

Dipolar temperature and Multiple Quantum NMR Dynamics in Dipolar Ordered Spin Systems

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We investigate analytically and numerically the Multiple Quantum (MQ) NMR dynamics in systems of nuclear spins $1/2$ coupled by the dipole-dipole interactions in the case of the dipolar ordered initial state. We suggest a new method of MQ NMR based on the measurement of the dipolar temperature in the quasi-equilibrium state which establishes after the time of order ω_{loc}^{-1} (ω_{loc} is the dipolar local field) after the MQ NMR experiment. Many-spin clusters and correlations are created faster in such experiment than in the usual MQ NMR experiments and can be used for the investigation of many-spin dynamics of nuclear spins in solids.

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1. Introduction. Multiple-quantum (MQ) NMR spin dynamics in solids [1] is a powerful tool for the investigation of structure and dynamical processes in solids, counting the number of spins in impurity clusters [2] and the simplification of ordinary NMR spectra [3]. 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 [1]. A systematic quantum-mechanical approach was developed [4–6] only for one-dimensional systems in the approximation of nearest neighbor dipolar interactions. Up to now the thermodynamic equilibrium density matrix in a strong external magnetic field has been considered as the initial condition for these experiments and theoretical interpretations. Recently, it has been suggested [7] to consider the dipolar ordered state as the 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 (ADRF) [8, 9] or with the Jeener-Broekaert (JB) two-pulse sequence [8, 10]. It has been shown that the spin system contains MQ coherences immediately following the second pulse of the JB pulse sequence [11]. 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 [12]. 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 [1].

In the present article we consider MQ NMR dynamics when the initial condition is determined by the dipolar ordered state. The motivation of this work comes, first of all, from the fact that the many-spin correlations are created faster in such experiments and can be used for the investigation of many-spin dynamics of nuclear spins in solids. We consider MQ NMR in systems prepared in the dipolar ordered states in Section 2. The method of MQ NMR for the systems in the dipolar ordered states is presented in Section 3. The method of Section 3 is based on the measurement of the dipolar temperature of the quasi-equilibrium state which establishes in the spin system after the time $t \sim \omega_{loc}^{-1}$ (ω_{loc} is the dipolar local field) after the MQ NMR experiment. Computer simulations of such experiments for the ten-spin system of cyclopentane and linear chains containing up to ten spins are presented in Section 4.

2. MQ NMR with the initial dipolar ordered state. We consider a system of nuclear spins ($s = 1/2$) coupled by the dipole-dipole interaction (DDI) in a strong external magnetic field. The secular part of the DDI Hamiltonian [8] has the following form

$$\mathcal{H}_{dz} = \sum_{j < k} D_{jk} \left[I_{jz} I_{kz} - \frac{1}{4} (I_j^+ I_k^- + I_j^- I_k^+) \right], \quad (1)$$

where

$$D_{jk} = \frac{\gamma^2 \hbar}{r_{jk}^3} (1 - 3 \cos^2 \theta_{jk})$$

is the coupling constant between spins j and k , γ is the gyromagnetic ratio, r_{jk} is the distance between spins j and k , θ_{jk} is the angle between the internuclear vector \mathbf{r}_{jk} and the external magnetic field \mathbf{H}_0 which is directed

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along the axis z . $I_{j\alpha}$ ($\alpha = x, y, z$) is the projection of the angular spin momentum operator on the axis α ; I_j^+ and I_j^- are the raising and lowering operators of spin j .

The basic scheme of MQ NMR experiments consists of four distinct periods of time: preparation, evolution, mixing and detection [1]. MQ coherences are created by the multipulse sequence consisting of eight-pulse cycles on the preparation period [1]. In the rotating reference frame (RRF) [8] the average Hamiltonian describing the MQ dynamics at the preparation period can be written as [1]

$$\mathcal{H}_{MQ} = \mathcal{H}^{(2)} + \mathcal{H}^{(-2)}, \quad (2)$$

$$\mathcal{H}^{(\pm 2)} = -\frac{1}{4} \sum_{j < k} D_{jk} I_j^{\pm} I_k^{\pm}.$$

