial state of the system determined by equation (3.1) is separable. Entanglement appears in the course of the preparation period of the MQ NMR experiment. In order to estimate the entanglement quantitatively, we apply the Wootters criterion [80]. According to Wootters [80], one needs to construct the
spin–flip density matrix

\[ \tilde{\rho}(\tau) = (\sigma_y \otimes \sigma_y)\rho(\tau)(\sigma_y \otimes \sigma_y), \]  

(3.4)

where the asterisk denotes complex conjugation in the standard basis |00⟩, |01⟩, |10⟩, |11⟩ and the Pauli matrix \( \sigma_y = 2I_y \). The concurrence of the two-spin system with the density matrix \( \rho(\tau) \) is equal to

\[ C = \max(0, 2\lambda_1 - \lambda_2 - \lambda_3 - \lambda_4), \quad \lambda = \max(\lambda_1, \lambda_2, \lambda_3, \lambda_4), \]  

(3.5)

where \( \lambda_1, \lambda_2, \lambda_3 \) and \( \lambda_4 \) are the square roots of the eigenvalues of the product \( \rho(\tau)\tilde{\rho}(\tau) \). Using equations (3.3), (2.6) and (3.5), one obtains

\[ \lambda_{1,2} = \sqrt{1 + \sin^2(D\tau)\sinh^2\beta \pm |\sin(D\tau)|\sinh\beta} \]  

and \[ \lambda_{3,4} = \frac{1}{4\cosh^2(\beta/2)}. \]  

(3.6)

As a result, the concurrence, \( C \), is

\[ C = \max \left(0, \frac{|\sin(D\tau)|\sinh\beta - 1}{2\cosh^2(\beta/2)} \right). \]  

(3.7)

The entangled state can appear only at \( \sinh\beta > 1 \). This condition means that the entanglement appears at temperatures

\[ T < \frac{\hbar \omega_0}{k_B \ln(1 + \sqrt{2})}. \]  

(3.8)

If one takes \( \omega_0 = 2\pi 500 \times 10^6 \text{s}^{-1} \), then the entangled state emerges at the temperature \( T_E \approx 27 \text{mK} \). It is interesting to note that in a linear chain of dipolar coupled nuclear spins with the thermodynamic equilibrium state, the entanglement appears only at microkelvin temperatures [81]. For the total DDIs (not for secular ones), the concurrence as a function of magnetic field strength, dipolar coupling constant and temperature was obtained in Furman et al. [82].

(b) Quantum discord in MQ NMR experiment

Note that the density matrix (3.3) is a particular case of the more general X-matrix whose discord has been analytically studied in Ali et al. [16]. By definition [14,16,83], the discord is a difference of two components: the total mutual information \( I(\rho) \) and the classical correlations \( C(\rho) \), i.e.

\[ Q(\rho) = I(\rho) - C(\rho). \]  

(3.9)

Here, the total mutual information \( I(\rho) \) is given by [14]

\[ I(\rho) = S(\rho^A) + S(\rho^B) + \sum_{j=0}^{3} \lambda_j \log_2 \lambda_j, \]  

(3.10)

where \( A \) and \( B \) mark the first and the second spins, respectively, \( \rho^A = \text{Tr}_B \rho = \text{diag}(\rho_{11} + \rho_{22}, \rho_{33} + \rho_{44}) \), \( \rho^B = \text{Tr}_A \rho = \text{diag}(\rho_{11} + \rho_{33}, \rho_{22} + \rho_{44}) \) are the reduced
density matrices and $\lambda_j$ are the eigenvalues of the density matrix (3.3):

$$
\lambda_0 = \frac{\cosh \beta + \sinh \beta}{2(1 + \cosh \beta)}, \quad \lambda_1 = \frac{\cosh \beta - \sinh \beta}{2(1 + \cosh \beta)} \quad \text{and} \quad \lambda_2 = \lambda_3 = \frac{1}{2(1 + \cosh \beta)}.
$$

(3.11)

