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Multiple Quantum Dynamics in Linear Chains and Rings of Nuclear Spins in Solids at Low Temperatures

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Multiple quantum spin dynamics is studied using analytical and numerical methods for one-dimensional finite systems of nuclear spins $\frac{1}{2}$ coupled by dipole–dipole interactions at low temperatures. Exact expressions for intensities of multiple quantum coherences at low temperatures were obtained in the approximation of the nearest neighbor interactions. The time growth of multiple quantum coherences was analyzed numerically when all the dipole–dipole interactions in one-dimensional systems consisting of $6 \div 8$ spins were taken into account. It is shown that the growth of multiple quantum coherences gets faster when the temperature decreases, and the intensities of multiple quantum coherences can be negative at low temperatures. © 2002 Elsevier Science (USA)

Key Words: **multiple quantum NMR; exactly solvable models; low temperatures; supercomputer simulations.**

1. INTRODUCTION

Multiple quantum (MQ) NMR is a powerful tool for investigations of structural properties in solids (*1*). Although many experimental and theoretical works consider a high-temperature region (*2–4*), MQ methods give much promise at low temperatures too. The point is that one can neglect the spin–lattice relaxation at low temperatures during the time scale of MQ spin dynamics and can hope to obtain exact and clear information about spin dynamics of one-dimensional systems in MQ NMR experiments. This will facilitate the comparison of MQ experiments with theory.

We study analytically and numerically the behavior of one-dimensional systems at low temperatures under MQ NMR experiments. At initial time $\tau = 0$ the system of nuclear spins is assumed to be at thermal equilibrium with the lattice and the equilibrium spin density operator ρ_{eq} given as

$$\rho_{\text{eq}} = \frac{1}{Z} e^{\beta\omega_0 I^z}, \qquad [1]$$

where ω_0 is the Larmor frequency, β^{-1} is proportional to the Zeeman temperature, I^z is the z component of the spin angular momentum operator, and $Z = \text{Tr}[\exp(\beta\omega_0 I^z)]$ is the partition function. Consider a two-dimensional time-resolved MQ NMR experiment (*1–3*) for one-dimensional systems (linear chains or rings). During the excitation period τ let the spin system be driven by a sequence of RF pulses and its behavior be described by the 2-spin/2-quantum Hamiltonian

$$H = H^{+2} + H^{-2}, \qquad [2]$$

where

$$H^{\pm 2} = -\frac{1}{2} \sum_{i<j} D_{ij} I_i^{\pm} I_j^{\pm}. \qquad [3]$$

The $I_j^{\pm}$ are the raising and lowering spin angular operators of spin j, and D_{ij} is the dipolar coupling constant between spins i and j given by

$$D_{ij} = \frac{\gamma^2 \hbar}{2 r_{ij}^3}(1 - 3\cos^2\theta_{ij}), \qquad [4]$$

where r_{ij} is the distance between spins i and j, and θ_{ij} is the angle between the internuclear vector $\mathbf{r}_{ij}$ and the Zeeman field. In the plane linear chains and rings (the external magnetic field is perpendicular to their planes) the angle θ_{ij} is the same for all pairs of spins. We shall assume at analytical calculations that the distances between nearest neighbors r_{ii+1} are the same. It means that the dipolar coupling constants are equal, i.e., $D_{ii+1} = D$. The dipole–dipole interaction (DDI) of the spins decreases as r^{-3} with the distance r. Thus the next nearest neighbors in plane linear chains interact eight times weaker than the nearest neighbors do (the corresponding factor is $8\cos^3(\frac{\pi}{N})$ for rings where N is the number of spins).

In the present work we investigate theoretically MQ dynamics of one-dimensional spin systems at low temperatures. In Section 3, we develop a new theoretical approach to MQ dynamics at low temperatures and find the exact expressions for intensities of MQ coherences in the approximation of nearest neighbor interactions. We demonstrate with computer simulations that MQ coherences of higher orders appear at earlier times than they do at high temperatures. One can hope to obtain a profile of MQ coherences at low temperatures without distortions caused

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by the spin–lattice relaxation. We also show that intensities of higher order MQ coherences can change their signs in the course of a time evolution of the spin system at low temperatures. This peculiarity of MQ dynamics can be useful for extracting new physical–chemical information.