Then the evolution period without any pulses follows. The transfer of the information about MQ coherences to the observable magnetization occurs during the mixing period. The density matrix of the spin system, $\rho(\tau)$, at the end of the preparation period is

$$\rho(\tau) = U(\tau)\rho(0)U^+(\tau), \quad (3)$$

where $U(\tau) = \exp(-i\tau(\mathcal{H}^{(2)} + \mathcal{H}^{(-2)}))$ and $\rho(0)$ is the initial density matrix of the system. Usually the thermodynamical equilibrium density matrix is used as the initial one for MQ NMR experiments [1]. Here we consider MQ NMR dynamics with the initial dipolar ordered state when the Hamiltonian of the system is determined by Eq. (1). Then the equilibrium state can be described as

$$\rho(0) = \frac{1}{Z} \exp(-\beta\mathcal{H}_{dz}) \approx (1 - \beta\mathcal{H}_{dz})/2^N, \quad (4)$$

where β is the inverse spin temperature, the partition function $Z = \text{Tr}\{\exp(-\beta\mathcal{H}_{dz})\}$ and N is the number of spins in the system. The high temperature approximation is taken into account in Eq. (4). The dipolar ordered state of the spin system can be reached by using the method of adiabatic demagnetization in a rotating frame (ADRF) [8, 9] or by applying a pair of phase-shifted rf-pulses (the Jeener-Brokaert (JB) method) [8, 10]. It is evident that the unit operator in Eq.(4) is not significant for the time evolution of the density matrix. For simplicity we will take

$$\rho(0) = \mathcal{H}_{dz} \quad (5)$$

as the initial condition. The use of the dipolar ordered state as the initial condition in MQ NMR experiments leads to the emergence of dipolar spin clusters with a greater number of spins faster than in the standard

method. It is well known [8] that NMR methods in solids use both the Zeeman equilibrium state and the dipolar ordered one as the initial conditions. Here the developed method together with the standard one [1] yield analogous possibilities for MQ NMR spectroscopy.

3. The dipolar temperature as a source of information about MQ NMR. The density matrix, $\rho_{\text{end}}(\tau, \bar{t})$, after the first three periods of the MQ NMR experiment can be written as

$$\rho_{\text{end}}(\tau, \bar{t}) = U^+(\tau)e^{-i\delta\bar{t}I_z}U(\tau)\mathcal{H}_{dz} \times U^+(\tau)e^{i\delta\bar{t}I_z}U(\tau), \quad (6)$$

where δ is the frequency offset on the evolution period of the duration \bar{t} which is a result of applying the time proportional phase incrementation (TPPI) method [1]. Then the evolution of the system in the RRF is governed by the Hamiltonian \mathcal{H}_{dz} of Eq. (1) and after the time $t \geq \omega_{\text{loc}}^{-1}$ ($\omega_{\text{loc}}^2 = \text{Tr}\{\mathcal{H}_{dz}^2\}/\text{Tr}\{I_z^2\}$) the system achieves the two-temperature quasi-equilibrium state with the density matrix ρ_{eq} ,

$$\rho_{\text{eq}} = \alpha\omega_0 I_z + \beta\mathcal{H}_{dz}, \quad (7)$$

where the inverse temperatures, α and β , can be found from the conservation laws:

$$\alpha = \frac{\text{Tr}\{\rho_{\text{end}}(\tau, \bar{t})I_z\}}{\omega_0 \text{Tr}\{I_z^2\}}, \quad \beta = \frac{\text{Tr}\{\rho_{\text{end}}(\tau, \bar{t})\mathcal{H}_{dz}\}}{\text{Tr}\{\mathcal{H}_{dz}^2\}}. \quad (8)$$

Applying the unitary transformation $V = e^{-i\frac{\pi}{2}I_z}e^{-i\pi I_x}$ to the expression $\rho_{\text{end}}(\tau, \bar{t})I_z$ one can obtain from Eq.(8) that $\alpha = 0$. It means that the quasi-equilibrium state of Eq.(7) is the dipolar ordered state. It is convenient to introduce the density matrix, $\rho_{\text{prep}}(\tau)$, at the end of the preparation period of the MQ NMR experiment

$$\rho_{\text{prep}}(\tau) = U(\tau)\mathcal{H}_{dz}U^+(\tau) \quad (9)$$

and represent it as [4]

$$\rho_{\text{prep}}(\tau) = \sum_n \rho_n(\tau), \quad (10)$$

where the term $\rho_n(\tau)$ is responsible for the MQ coherence of the n -th order. One can find

$$e^{-i\delta I_z t} \rho_n(\tau) e^{i\delta I_z t} = e^{-in\delta t} \rho_n(\tau). \quad (11)$$

By using Eqs.(9)–(11) one can rewrite the temperature β as

$$\beta = \sum_n e^{-in\delta t} J_n(\tau), \quad (12)$$

where the intensities of MQ coherences

$$J_n(\tau) = \frac{\text{Tr}\{\rho_n(\tau)\rho_{-n}(\tau)\}}{\text{Tr}\{\mathcal{H}_{dz}^2\}}. \quad (13)$$

The temperature β can be measured using the magnetization component which is in phase with the exciting radio-frequency (rf)pulse [8]. Different frequency components of the temperature β yield MQ coherences of different orders. Although the idea to use the dipolar ordered state as the initial one in MQ NMR experiments was formulated in [7] the physical realization of this idea is developed here for the first time.