The entropies $S(\rho^A)$ and $S(\rho^B)$ of the subsystems $A$ and $B$ ($S(\rho^{A,B}) = -\text{Tr}(\rho^{A,B} \log_2 \rho^{A,B})$) [14] read in our case

$$
S(\rho^A) = S(\rho^B) = -\frac{1}{2} \log_2 \left( \frac{(\cosh \beta + 1)^2 - \xi^2 \sinh^2 \beta}{4(1 + \cosh \beta)^2} \right)
- \frac{\xi \sinh \beta \cosh \beta}{2(1 + \cosh \beta)} \log_2 \frac{\cosh \beta + 1 + \xi \sinh \beta}{\cosh \beta + 1 - \xi \sinh \beta},
$$

(3.12)

where we introduce the parameter $\xi = |\cos(D\tau)|$, $0 \leq \xi \leq 1$. Following Ali et al. [16], we assume that the projective measurements are performed over the subsystem $B$. The expression for the classical correlations $C(\rho)$ (see recent studies [14, 16]) in equation (3.9) is simplified in our case:

$$
C(\rho) = S(\rho^A) - \min_{\eta=\{0,1\}} \Omega(\eta, \beta, \xi), \quad \Omega(\eta, \beta, \xi) = p_0 S_0 + p_1 S_1
$$

(3.13)

with [20]

$$
S_i = -\frac{1 - \theta^{(i)}}{2} \log_2 \frac{1 - \theta^{(i)}}{2} - \frac{1 + \theta^{(i)}}{2} \log_2 \frac{1 + \theta^{(i)}}{2},
$$

(3.14)

$$
p_i = \frac{1}{2} (1 + (-1)^i \eta (2(\rho_{11} + \rho_{33}) - 1))
$$

(3.15)

and

$$
\theta^{(i)} = \frac{1}{p_i} \left[ (1 - \eta^2) |\rho_{14}|^2 + \frac{1}{4} (2(\rho_{11} + \rho_{22}) - 1 + (-1)^i \eta (1 - 2(\rho_{22} + \rho_{33})))^2 \right]^{1/2},
$$

(3.16)

Here, $\eta$ is an arbitrary parameter, $0 \leq \eta \leq 1$.

It was shown in Kuznetsova & Zenchuk [84] that the minimum of $\Omega(\eta, \beta, \tau)$ in equation (3.13) corresponds to $\eta = 0$ with

$$
\Omega(0, \beta, \xi) = \log_2 (1 + e^\beta) - \frac{\beta e^\beta}{\ln 2(1 + e^\beta)}.
$$

(3.17)

Thus, the optimization problem, which is inherent in the definition of the quantum discord [14], is completely solved analytically for the dimer in the MQ NMR experiment.

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Finally, by combining equations (3.9)–(3.13) and (3.17), we obtain the following expression for the quantum discord:

\[
Q(\beta, \xi) = S(\rho^A) - \Omega(0, \beta, \xi) = \log_2(1 + e^{\beta}) - \frac{\beta}{\ln 2(1 + e^{\beta})} - \frac{1}{2} \log_2((\cosh \beta + 1)^2 - \xi^2 \sinh^2 \beta) - \frac{\xi \sinh \beta}{2(1 + \cosh \beta)} \log_2 \frac{\cosh \beta + 1 + \xi \sinh \beta}{\cosh \beta + 1 - \xi \sinh \beta},
\]

(c) Quantum discord and concurrence as functions of second-order coherence intensity

Because the discord has been introduced as a measure of quantum information, it is important to have a tool allowing one to measure the discord in experiments [85]. Regarding the MQ NMR experiment, the MQ coherence intensities should be taken as measurable quantities for this purpose.

Let us remember that only the zeroth- and plus/minus-second-order MQ NMR coherence intensities [41,46,52] are generated in the case of a dimer (which might be considered as a particular model with the NN interaction) and the intensities \( J_{\pm 2} \) for the state (3.3) are defined by equation (2.11) [47,86]

\[
J \equiv J_{\pm 2} = \rho_{14}(\tau)\rho_{41}^{ht}(\tau) = \frac{1}{2} \tanh \left( \frac{\beta}{2} \sin^2(D\tau) \right) = \frac{1}{2} \tanh \frac{\beta}{2}(1 - \xi^2), \quad (3.19)
\]

where \( \rho^{ht} \) is given in equation (2.8). Following Fel’dman & Pyr'kov [86], we show that the second-order coherence intensity is an appropriate observable quantity, which may serve to detect the quantum discord in the MQ NMR experiment with dimers.

