Multiple Quantum NMR Dynamics in Dipolar Ordered Spin Systems

S. I. Doronin, E. B Fel’dman, E. I. Kuznetsova

Institute of Problems of Chemical Physics of Russian Academy of Sciences,
Chernogolovka, Moscow Region, 142432, Russia

G. B. Furman, S.D. Goren

Department of Physics, Ben Gurion University, Beer Sheva 84105, Israel

Abstract

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 two different methods of MQ NMR. One of them is based on the measurement of the dipolar temperature in the quasi-equilibrium state which establishes after the time of order T2 after the MQ NMR experiment. The other method uses an additional resonance 45°-0-pulse after the preparation period of the standard MQ NMR experiment in solids. Many-spin clusters and correlations are created faster in such experiments than in the usual MQ NMR experiments and can be used for the investigation of many-spin dynamics of nuclear spins in solids.
I. INTRODUCTION

Multipe-quantum (MQ) NMR spin dynamics in solids is a powerful tool for the investigation of structure and dynamical processes in solids, counting the number of spins in impurity clusters and the simplification of ordinary NMR spectra. 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. A systematic quantum-mechanical approach was developed 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 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) or with the Jeener-Broekaert (JB) two-pulse sequence. It has been shown that the spin system contains MQ coherences immediately following the second pulse of the JB pulse sequence. 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. 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 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 article we consider MQ NMR dynamics when the initial condition is determined by the dipolar ordered state. Our motivation of performance of this work is defined first of all by 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 peculiarities of MQ NMR in systems prepared in the dipolar ordered states in Section II. Two methods of MQ NMR for the systems in the dipolar ordered states are presented in Sections III and IV. The method of Section III is based on the measurement of the dipolar temperature of the quasi-equilibrium state which establishes after the time \( t \sim \omega_{\text{loc}}^{-1} \) (\( \omega_{\text{loc}} \) is the dipolar local field) after the MQ NMR experiment. The method of Section IV is a
simple modification of the usual MQ NMR experiment [1]. The additional \(\pi/4\)-pulse after the preparation period allows the observation of a non-zero signal as in the usual MQ NMR experiments. Computer simulations of such experiments for linear chains containing up to eight spins are presented in Section V.

II. 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

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

where \(D_{jk} = \frac{\gamma^2 \hbar}{r_{jk}^3} (1 - 3 \cos^2 \theta_{jk})\) is the coupling constant between spins \(j\) and \(k\), \(\gamma\) is the gyromagnetic ratio, \(r_{jk}\) is the distance between spins \(j\) and \(k\), \(\theta_{jk}\) is the angle between the internuclear vector \(\vec{r}_{jk}\) and the external magnetic field \(\vec{H}_0\) which is directed along the axis \(z\). \(I_j \alpha(\alpha = x, y, z)\) is the projection of the angular spin momentum operator on the axis \(\alpha\); \(I_j^+\) and \(I_j^-\) are the raising and lowering operators of spin \(j\).

The basic scheme of the standard MQ NMR experiments consists of four distinct periods of time (Fig.1a): preparation \((\tau)\), evolution \((t_1)\), mixing \((\tau)\) and detection \((t_2)\) [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]

\[
\mathcal{H}_{MQ} = \mathcal{H}^{(2)} + \mathcal{H}^{(-2)},
\]

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

\[
\rho(\tau) = U(\tau) \rho(0) U^+ (\tau),
\]

where \(U(\tau) = \exp(-i \tau (H^{(2)} + H^{(-2)}))\) is the evolution operator on the preparation period and \(\rho(0)\) is the initial density matrix of the system. On the mixing period the spin system is irradiated with sequence of the pulses shifted on a \(\pi/2\)-phase regarding the pulses of the
preparation period. As a result the average Hamiltonian describing evolution of the spin system on the mixing period changes a sign on opposite to the sign of the Hamiltonian (2), and the evolution operator, \( U(\tau) \), is replaced by the operator \( U^+(\tau) \). Usually the thermodynamical 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). Then the equilibrium state can be described as