4. The numerical analysis of the time evolution of MQ coherences. We restrict ourselves to numerical simulations of MQ NMR dynamics of quasi-one-dimensional hydroxyl proton chains in calcium hydroxapatite $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ [13], fluorine chains in calcium fluorapatite $\text{Ca}_5\text{F}(\text{PO}_4)_3$ [13], and the ten-spin system of protons of cyclopentane C_5H_{10} , consisting of two pentagon cycles [14], are suitable objects to study MQ dynamics in dipolar ordered systems.

The numerical calculations were performed with the developed method for MQ NMR dynamics of linear chains of 8 (Fig.1) and 10 (Fig.2) spins. The DDI coupling constant of the nearest neighbors is chosen to be $D = 1\text{s}^{-1}$. Then the coupling constant of spins j and k is $D/|j - k|^3$. The dependence of the intensities of MQ coherences on the dimensionless time $t = D\tau$ in spin chains containing eight and ten spins is presented in Figs.1 and 2. One can compare the intensities of MQ coherences in the suggested experiment with the standard ones (see Figs.1 and 2). It is evident that the suggested method can be considered as a useful addition to the standard MQ NMR methods. The intensities of the fourth, sixth and eighth order MQ coherences in a linear chain of eight spins coupled by the DDI (Fig.1) in the developed method are greater than in the usual MQ NMR experiments. In contrast to the initial equilibrium state [1], the dipolar one results in a creation of the non-zero highest order MQ coherences in a cluster of eight dipolar-coupled nuclear spins. A tendency of the faster growth of MQ coherences of high orders takes place for the linear chain containing ten spins (Fig.2). This peculiarity is connected with the initial dipolar ordered state. As a result, many-spin clusters and connected with them MQ coherences appear faster than in the usual NMR with the one-spin initial condition.

This conclusion can be proved by simulating the MQ dynamics for a cluster consisting of ten spins with 1024 quantum states. As a modelling system consisting of ten spins we consider cyclopentane molecules with ten hydrogen atoms in a liquid crystalline solvent. Since

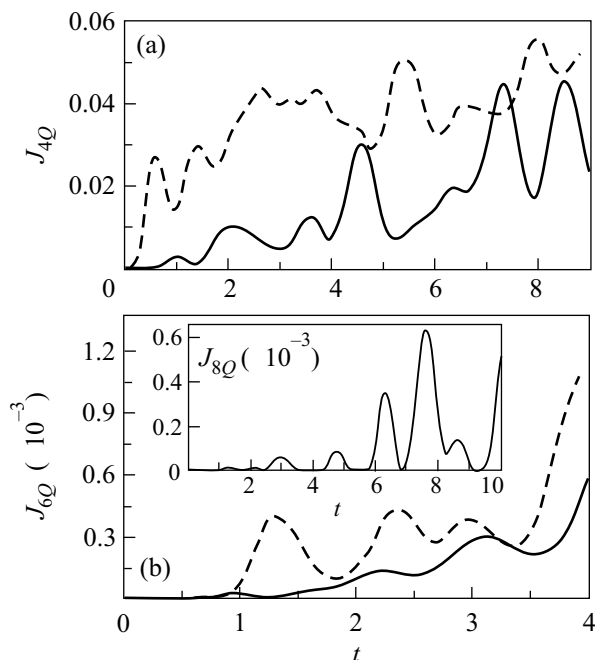


Fig.1. The time dependence of the intensities of the fourth, sixth and eighth order MQ coherences in a linear chain of eight spins coupled by the DDI: (a) the intensity of MQ coherence of the fourth order, J_4 , (solid) for $\rho(0) = I_z$, (dash) for $\rho(0) = H_{dz}$; (b) the intensity of MQ coherence of the sixth order, J_6 , (solid) for $\rho(0) = I_z$, (dash) for $\rho(0) = H_{dz}$. The inset shows the intensity of MQ coherence of the eighth order, J_8 , for $\rho(0) = H_{dz}$. Note that the intensity $J_8 = 0$ for $\rho(0) = I_z$