2. MQ COHERENCES AT LOW TEMPERATURES

A two-dimensional time-resolved MQ NMR experiment has the four periods: preparation, evolution, mixing, and detection (see Fig.1 and Ref. (*1*)). In the preparation period the system is exposed to a sequence of pulses which leads to the appearance and the evolution of MQ coherences. We assume that this sequence is periodic and that one period contains eight RF pulses (*1*),

$$\frac{\Delta}{2} - X - \Delta' - X - \Delta - X - \Delta' - X - \Delta - \bar{X} - \Delta' - \bar{X} - \Delta - \bar{X} - \Delta' - \bar{X} - \frac{\Delta}{2}, \quad [5]$$

where $\Delta' = 2\Delta + t_p$ are the time intervals between pulses (t_p is the pulse duration), and X and $\bar{X}$ are resonant pulses having the phase difference π which flip the spins by 90° about the x axis of the reference frame rotating at the pulse carrier frequency. Then the average Hamiltonian determining the dynamics of the nuclear spin system is given by Eq. [2] and the resulting signal $G(\tau, t)$ stored as population information reads (*1, 7*)

$$G(\tau, t) = \mathrm{Tr}\left[I^z e^{\mathrm{i}H\tau} e^{\mathrm{i}\Delta\omega t I^z} e^{-\mathrm{i}H\tau} \rho_{\mathrm{eq}} e^{\mathrm{i}H\tau} e^{-\mathrm{i}\Delta\omega t I^z} e^{-\mathrm{i}H\tau}\right], \quad [6]$$

where $\Delta\omega$ is the RF offset, chosen to be larger than the local dipolar field frequency, τ is the excitation time, and t is the evolution time. Such an experiment allows us to obtain the integrated intensities over all the dipolar frequencies of the different MQ orders. It is sufficient to obtain the important information in MQ clustering experiments (*8*). We denote the density operator at the end of the preparation period at high temperatures $\rho^{\mathrm{ht}}(\tau) = \exp(-\mathrm{i}H\tau) I^z \exp(\mathrm{i}H\tau)$. It was calculated in (*4–6*). Taking into account that $\rho^{\mathrm{ht}}(\tau) = \sum_n \rho_n^{\mathrm{ht}}(\tau)$, where n is the order of the MQ coherence, we can rewrite Eq. [6] as

$$G(\tau, t) = \sum_n \mathrm{Tr}\left[\rho(\tau) e^{-\mathrm{i}\Delta\omega t I^z} \rho_n^{\mathrm{ht}}(\tau) e^{\mathrm{i}\Delta\omega t I^z}\right] = \sum_n e^{-\mathrm{i}n\Delta\omega t} \mathrm{Tr}\left[\rho(\tau)\rho_n^{\mathrm{ht}}(\tau)\right], \quad [7]$$

where $\rho(\tau) = \exp(-\mathrm{i}H\tau)\rho_{\mathrm{eq}} \exp(\mathrm{i}H\tau)$ is the low-temperature spin density operator. Then the spectral intensities $J_n(\tau)$ of order n and the partition function Z are (*7*)

$$J_n(\tau) = \mathrm{Tr}\left[\rho(\tau)\rho_n^{\mathrm{ht}}(\tau)\right], \quad Z = \mathrm{Tr}\left[e^{\beta\omega_0 I^z}\right] = 2^N \cosh^N \frac{\beta\omega_0}{2}, \quad [8]$$

where N is the number of the spins in the one-dimensional system. Equation [8] can be rewritten as

$$J_n(\tau) = \mathrm{Tr}\left[\rho(\tau)\rho_n^{\mathrm{ht}}(\tau)\right] = \mathrm{Tr}\left[\rho^+(\tau)\left(\rho_n^{\mathrm{ht}}(\tau)\right)^+\right] = \mathrm{Tr}\left[\rho(\tau)\rho_{-n}^{\mathrm{ht}}(\tau)\right] = J_{-n}(\tau). \quad [9]$$

For analytical calculations of MQ coherences it is convenient to use the following form of Eq. [8]

$$J_n(\tau) = \frac{1}{Z}\mathrm{Tr}\left[\rho_n^{\mathrm{ht}}(\tau) e^{\beta\omega_0 \rho^{\mathrm{ht}}(\tau)}\right]. \quad [10]$$