\[
\rho(0) = \frac{1}{Z} \exp(-\beta H_{dz}) \approx (1 - \beta H_{dz}) / 2^N, \tag{4}
\]

where \( \beta \) is the inverse spin temperature, the partition function \( Z = Tr\{\exp(-\beta H_{dz})\} \) 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 radiofrequency (rf)-pulses (the Jeener-Broekaert (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

\[
\rho(0) = H_{dz} \tag{5}
\]

as the initial condition. The use of the dipolar ordered state as the initial condition in MQ NMR experiments leads to the emergence of 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 methods together with the standard one \[1\] yield analogous possibilities for MQ NMR spectroscopy. Below we describe two different methods of MQ NMR of the dipolar ordered systems.

### III. THE DIPOLAR TEMPERATURE AS A SOURCE OF INFORMATION ABOUT MQ NMR

Starting with the initial condition (5), the density matrix, \( \rho(t) \), after the three periods of the standard MQ NMR experiment (Fig.1a) can be written as

\[
\rho(t) = U^+(\tau) e^{-i\delta t_1 I_z} \rho(\tau) e^{i\delta t_1 I_z} U(\tau), \tag{6}
\]
where $\rho(\tau)$ is the density matrix at the end of the preparation period according to Eq. (3) and $t = 2\tau + t_1$, $\delta$ is the frequency offset on the evolution period of the duration $t_1$ which is a result of applying the time proportional phase incrementation (TPPI) method [1]. The last unitary transformation in (6) with operator $U(\tau)$ describes the mixing period. Then the evolution of the system in the RRF is governed by the Hamiltonian $H_{dz}$ of Eq. (1) and after the time $t \geq \omega_{loc}^{-1} (\omega_{loc}^2 = Tr\{H_{dz}^2\}/Tr\{I_z^2\})$ the system achieves the two-temperature quasi-equilibrium state with the density matrix $\rho_{eq}$,

$$\rho_{eq} = \alpha \omega_0 I_z + \beta H_{dz}, \quad (7)$$

where the inverse temperatures, $\alpha$ and $\beta$, can be found from the conservation laws:

$$\alpha = \frac{Tr\{\rho(t)I_z\}}{\omega_0 Tr\{I_z^2\}}, \quad \beta = \frac{Tr\{\rho(t)H_{dz}\}}{Tr\{H_{dz}^2\}}. \quad (8)$$

Applying the unitary transformation $V = e^{-i\pi/2}I_z e^{-i\pi I_x}$ to the expression $\rho(t)I_z$ 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 expand the density matrix, $\rho(\tau)$, at the end of the preparation period of the MQ NMR experiment (Fig. 1a) with the initial condition (5) as

$$\rho(\tau) = \sum_n \rho_n(\tau), \quad (9)$$

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

$$e^{-i\delta t} \rho_n(\tau) e^{i\delta t} = e^{-in\delta t} \rho_n(\tau). \quad (10)$$

By using Eqs. (8)-(10) one can rewrite the temperature $\beta$ as

$$\beta = \sum_n e^{-in\delta t} J_n(\tau), \quad (11)$$

where the intensities of MQ coherences

$$J_n(\tau) = \frac{Tr\{\rho_n(\tau)\rho_{-n}(\tau)\}}{Tr\{H_{dz}^2\}}. \quad (12)$$

The temperature $\beta$ can be measured using the magnetization component which is in phase with the exciting rf-pulse [8]. Different frequency components of the temperature $\beta$ yield MQ coherences of different orders.
IV. THE MODIFICATION OF THE STANDARD MQ NMR EXPERIMENT IN SOLIDS