The dependence of the discord \( Q \) and the concurrence \( C \) on the coherence intensity \( J \) can be derived in one of two ways.

(i) Discord and concurrence as functions of the inverse temperature \( \beta \) and the coherence intensity \( J \)

To obtain the relation between the measures of quantum correlations (discord and concurrence) and the second-order coherence intensity, we use equation (3.19) to express \( \xi \) in terms of \( J \),

\[
\xi = \sqrt{1 - \frac{2J}{\tanh(\beta/2)}.} \quad (3.20)
\]

Equation (3.20) means that \( \xi \) is a monotonic function of \( J \) at fixed \( \beta \), so that the change of variables \( (\beta, \xi) \rightarrow (\beta, J) \) is valid. Substituting \( \xi \) from equation (3.20) into equation (3.18), we obtain the discord \( Q \) as a function of two variables \( \beta \).
Figure 2. The discord, $Q$ (solid line), and the concurrence, $C$ (dashed line), versus the second-order coherence intensity, $J$, at different $\beta = 1, 2, 5$. The appropriate maximal values of $J$ are the following: $J_{\text{max}}^{(1)} = 0.231, 0.381, 0.493$; at these $J$, the discord and the concurrence reach their maximal values: $Q_{\text{max}} = 0.160, 0.473, 0.942, C_{\text{max}} = 0.069, 0.552, 0.973$.

and $J$: $Q(\beta, J)$. The explicit expression for $Q(\beta, J)$ is very complicated and is not represented here. In this case, $J$ varies in the range

$$0 \leq J \leq J_{\text{max}}^{(1)} = \frac{1}{2} \tanh \left( \frac{\beta}{2} \right), \quad (3.21)$$

so that the maximal value of the discord is $Q(\beta, J_{\text{max}}^{(1)})$. Substituting equation (3.20) for $\xi$ into equation (3.5), we obtain the concurrence as a function of $\beta$ and $J$ [86]:

$$C = \max \left( 0, \sqrt{2J(\tau) \tanh \frac{\beta}{2} - \frac{1}{2 \cosh^2(\beta/2)}} \right). \quad (3.22)$$

Thus, the state is entangled if

$$J(\tau, \beta) > J_{\text{min}}^{(1)}(\beta) = \frac{1}{4 \sinh \beta \cosh^2(\beta/2)}. \quad (3.23)$$

Concurrence $C$ and discord $Q$ as functions of $J$ at three different values of $\beta$ are compared in figure 2. We see that the concurrence appears at some $J_{\text{min}}^{(1)} > 0$, while the discord is bigger than zero over the whole interval $0 \leq J \leq J_{\text{max}}^{(1)}$.

(ii) Discord and concurrence as functions of the coherence intensity $J$ and the parameter $\xi$ ($\xi = |\cos(D\tau)|$)

Similarly, we may express $\beta$ in terms of $J$ from equation (3.19),

$$\beta = 2 \tanh^{-1}(2J/(1 - \xi^2)). \quad (3.24)$$
Equation (3.24) means that $\beta$ is a monotonic function of $J$ at fixed $\xi$. Thus, the change of variables $(\beta, \xi) \to (J, \xi)$ is valid. By substituting $\beta$ from equation (3.24) into equation (3.18), we obtain the discord $Q$ as a function of $J$ and $\xi$: $Q(J, \xi)$. The explicit expression for $Q(J, \xi)$ is very complicated and it is not represented here. In this case, $J$ varies in the range

$$0 \leq J < J_{\text{max}}^{(2)} = \frac{1}{2}(1 - \xi^2),$$

so that the maximal value of the discord is $Q(J_{\text{max}}^{(2)}, \xi)$.