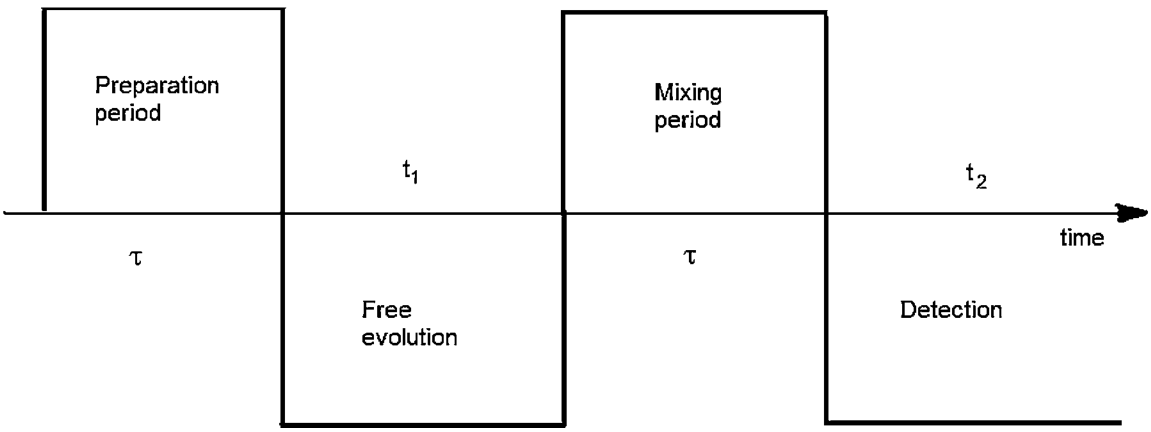

FIG. 1. A schematic presentation of a time-domain MQ experiment.

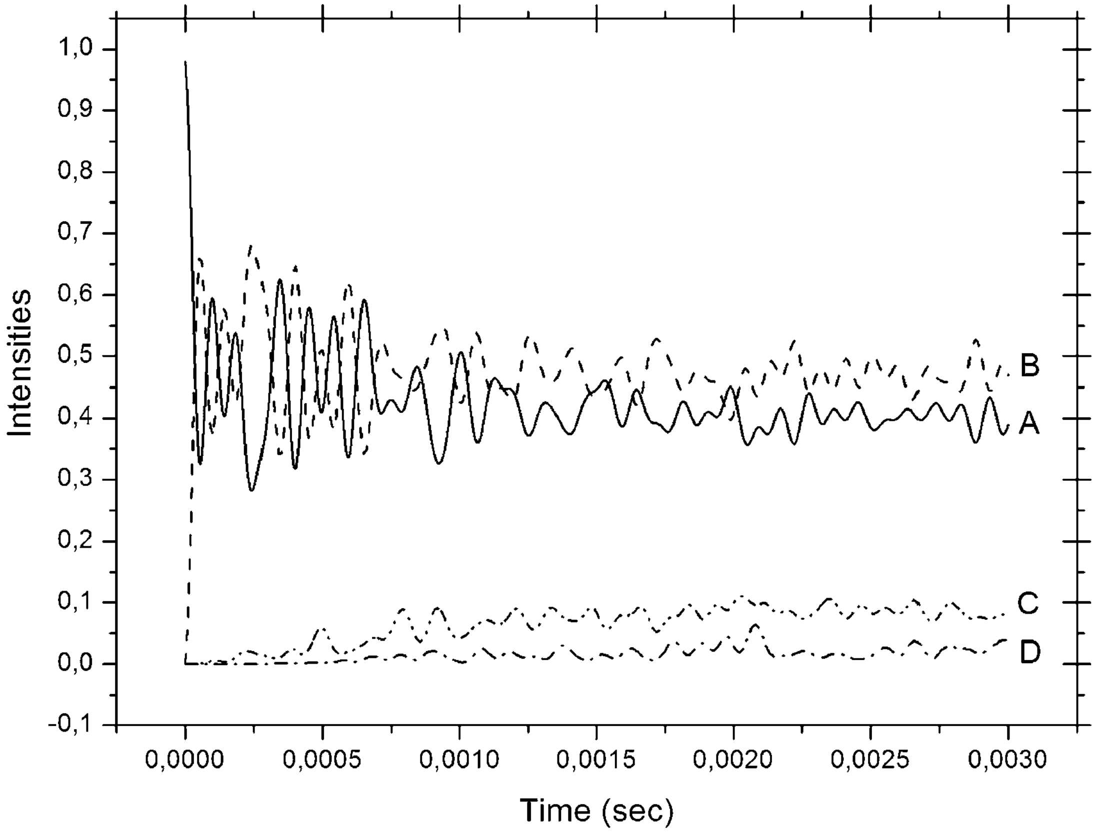

FIG. 2. Time-course of MQ coherences for a spin ring of $N = 8$ spins at $\beta\omega_0 = 0.5$ (20 mK). MQ coherence of (A) the zeroth $J_0(\tau)$ order (—), (B) $J_2(\tau) + J_{-2}(\tau)$ the second order (— —), (C) $J_4(\tau) + J_{-4}(\tau)$ the fourth order (- - - - -), (D) $J_6(\tau) + J_{-6}(\tau)$ the sixth order (- · · · -).