In the previous section we showed that at the initial condition of Eq. (5) the standard scheme of MQ NMR experiments does not lead to any observable magnetization. In order to overcome this problem we introduce a $\phi_y$-pulse turning spins around the axis $y$ by the angle $\phi$ after the preparation period (Fig. 1b). Then starting with $\rho(0) = H_{dz}$, after the mixing period (Fig. 1b) the longitudinal magnetization, $M_z(t)$, is

$$M_z(t) = Tr \{\rho(t)I_z\}$$  \hspace{1cm} (13)

where the density matrix after the three periods of the modified MQ NMR pulse sequence (Fig. 1b) can be written as

$$\rho(t) = U^+(\tau)e^{-i\delta I_z t_1}\rho(\tau)e^{i\delta I_z t_1}U(\tau)$$  \hspace{1cm} (14)

and $\rho(\tau)$ is the density matrix just after the $\phi_y$-pulse (Fig. 1b)

$$\rho(\tau) = e^{-i\phi I_y}U(\tau)\rho(0)U^+(\tau)e^{i\phi I_y}.$$  \hspace{1cm} (15)

It is worth to notice that here the TPPI method [1] is applied in the mixing period in contrast to the method of Section III when it was applied in the preparation period of the MQ NMR experiment. Using Eqs. (14) and (15) and the initial condition (5) it is convenient to present the formula (13) for the longitudinal magnetization, $M_z(t)$, as follows

$$M_z(t) = Tr \{e^{-i\delta I_z t}e^{-i\phi I_y}U(\tau)H_{dz}U^+(\tau)e^{i\phi I_y}e^{i\delta I_z t}\rho_{MQ}(\tau)\}$$  \hspace{1cm} (16)

where

$$\rho_{MQ}(\tau) = U(\tau)I_zU^+(\tau),$$  \hspace{1cm} (17)

coincides with the density matrix at the end of the preparation period of the standard MQ NMR experiment with the thermodynamical equilibrium density matrix as the initial condition [1]. The density matrix $\rho_{MQ}(\tau)$ can be represented in the following form [4]

$$\rho_{MQ}(\tau) = \sum_n \rho_{nMQ}(\tau)$$  \hspace{1cm} (18)
where again the term $\rho^\text{MQ}_n(\tau)$ is responsible for the MQ coherence of the $n$-th order and satisfies to the relationship of Eq. (10). By using Eqs. (10), (17), and (18) one can rewrite the expression for the observable signal in terms of the intensities of MQ coherences

$$M_z(t) = -i \sum_n e^{-in\delta t} J_n(\tau) = i \sum_n e^{in\delta t} J_n^*(\tau) = i \sum_n e^{-in\delta t} J_{-n}^*(\tau),$$

where

$$J_n(\tau) = i Tr \{ \rho_\phi(\tau) \rho^\text{MQ}_n(\tau) \}$$

and the longitudinal magnetization, $M_z(t)$, is always real. Thus, one can find from Eq.(19) that

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

One can notice that

$$I_z(\delta) = -I_z(-\delta)$$

by applying a $\pi$-rotation around the $y$-axis to all operators in Eq. (13). It follows immediately from Eqs. (19) and (22) that

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

It is evident that with the method of Section III $J_n(\tau) = J_{-n}(\tau)$, and the longitudinal magnetization, $M_z(t)$, is determined as

$$M_z(t) = \sum_n \cos(n\delta t) J_n(\tau).$$

By using the modified pulse sequence (Fig. 1b) the longitudinal magnetization can be expressed as

$$M_z(t) = -\sum_n \sin(n\delta t) J_n(\tau).$$

Thus the phases of the MQ NMR coherences in the modified MQ NMR pulse excitation scheme are shifted by $\pi/2$ from the phases in standard MQ NMR [1]. It is clear from Eq. (23) that the intensity of the MQ coherence of the zeroth order, $J_0(\tau)$, is equal to zero in the considered experiments.