By eliminating $\beta$ from equation (3.5) using equation (3.24), we obtain the concurrence as a function of $J$ and $\xi$:

$$C = \max \left(0, \frac{2J(\tau)}{|\sin(D\tau)|} + \frac{2J^2(\tau)}{\sin^4(D\tau)} - \frac{1}{2}\right).$$

(3.26)

Thus, the state is entangled if

$$J(\tau) > J_{\text{min}}^{(2)}(\tau) = \frac{1}{2} \left(\sin^2(D\tau)\sqrt{\sin^2(D\tau) + 1 - |\sin(D\tau)|^3}\right).$$

(3.27)

The discord and the concurrence as functions of $J$ at three different values of $\xi$ are compared in figure 3. Similar to figure 2, the concurrence appears at some $J_{\text{min}}^{(2)} > 0$, while the discord is bigger than zero over the whole interval $0 \leq J \leq J_{\text{max}}^{(2)}$. The almost linear behaviour of the concurrence $C$ is explained by equation (3.26), which means that $C \sim J$ for $J < 1$.

Having functions $Q(\beta, J)$ and $C(\beta, J)$ (or $Q(J, \xi)$ and $C(J, \xi)$), we are able to find the discord and concurrence measuring the second-order coherence intensity at the given inverse temperature $\beta$ (or at the given value of the parameter $\xi$, $\xi = |\cos(D\tau)|$).

(d) Effect of spin–lattice relaxation on concurrence

The MQ coherences in a system of dipolar coupled spins can be detected by MQ NMR methods [40,57]. In the simplest cases (one-dimensional spin chains and rings, a system of spin-carrying atoms (molecules) in nanopores), analytical and numerical methods were developed [41,76] in order to calculate the intensities of MQ NMR coherences. Usually, spin–lattice relaxation is not taken into account in the investigations of MQ NMR dynamics, because the characteristic times of spin–lattice relaxation are longer than the characteristic time of MQ NMR dynamics [40]. At the same time, the MQ NMR methods have been also used to measure decoherence for highly correlated spin states [68,69] and to study the scaling of the decoherence rate with the number of correlated spins [68]. The MQ NMR investigations showed both experimentally [87] and numerically for a system of equivalent spins [88] that the relaxation time decreases with the increase in the MQ coherence order and in the number of spins. The relationships between the intensity of the MQ coherence of the second order and measures of the quantum correlations (which are entanglement and discord) (see §3c and Fel’dman & Pyrkov [86]) were found without taking into account the effects of

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Figure 3. The discord, $Q$ (solid line), and the concurrence, $C$ (dashed line), versus the second-order coherence intensity, $J$, at different $\xi = 0.9, \sqrt{2}/2, 0$. The appropriate maximal values of $J$ are the following: $J^{(2)}_{\text{max}} = 0.095, 0.250, 0.500$; at these $J$, the discord and the concurrence reach their maximal values: $Q_{\text{max}} = 0.286, 0.601, 1$, $C_{\text{max}} = 0.436, 0.707, 1$.

spin–lattice relaxation. A theoretical interpretation of such results is impossible without taking into account those effects. A theory of spin–lattice relaxation is also useful for traditional problems of NMR (paramagnetic impurities, internal molecular motions, etc.) [89].

We develop a phenomenological theory of spin–lattice relaxation for a system consisting of two dipolar-coupled spins in the MQ NMR experiment at low temperatures and obtain a connection between the quantum entanglement and the intensity of the second-order MQ NMR coherence at different spin–lattice relaxation times [90] (effect of the spin–lattice relaxation on the discord may be derived in a similar manner).

In order to take into account the spin–lattice relaxation, one has to introduce, generally speaking, a nonlinear term with respect to the density matrix $\rho(t)$ on the right-hand side of equation (2.4). In practice, such equations can be solved expanding the earlier-mentioned nonlinear term on the right-hand side of the Liouville equation in powers of $\rho(t) - \bar{\rho}$, where $\bar{\rho}$ is the equilibrium density matrix in the RRF. This procedure is valid if the deviation of $\rho(t)$ from $\bar{\rho}$ is small. One can expect a small deviation if the time-independent $\rho = \bar{\rho}$ is a solution to the Liouville equation. It is reasonable to suppose that [61]

$$\bar{\rho} = \frac{\exp(-\hbar H_{\text{MQ}}/k_B T)}{\text{Tr}(\exp(-\hbar H_{\text{MQ}}/k_B T))},$$

(3.28)

where the temperature $T$ is of the order of the lattice temperature.

