

# Multiple Quantum NMR Dynamics in Spin Systems in Dipolar Ordered State

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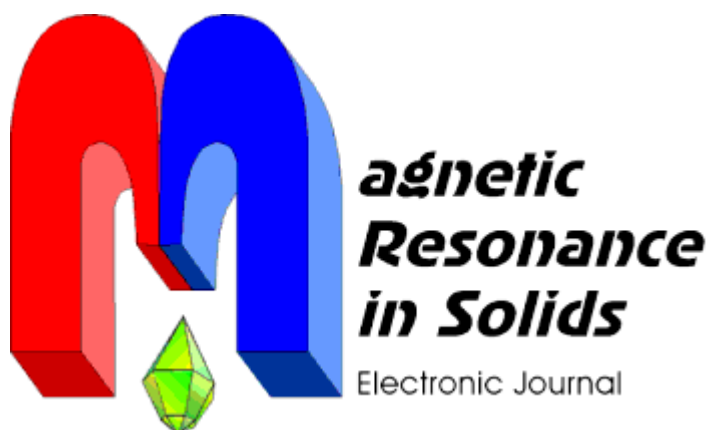
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Received November 18, 2006

Revised November 30, 2006

Accepted December 3, 2006



*Volume 8, No. 1,  
pages 10-14, 2006*

<http://mrsej.ksu.ru>

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Multiple quantum (MQ) NMR dynamics in a system which was prepared initially in dipolar ordered state is investigated with analytical and numerical methods for linear open chains of nuclear spins  $1/2$  coupled by dipole-dipole interactions. We show that the phases of the signals of MQ coherences are shifted by  $\pi/2$  with respect to the signals of the ordinary MQ NMR experiment. The sum of the intensities of MQ coherences of arbitrary opposite orders in this experiment is equal to zero. Many-spin correlations are created faster in the such experiments and can be used for investigations of many-spin dynamics of nuclear spins in solids.

**PACS:** 05.30.-d, 76.20.+q

**Keywords:** multiple quantum NMR spin dynamics, multiple quantum coherences, density matrix, high temperature approximation, dipolar ordered state

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 thermodynamical 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-Brokaert (JB) two-pulse sequence [8,10]. As a result of such initial condition, many-spin correlations appear faster than in the ordinary MQ NMR experiments in solids [1] 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.

In the present work we consider MQ NMR dynamics when the initial condition is determined by the dipolar ordered state. However, the observable is the longitudinal magnetization as in the usual MQ experiments. MQ NMR dynamics in the suggested experiment is strongly different from the standard one [1]. In particular, the sum of intensities of MQ coherences of arbitrary opposite orders equals zero in contrast to the usual MQ NMR experiments where these intensities are equal. It is interesting to underline that the phases of signals of MQ coherences are shifted over  $\pi/2$  in comparison with the signals of the standard experiments [1]. Computer simulations of such experiments for linear chains containing up to eight spins are presented in this paper.

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

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

where

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

is the coupling constant between spins  $j$  and  $k$ ,  $r_{jk}$  is the distance between spins  $j$  and  $k$ ,  $\gamma$  is the gyromagnetic ratio,  $\theta_{jk}$  is the angle between the internuclear vector  $r_{jk}$  and the external magnetic field  $\mathbf{H}_0$  is directed along the  $z$ -axis.  $I_{j\alpha}$  is the projection of the angular spin momentum operator on the axis  $\alpha$  ( $\alpha = x, y, z$ );  $I_j^+$  and  $I_j^-$  are the raising and lowering operators of spin  $j$ .

The basics scheme of MQ NMR experiments consists of four distinct periods: the preparation, free 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 [8] the average Hamiltonian, describing spin dynamics in the preparation period can be written as [1]:

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

where

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

The density matrix of the spin system at the end of the preparation period is

$$\rho(\tau) = U(\tau) \rho(0) U^\dagger(\tau),$$

where

$$U(\tau) = \exp(-i\tau(H^{(2)} + H^{(-2)}))$$

and  $\rho(0)$  is the initial density matrix of the system. Usually the thermodynamic equilibrium density matrix is used as the initial one for MQ NMR experiments. Here we consider MQ NMR dynamics with the initial dipolar ordered state when the Hamiltonian of the system is determined by Eq.(1).

We introduce  $\varphi_y$ -pulse turning spins around the axis  $y$  on the angle  $\pi/4$  after the preparation period. Without this additional pulse it is not possible to obtain a nonzero signal at the end of the MQ NMR experiment. As a result, we have the following expression for the observable signal

$$I_z(\tau, t) = Tr \left\{ e^{-i\varphi I_y} U(\tau) H_{dz} U^\dagger(\tau) e^{i\varphi I_y} e^{i\delta I_z} U(\tau) I_z U^\dagger(\tau) e^{-i\delta I_z} \right\}, \quad (3)$$

where  $\delta$  is the frequency offset on the evolution period of the duration  $t$  which is a result of applying the TPPI method [1].