3. INTENSITIES OF MQ NMR COHERENCES IN ONE-DIMENSIONAL SYSTEMS IN THE APPROXIMATION OF THE NEAREST NEIGHBOR DDI AT LOW TEMPERATURES

In order to calculate MQ intensities, one has first to diagonalize the operator $\rho^{\mathrm{ht}}(\tau)$. At first, we shall calculate the MQ intensities for linear spin chains. In order to diagonalize the operator $\rho^{\mathrm{ht}}(\tau)$ we use the expression for $\rho_n(\tau)$ for a linear chain which was obtained earlier in Ref. (*4*). Applying the unitary transformation U which is the composition of π-pulses applied to even spins $(2, 4, 6, \ldots)$ (*4*)

$$U = e^{i\pi I_2^z} e^{i\pi I_4^z} e^{i\pi I_6^z} \ldots, \qquad [11]$$

we transform the Hamiltonian of Eq. [2] into the flip-flop Hamiltonian (*4*),

$$H_{\mathrm{flip}} = UHU^{+} = b \sum_{i=1}^{N-1} (I_i^{+} I_{i+1}^{-} + I_i^{-} I_{i+1}^{+}), \qquad [12]$$

with $b = -\frac{1}{2}D$. It is worth noticing the identity

$$UI^z U^{+} = \sum_{j=1}^{N} (-1)^{j-1} I_j^z. \qquad [13]$$

The Liouville–von Neumann equation $i\dot{\rho} = [H, \rho]$ with the Hamiltonian of Eq. [12] and the initial condition $\rho(0) = UI^z U^{+}$ has an exact solution (*4, 9*) which can be written as

$$\rho^{\mathrm{ht}}(\tau) = U^{+}\left[-\frac{2}{N+1}\sum_k e^{2i\epsilon_k\tau} \sum_{n,m=1}^{N} (-1)^m 2^{n+m-2} \sin(kn) \times \sin(km) I_1^z \cdots I_{n-1}^z I_n^{+} I_1^z \cdots I_{m-1}^z I_m^{-} - \frac{1}{4}(1-(-1)^N)\right] U, \qquad [14]$$

where $\epsilon_k = D\cos k$ with $k = \frac{\pi n}{N+1}$, $n = 1, 2, \ldots, N$.

At the next step we use the Jordan–Wigner transformation (*9*)

$$\beta_k = \sqrt{\frac{2}{N+1}} \sum_{j=1}^{N} \sin(kj)(-2)^{j-1} I_1^z \cdots I_{j-1}^z I_j^{-}, \qquad [15]$$

and express the MQ intensities via the fermion operators β_k,

$$J_n(\tau) = \frac{1}{Z}\mathrm{Tr}\left[\tilde{\rho}_n(\tau) e^{\beta\omega_0 \sum_k \exp(-2i\epsilon_k\tau)\beta_k^{+}\beta_{\pi-k}}\right], \qquad [16]$$

where $\tilde{\rho}_n(\tau) = U\rho_n^{\mathrm{ht}}(\tau)U^{+}$ is the transformed part of the