We will consider the millikelvin temperature range, where one can suppose [91] that $\hbar D/k_B T \ll 1$, $\bar{\rho} = 1/4e$ and $e$ is the $4 \times 4$ unit matrix. Then, the Liouville
equation with a linearized phenomenological term for spin–lattice relaxation reads
\[
\frac{d\rho(t)}{dt} = -i[H_{MQ}, \rho(t)] - \frac{\rho(t) - \bar{\rho}}{T_{MQ}},
\] (3.29)

where \( T_{MQ} \) is the spin–lattice relaxation time of MQ NMR coherences. A reorientation of groups of spins can be responsible for the relaxation [92]. We consider relaxation as a perturbation only to the MQ NMR dynamics assuming \( D \gg 1/T_{MQ} \). We assume also that the spin–lattice relaxation time \( T_1 \) in the laboratory reference frame is large (\( T_1 \gg T_{MQ} \)) and we neglect it. It is worth emphasizing that the equilibrium density matrix \( \bar{\rho} \) describes the spin system in the RRF, where there is no external magnetic field, i.e. the Zeeman reservoir is absent in the considered case. Thus, relaxation of MQ NMR coherences can be described with only one relaxation time, \( T_{MQ} \). After the mixing period \( \tau \), the density matrix \( \rho(2\tau + t) \) reads [90]
\[
\rho(2\tau + t) = e^{iH_{MQ}\tau} e^{-i\Delta t I_z} e^{-iH_{MQ}\tau} \rho_0 e^{iH_{MQ}\tau} e^{i\Delta t I_z} e^{-iH_{MQ}\tau} e^{-2\tau/T_{MQ}} + (1 - e^{-2\tau/T_{MQ}})\bar{\rho},
\] (3.30)

where \( \rho_0 \) is given in equation (3.1). Calculating the longitudinal magnetization \( I_z(2\tau + t) \) at the end of the MQ NMR experiment [57] and taking into account that \( Tr(I_z\bar{\rho}) = 0 \), one can find that only the MQ NMR coherences of zeroth and plus/minus second orders emerge in our system and their intensities \( J_0(\tau), J_{\pm 2}(\tau) \) read
\[
J_0 = \tanh \frac{\beta}{2} \cos^2(D\tau) e^{-2\tau/T_{MQ}} \quad \text{and} \quad J = J_{\pm 2} = \frac{1}{2} \tanh \frac{\beta}{2} \sin^2(D\tau) e^{-2\tau/T_{MQ}}.
\] (3.31)

Thus, we have found a simple exponential law for the spin–lattice relaxation of the MQ NMR coherences.

(i) Quantum entanglement

By calculating the concurrence using equations (3.4) and (3.5), we obtain
\[
C(\tau) = \max \left[ 0, e^{-\tau/T_{MQ}} |\sin(D\tau)| \tanh \frac{\beta}{2} + \frac{1}{2} \left( e^{-\tau/T_{MQ}} \tanh^2 \frac{\beta}{2} - 1 \right) \right].
\] (3.32)

This expression coincides with equation (3.7) [86] in the limit of the infinite spin–lattice relaxation time. The entangled state emerges at temperatures
\[
T < T_E = \frac{\hbar \omega_0}{k_B \ln(\sqrt{2 + a/(2 - \sqrt{2 + a}))},
\] (3.33)

where \( a = e^{\tau/T_{MQ}} - 1 \). If one takes \( \omega_0 = 2\pi 500 \times 10^6 \text{ s}^{-1} \) the entangled state emerges at the temperature \( T_E \approx 27 \text{ mK} \) when \( T_{MQ} \to \infty \) [86]. According to equation (3.33), the entangled states emerge at \( \tau/T_{MQ} < \ln 3 \). The temperature \( T_E \) decreases with the decrease in the spin–lattice relaxation time.

Similar to §3c, the relation between the concurrence \( C \) and the coherence intensity \( J \) can be derived in one of two ways.
Using equation (3.31), we eliminate $\sin(D\tau)$ from equation (3.32) to derive a simple relationship between intensities of MQ NMR coherences of the second order and the concurrence:

$$C = \max \left(0, \sqrt{2J \tanh \frac{\beta}{2}} + \frac{1}{2} \left( e^{-\tau/T_{MQ}} \tanh^2 \frac{\beta}{2} - 1 \right) \right).$$ \hspace{1cm} (3.34)

This formula coincides with equation (3.22) \cite{86} at $T_{MQ} \to \infty$.