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 [13]. This is also right for the method described in Section III. Here this law has a specific form. According to Eq. (23) the sum of intensities of orders $n$ and $-n$ is equal to zero for all $n$. Thus, the sum of the intensities of all MQ coherences equals zero.
V. THE NUMERICAL ANALYSIS OF THE TIME EVOLUTION OF MQ COHERENCES

We restrict ourselves to numerical simulations of MQ NMR dynamics of one-dimensional systems. For example, quasi-one-dimensional hydroxyl proton chains in calcium hydroxyapatite \( \text{Ca}_5(OH)(PO_4)_3 \) [14] and fluorine chains in calcium fluorapatite \( \text{Ca}_5F(PO_4)_3 \) [14] are suitable objects to study MQ dynamics in dipolar ordered systems. The numerical calculations were performed with the methods of Sections III, IV for MQ NMR dynamics of linear chains of 6 and 8 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 \( D/|j-k|^3 \). In order to compare the results of the numerical simulations with the analogous ones for the ordinary MQ NMR dynamics we introduce the normalized intensities of MQ coherences for the method of Section IV, \( J_n(\tau)/\{T_r(I_z^2)T_r(H_{dz}^2)\}^{1/2} \). The dependence of the intensities of MQ coherences on the dimensionless time, \( t = D\tau \), of the preparation period in spin chains containing six and eight spins is presented in Figs. 2 and 3 for the both methods of Sections III and Sections IV. One can compare the intensities of MQ coherences in the suggested experiments with the standard ones (see Figs. 2 and 3). It is evident that the suggested methods can be considered as a useful addition to the standard MQ NMR methods. Comparison of the suggested methods of MQ NMR of the systems in the dipolar ordered state is given in Fig. 2 for MQ coherences of the second and fourth orders. One can see (Figs. 2a, 2b) that the method of Section III is more preferable for experimental realizations in some cases.

Fig. 2a demonstrates that the method of Section III yields the intensities of MQ coherences of the fourth order which several times higher than the analogous coherence in the standard MQ NMR experiment. It is clear from the inset of Fig. 3a that MQ coherence of the sixth order, obtained with the method of Section IV, appears little earlier than in the usual MQ NMR in a linear chain of six spins. At the same time, the intensity of this MQ coherence obtained with the method of Section III is equal zero. In fact, the both methods supplement each other at the study of MQ NMR dynamics. A tendency of the faster growth of MQ coherences of high orders takes place for the linear chain containing eight spins (Fig. 3b). This peculiarity is connected with the initial dipolar ordered state, \( \rho(0) = H_{dz} \). As a result, many-spin clusters and connected with them MQ coherences appear faster than in the standard MQ NMR with the initial condition, \( \rho(0) = I_z \). The numerical calculations
confirm also the results obtained in the previous section. In particular, the growth of MQ coherences (for the method of Section IV) occurs in accordance with Eq. (23) and $J_0(t) \equiv 0$.

One can see from Figs. 2 and 3 and Eq. (23) that the observable intensities can be negative in contrast to the ordinary MQ NMR experiments at high temperatures [1, 4, 5]. At the same time, it was shown [15] that the intensities of MQ coherences can be negative in the standard NMR experiments at low temperatures. It is a terminological problem only. In fact, in MQ NMR experiments the observable is the longitudinal magnetization modulated by rf pulses. The distinct frequency components of the magnetization can have an arbitrary sign [15].

VI. CONCLUSIONS

The MQ NMR methods for the detection of MQ coherences starting from the dipolar ordered state are proposed. The first method is based on the quasi-equilibrium state which establishes after the time $t \gtrsim \omega_{\text{loc}}^{-1}$ after the MQ NMR experiment. This state is the dipolar ordered one and its temperature is a source of information about MQ NMR dynamics. In order to observe a non-zero signal of MQ coherences in the second method an additional resonance $(\pi/4)_y$-pulse should be applied after the preparation period of the standard MQ NMR experiment in solids. 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 initial condition without any correlation between the spins. This paper focuses on simple one-dimensional examples 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.