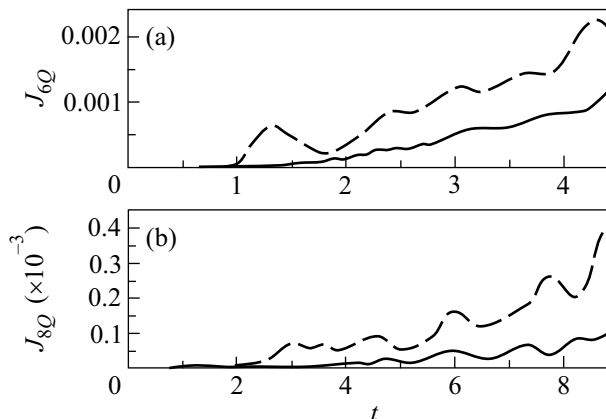


Fig.2. The time dependence of the intensities of the sixth and eighth order MQ coherences in a linear chain of ten spins coupled by the DDI: (a) the intensity of MQ coherence of the sixth order, J_6 , (solid) for $\rho(0) = I_z$; (dash) obtained by the developed method; (b) the intensity of MQ coherence of the eighth order, J_8 , (solid) for $\rho(0) = I_z$; (dash) obtained by the developed method

the DDI of different molecules are averaged due to the fast molecular motions MQ NMR dynamics is determined by the intramolecular DDI. The molecule cy-

clopontan has two pentagon cycles [14] and the reduced DDI coupling constants, $\overline{D}_{ij} = D_{ij}/D_{11'}$, are the following: $\overline{D}_{11'} = +1$ (by definition), $\overline{D}_{12} = -0.178$, $\overline{D}_{12'} = -0.002$, $\overline{D}_{13} = -0.093$, $\overline{D}_{13'} = -0.026$. MQ coherences of the sixth and eighth orders are represented in Fig.3 for the molecule cyclopentane. One can obtain

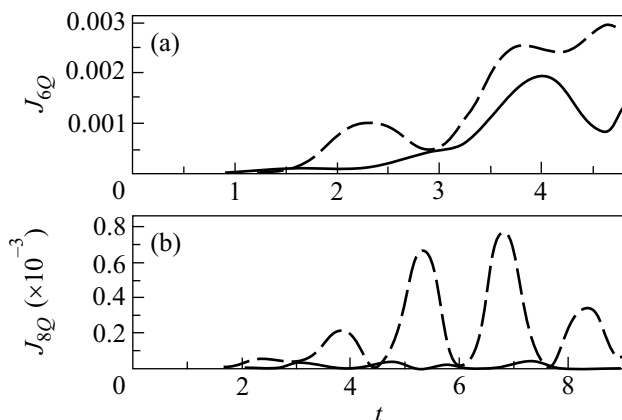


Fig.3. The time dependence of the intensities of the sixth and eighth order MQ coherences in the molecule cyclopentane (C_5H_{10}) consisting of 10 spins 1H coupled by the DDI: (a) the intensity of MQ coherence of the sixth order, J_6 , (solid) for $\rho(0) = I_z$, (dash) for $\rho(0) = H_{dz}$; (b) the intensity of MQ coherence of the eighth order, J_8 , (solid) for $\rho(0) = I_z$, (dash) for $\rho(0) = H_{dz}$

from Fig.3 the same conclusions as for one-dimensional systems. The intensities of these coherences, which were obtained by the developed method, are several times greater than in the standard MQ NMR (see Fig.3). These coherences appear faster in the MQ NMR in the dipolar ordered systems than in the ordinary conditions.

5. Conclusions. The MQ NMR method for the detection of MQ coherences starting from the dipolar ordered state is proposed. The method is based on the measurement of the dipolar temperature of quasi-equilibrium state which establishes after the time $t \gtrsim \omega_{loc}^{-1}$ after the MQ NMR experiment. This state is the dipolar ordered one and its temperature is a source of information about MQ NMR dynamics. It is well known [8] that the dipolar temperature is very useful for investigations of dynamics and relaxation processes in solids. The suggested method shows that this is also true for MQ NMR spectroscopy. Investigations of MQ NMR

dynamics in the dipolar ordered states can be considered as a supplementary method which complements the usual NMR in order to study structures and dynamical processes in solids. Many-spin clusters and many-spin correlations are created faster in such experiments than in the usual MQ NMR with the one-spin initial condition without any correlation between the spins. This paper focuses on simple examples of MQ NMR dynamics but the physical picture obtained here is not limited to the performed simulations and experiments and opens new possibilities for the study of many-spin systems.

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