Concurrence as a function of the coherence intensity $J$ and time $\tau$. Eliminating $\beta$ from equation (3.32) using equation (3.31), we obtain

$$C = \max \left(0, \frac{2J e^{\tau/T_{MQ}}}{\sin(D\tau)} + \frac{2J^2 e^{3\tau/T_{MQ}}}{\sin^4(D\tau)} - \frac{1}{2} \right),$$ \hspace{1cm} (3.35)

which coincides with equation (3.26) at $T_{MQ} \to \infty$.

The dependencies of both the double second-order MQ NMR coherence intensity and the concurrence $C(\tau)$ on the dimensionless spin–lattice relaxation rate $\tau/T_{MQ}$ at $\beta = 6$ are shown in figure 4. At long spin–lattice relaxation times, the concurrence approximately coincides with $2J$, which agrees with Fel’dman & Pyrkov \cite{86}. At $DT_{MQ} \gg 1$, the MQ NMR dynamics determines the entanglement. Spin–lattice relaxation is the dominant factor when $DT_{MQ} \approx 1$. We note also that the concurrence decreases with a decrease in the spin–lattice relaxation time.
4. The MQ NMR spin dynamics in a nanopore

To realize the enormous potential of quantum computers, well-controlled quantum systems consisting of hundreds (or even thousands) of qubits are required. In order to reliably operate, such large systems must meet a set of requirements. In particular, they must be able to perform a large number of quantum operations within the decoherence time of the system. The experimental investigation of the decoherence time was performed in recent studies [68,87,93]. However, the theoretical approach to the decoherence time in large systems of correlated spins is a complicated computational problem because of the exponential growth of the matrix dimensionality with the spin number involved in the calculations. Meanwhile, the theoretical study might affect the traditional standpoints on the spin dynamics in large systems.

For this reason, a particular model allowing one to describe the spin dynamics (in particular, the decoherence time) theoretically (numerically) would be of great interest. We consider a system of equivalent spins as an example of the theoretically solvable models. This system can be realized, for instance, in a solid nanopore filled with the spin-carrying particles [76,77,88]. In this case, we deal with the highly symmetrical model where any two spins interact with the same constant of DDI, because the diffusion characteristic time in the nanopore is much shorter than the dipolar spin flip–flop time [94,95]. This fact simplifies the numerical calculations significantly since all particles are ‘nearest neighbours’ in this model and we consider interactions among all of them. Therefore, the theoretical investigation of many aspects of the spin dynamics in MQ NMR experiments becomes possible. In particular, the profiles of the MQ NMR coherence intensities have been constructed, and it was shown that they are well approximated by the exponential (rather than by phenomenological Gaussian [57]) distribution function.

The Hamiltonians $H_{MQ}$ (2.1) and $H_{dz}$ (2.3) in the nanopore are averaged (but not to zero) by the fast molecular diffusion [94,95]. As a result, we obtain the Hamiltonians with the averaged coupling constant $D$ ($D\tau_c \ll 1$) that read [76,77]

$$
\bar{H}_{MQ} = -\frac{D}{4} \left\{ (I^+)^2 + (I^-)^2 \right\}, \quad \bar{H}_{dz} = \frac{D}{2} \{ 3 I_z^2 - I^2 \},
$$

where $I^\pm = \sum_{j=1}^{N} I_j^\pm$ ($N$ is the number of spins), $I_z = \sum_{j=1}^{N} I_{zj}$ and the operator $I^2$ is the square of the total spin angular momentum.

Later in this section, we use the high-temperature approximation of the thermodynamic equilibrium initial density matrix $\rho_0 \approx (1/2^N)(1 + \beta I_z)$.

Consider the time evolution of the coherences in the MQ NMR experiment [57]. The Hamiltonian on the evolution period $H_{ev}$ (2.2) is averaged as well: $H_{ev} = \bar{H}_{dz} + \Delta I_z$. The averaged Hamiltonians $\bar{H}_{MQ}$ and $\bar{H}_{dz}$ will be used in the following formulae. In addition, in the high-temperature approximation, there is a tradition [57,66] to use the ‘normalized’ coherence intensities defined as

$$
J_k^{ht} (2\tau + t) = \frac{\text{Tr}\{e^{-i\bar{H}_{dz}t}\rho_k^{ht}(\tau) e^{i\bar{H}_{dz}t}\rho_{-k}^{ht}(\tau)\}}{\text{Tr} I_z^2}
$$

(4.2)
instead of the coherence intensities defined in equation (2.11). Here, $\rho^{ht}$ is defined by equation (2.8) where the Hamiltonian $H_{MQ}$ is replaced with $\bar{H}_{MQ}$.