Acknowledgements

We are grateful for financial support for this work through a grant from the Russian Foundation for Basic Research (grant no. 07-07-00048). G.F. acknowledges financial support
from the US-Israel Binational Science Foundation (grant no. 2002054).

[1] J. Baum, M. Munovitz, A. N. Garroway, A. Pines, J. Chem. Phys. **83**, 2015 (1985).

[2] J. Baum, K. K. Gleason, A. Pines, J. Chem. Phys., **56**, 1377 (1986).

[3] W. S. Warren, D. P. Weitekamp, A. Pines, J. Chem. Phys., **73**, 2084 (1980).

[4] E. B. Fel’dman, S. Lacelle, J. Chem. Phys., **107**, 7067 (1997).

[5] S. I. Doronin, I. I. Maximov, E. B. Fel’dman, Zh. Eksp. Teor. Fiz., **118**, 687 (2000), JETP, **91**, 597 (2000).

[6] S. I. Doronin, E. B. Fel’dman, Solid State Nucl. Magn. Reson., **28**, 111 (2005).

[7] G. B. Furman, S. D. Goren, J. Phys.: Condens. Matter, **17**, 4501 (2005).

[8] M. Goldman. *Spin Temperature and Nuclear Magnetic Resonance in Solids*, Oxford. Clarendon Press. 1970.

[9] C. P. Slichter, W. C. Holton, Phys. Rev., **122**, 1701 (1961).

[10] J. Jeener, P. Broekaert, Phys. Rev., **157**, 232 (1967).

[11] S. Emid, A. Bax, J. Konijnendijk, J. Smidt, A. Pines, Physica B, **96**, 333 (1979).

[12] H. Cho, D. G. Cory, C. Ramanathan, J. Chem. Phys., **118**, 3686 (2003).

[13] D. A. Lathrop, E. S. Handy, K. K. Gleason, J. Magn. Reson. A , **111**, 161 (1994).

[14] G. Cho, J. P. Yesinowski, J. Phys. Chem., **100**, 15716 (1996).

[15] E. B. Fel’dman, I. I. Maximov, J. Magn. Reson., **157**, 106 (2002).

Caption figures

Fig. 1 The basic schemes for MQ NMR: a) the scheme of the standard MQ NMR experiment; b) the scheme of the modified MQ NMR experiment.

Fig. 2 The time dependence of the intensities of the MQ coherences of the second order in a linear chain of six spins coupled by the DDI for \( \rho(0) = H_{dz} \); the intensities \( J_{-2} \) (solid) and \( J_{+2} \) (dash) obtained by the method of Section IV at \( \phi = \pi/4 \). The intensity \( J_{2} \) (dot) is obtained by the method of Section III. (b) The time dependence of the intensities of the fourth order MQ coherences in a linear chain of six spins coupled by the DDI: the intensity of the MQ coherence of the fourth order (solid) for \( \rho(0) = I_{z} \); \( J_{-4} \) (dash) and \( J_{+4} \) (dot) for \( \rho(0) = H_{dz} \) obtained by the method of Section IV at \( \phi = \pi/4 \), and the intensity \( J_{4} \) (dash-dot) is obtained by the method of Section III.
Fig. 3 The 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 $\rho(0) = I_z$; $J_{-6}$ (dash) for $\rho(0) = H_{dz}$ obtained by the method of Section IV with using $(\pi/4)_{y_{\gamma}}$-pulse and $J_6$(dot) obtained by the method of Section III. (b) The 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 $\rho(0) = I_z$; $J_{-6}$ (dash) for $\rho(0) = H_{dz}$ obtained by the method of Section IV with $(\pi/4)_{y_{\gamma}}$-pulse; $J_6$ (dot-dash) and $J_8$ (dot) obtained by the method of Section III. The insets show that the MQ coherences in the dipolar ordered state obtained by the method of Section IV with applied $(\pi/4)_{y_{\gamma}}$-pulse appears little earlier than in the usual MQ NMR and in the method of Section III.