Density matrix  $\rho_{MQ}(\tau)$  at the end of the preparation period can be represented as follows:

$$\rho_{MQ}(\tau) = U(\tau)I_z U(\tau) = \sum_n \rho_n(\tau). \quad (4)$$

The term  $\rho_n(\tau)$  is responsible for MQ coherence of the  $n$ -th order. The observable signal can be presented as

$$I_z(\tau, t) = \sum_n e^{-in\delta t} J_n(\tau) = \sum_n e^{in\delta t} J_n^*(\tau) = \sum_n e^{-in\delta t} J_{-n}^*(\tau). \quad (5)$$

The intensity,  $J_n(\tau)$ , of MQ coherence of the  $n$ -th order is

$$J_n(\tau) = \text{Tr}\{A(\tau)\rho_n(\tau)\},$$

where

$$A(\tau) = e^{-i\varphi I_y} U(\tau) H_{dz} U^+(\tau) e^{i\varphi I_y}.$$

From (5) it follows that

$$J_n(\tau) = J_{-n}^*(\tau).$$

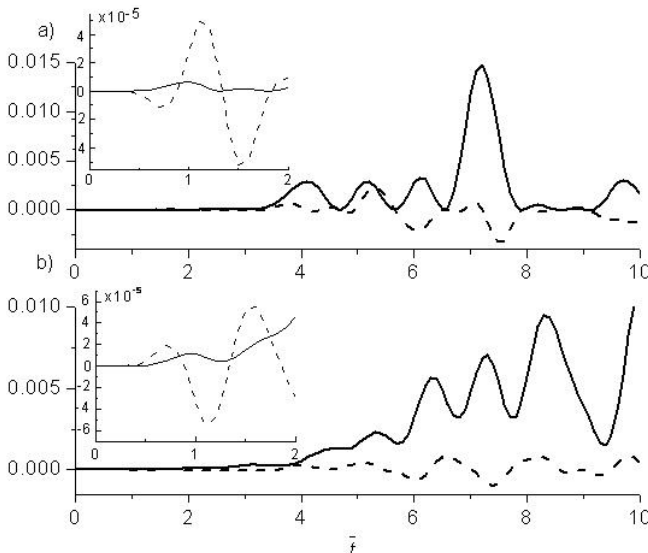
Expanding the density matrix,  $\rho_{MQ}(\tau)$  in the Taylor series over the parameter  $t$ , one can prove [11] that

$$J_n(\tau) + J_{-n}(\tau) = 0 \quad (6)$$

Eq.(6) allows us to conclude that  $J_n(\tau)$  is imaginary for all  $n \neq 0$ . Thus, the phases of the MQ NMR coherences in this experiment are shifted by  $\pi/2$  from the signals of usual MQ NMR [1]. It is well-known that in the usual MQ NMR experiments the sum of the intensities of all MQ coherences does not depend on time [12]. Here this law has a specific form. According to Eq.(6) the sum of intensities of orders  $-n$  and  $n$  is equal to zero for all  $n$ .

The numerical calculations are performed for MQ dynamics of linear chains consisting of 6 and 8 spins. The DDI constant of the nearest neighbors is chosen to be  $D = 1 \text{ c}^{-1}$ . Then the DDI constant of spins  $j$  and  $k$  is  $D_{jk} = D/|j-k|^3$ . We introduce normalized intensities of MQ coherences  $\text{Im}\{J_n\} / \{Tr(I_z)^2 Tr(H_{dz})^2\}^{1/2}$ . The dependence of normalized intensities of MQ coherences on dimensionless time in spin chains containing six and eight spins is presented in Fig.1. It is clear that MQ coherence of the sixth order in a linear chain of six spins appears little earlier than in the usual MQ NMR. This can be seen in the inset of Fig.1a. An analogous tendency takes place for the linear chain containing eight spins (Fig.1b). This peculiarity is connected with the initial dipolar ordered state. The numerical calculations confirm the results obtained in the previous section. In particular, the computer simulations yield the following: i) all intensities,  $J_n(n \neq 0)\sigma_x$ , are imaginary, ii)  $J_0 = 0$ ,  $J_n + J_{-n} = 0$ . The growth of MQ coherences in time occurs in accordance with the condition  $J_n + J_{-n} = 0$  for all  $n$ .

Thus, the growth of MQ coherences in the systems with dipolar ordered state has some peculiarities which are related to the initial spin correlations. The spin-lattice dipolar relaxation in such systems is slower than the Zeeman one and it does not hamper the investigations of the MQ NMR coherences of high orders.



**Fig.1.** (a) time dependence of the intensities of the sixth order MQ coherences in a linear chain of six spins coupled by the DDI: the intensity of MQ coherence of the sixth order (solid) for  $\rho(0) = I_z$ ;  $\text{Im}(J_{-6})$  (dash) for  $\rho(0) = H_{dz}$ . (b) time dependence of the intensities of the sixth order MQ coherences in a linear chain of eight spins coupled by the DDI: the intensity of MQ coherence of the sixth order (solid) for  $\rho(0) = I_z$ ;  $\text{Im}(J_{-6})$  (dash) for  $\rho(0) = H_{dz}$ . The intensity of MQ coherence of the eighth order is equal to 0. The insets show that the MQ coherence appears some earlier than in the usual MQ NMR.

We are grateful for financial support for this work through a grant from the Russian Foundation for Basic Researches (grant no. 04-03-32528).

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