Our calculations show [76] that the MQ NMR coherence intensities are quickly oscillating functions. For this reason, we consider the averaged intensities [76]

$$\bar{J}_k(\bar{t}) = \frac{1}{2T} \int_{t_0}^{t_0+2T} J_k^{ht} \left( \frac{2\bar{t} + \bar{t}}{D} \right) d\bar{t}, \quad t_0 = 31, \quad T = \frac{4\pi}{\sqrt{3}}. \quad (4.3)$$

The averaged intensities decay with the dimensionless time $\bar{t} = Dt$ of the evolution period ($\bar{t} = D\tau$ is the dimensionless duration of the mixing period). The time moments $t_e$ (such that $\bar{J}_k(0)/\bar{J}_k(\bar{t})|_{\bar{t}=t_e} = e, \forall k$) versus MQ coherence order in systems with 201, 401 and 601 spins are shown in figure 5. We can see from this figure that (i) the MQ NMR coherence decay times decrease with the increase in the number of spins and (ii) the MQ NMR coherence decay times decrease with the increase in their order. The times $t_e(k)$ of the decay of MQ NMR coherences of order $k > 0$ can be approximated by the hyperbolic cotangent, as is shown in figure 5: $t_e(k) = a_1 \coth(a_2k + a_3)$, where parameters $a_1, a_2, a_3$ are calculated in Doronin et al. [88].

It is worthwhile to note that the dynamics of growth of the multi-spin cluster during the evolution of the solid spin system (considered, for instance, in earlier studies [57,96]) is essentially different in comparison with that in the system of equivalent spins. The matter is that only the strongly interacting spins are joined in the clusters initially, usually the nearest neighbours in the crystal lattice [57,96]. After that, the next neighbours become involved in the cluster and so on. Thus, more and more remote spins become embedded in the cluster with time. As a result, it becomes possible to observe the growth of the multi-spin clusters in MQ NMR experiments [57,96]. However, the dynamics of the spin clusters is quite different in the high symmetrical spin system such as the system of equivalent spins.
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spins. All spins are ‘nearest neighbours’ in this case, so that the spin cluster consisting of all \( N \) spins is formed much more quickly during the time interval \( \sim 1/D \), where \( D \) is the constant of DDI, which is the same for any two spins.

Now let us turn to the decay of MQ NMR coherences. We consider the ‘cluster’ of MQ NMR coherences as a family of such coherences whose intensities exceed some fixed value \( J_{\text{min}} \), say, \( J_{\text{min}} = 0.005 \). This minimal value is taken, because the smaller intensities are hardly observable in the experiment. The size \( N_c \) of the cluster of MQ coherences does evolve, which is demonstrated in figure 6. This evolution is a consequence of the fact that the decay rate of the coherence intensities increases with the increase in the order of MQ NMR coherences. We see also that the rate of decrease of the coherence cluster size increases with the increase in \( N \). The described experiment may be used in order to prepare the coherence clusters of desirable size by varying the duration of the evolution period.

5. Conclusions

We consider the MQ NMR experiment in solids as a tool for realization of devices for QIP. Although the detailed study of quantum correlations is proposed for dimers, the obtained results may be useful in analysis of larger quantum systems, for instance, in the study of the biparticle quantum correlations therein. The relation between the measures of quantum correlations (such as the entanglement and the discord) and the second-order MQ NMR coherence intensity may be used for the experimental detection of the quantum correlations. The consequent development of this idea together with higher-order coherence intensities might be useful for the experimental observation of the quantum correlations in large
quantum systems. In the latter case, the decoherence time becomes an important parameter characterizing the applicability of the given system in QIP devices. This decoherence time is theoretically studied for the systems of equivalent spin-$\frac{1}{2}$ particles in nanopores.

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