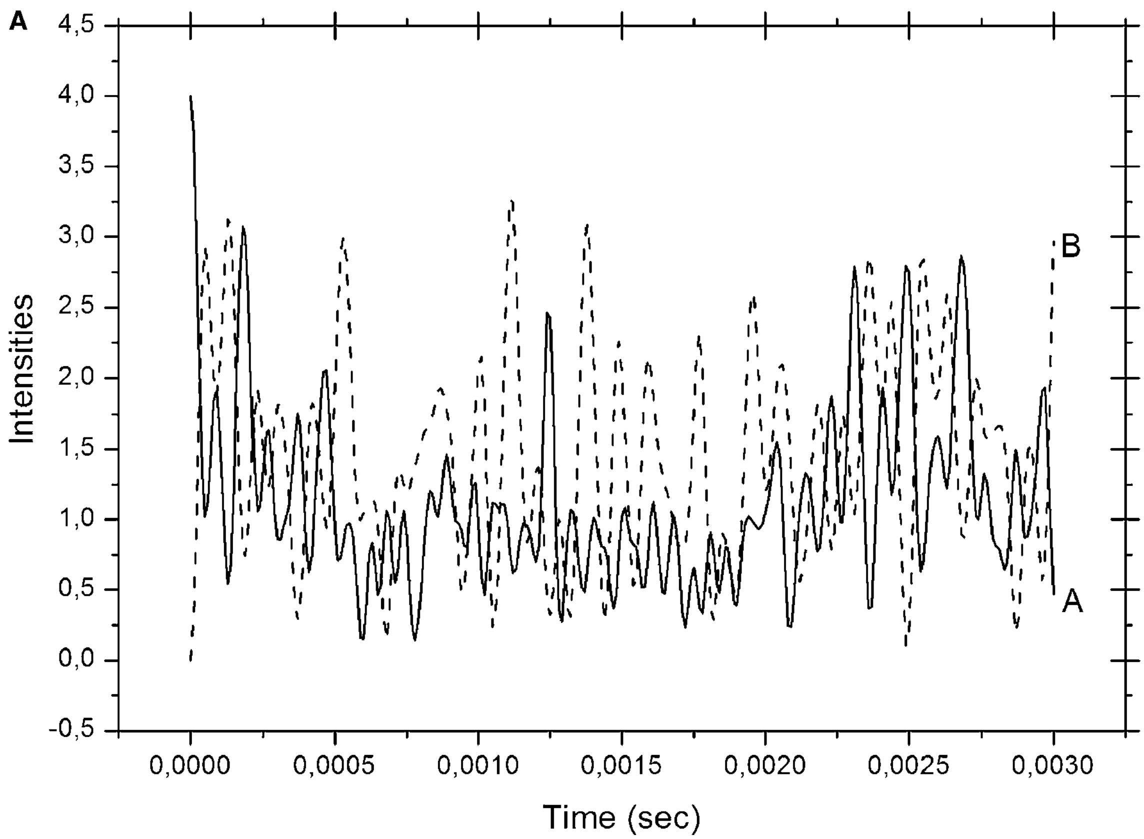

FIG. 3A. Time-course of MQ coherences for a spin ring of $N = 8$ spins at $\beta\omega_0 = 10$ (1 mK). MQ coherence of (A) the zeroth $J_0(\tau)$ order(—), (B) $J_2(\tau)+J_{-2}(\tau)$ the second order (— —).

high-temperature density operator. The exponential operator in Eq. [16] can be written in the symmetric form for an even number of spins N taking into account that

$$\sum_k e^{-2i\epsilon_k\tau}\beta_k^+\beta_{\pi-k} = \sum_{0<k<\pi/2}\left(e^{-2i\epsilon_k\tau}\beta_k^+\beta_{\pi-k} + e^{2i\epsilon_k\tau}\beta_{\pi-k}^+\beta_k\right). \tag{17}$$

Finally, we use the transformations which are analogous to the Bogolyubov ones (*10*),

$$\begin{aligned}\beta_k &= p_k\gamma_k + q_k\gamma_{\pi-k},\\ \beta_{\pi-k} &= r_k\gamma_k + s_k\gamma_{\pi-k},\end{aligned} \tag{18}$$

with the new fermion operators γ_k, γ_k^+. If one chooses the coefficients in Eq. [18] as

$$\begin{aligned}p_k = q_k &= \frac{1}{\sqrt{2}}e^{-i\epsilon_k\tau},\\ r_k = -s_k &= \frac{1}{\sqrt{2}}e^{i\epsilon_k\tau},\end{aligned} \tag{19}$$

the exponential operator of Eq. [16] becomes diagonal and has the form

$$e^{\beta\omega_0\sum_{0<k<\pi/2}(\gamma_k^+\gamma_k-\gamma_{\pi-k}^+\gamma_{\pi-k})}. \tag{20}$$

Analogous transformations can be performed with the operators $\tilde{\rho}_n^{\mathrm{ht}}(\tau)$. The corresponding diagonal parts are

$$\begin{aligned}\rho_0^{\mathrm{diag}}(\tau) &= \sum_{0<k<\pi/2}\cos^2(2\epsilon_k\tau)(\gamma_k^+\gamma_k - \gamma_{\pi-k}^+\gamma_{\pi-k}),\\ \rho_{\pm2}^{\mathrm{diag}}(\tau) &= \frac{1}{2}\sum_{0<k<\pi/2}\sin^2(2\epsilon_k\tau)(\gamma_k^+\gamma_k - \gamma_{\pi-k}^+\gamma_{\pi-k}).\end{aligned} \tag{21}$$

According to Eq. [8] the intensities of multiple quantum coherences read

$$\begin{aligned}J_0(\tau) &= \tanh\left(\frac{\beta\omega_0}{2}\right)\sum_{0<k<\pi/2}\cos^2(2\epsilon_k\tau),\\ J_{\pm2}(\tau) &= \frac{1}{2}\tanh\left(\frac{\beta\omega_0}{2}\right)\sum_{0<k<\pi/2}\sin^2(2\epsilon_k\tau).\end{aligned} \tag{22}$$

Equations [22] show that the profile of MQ coherences at low

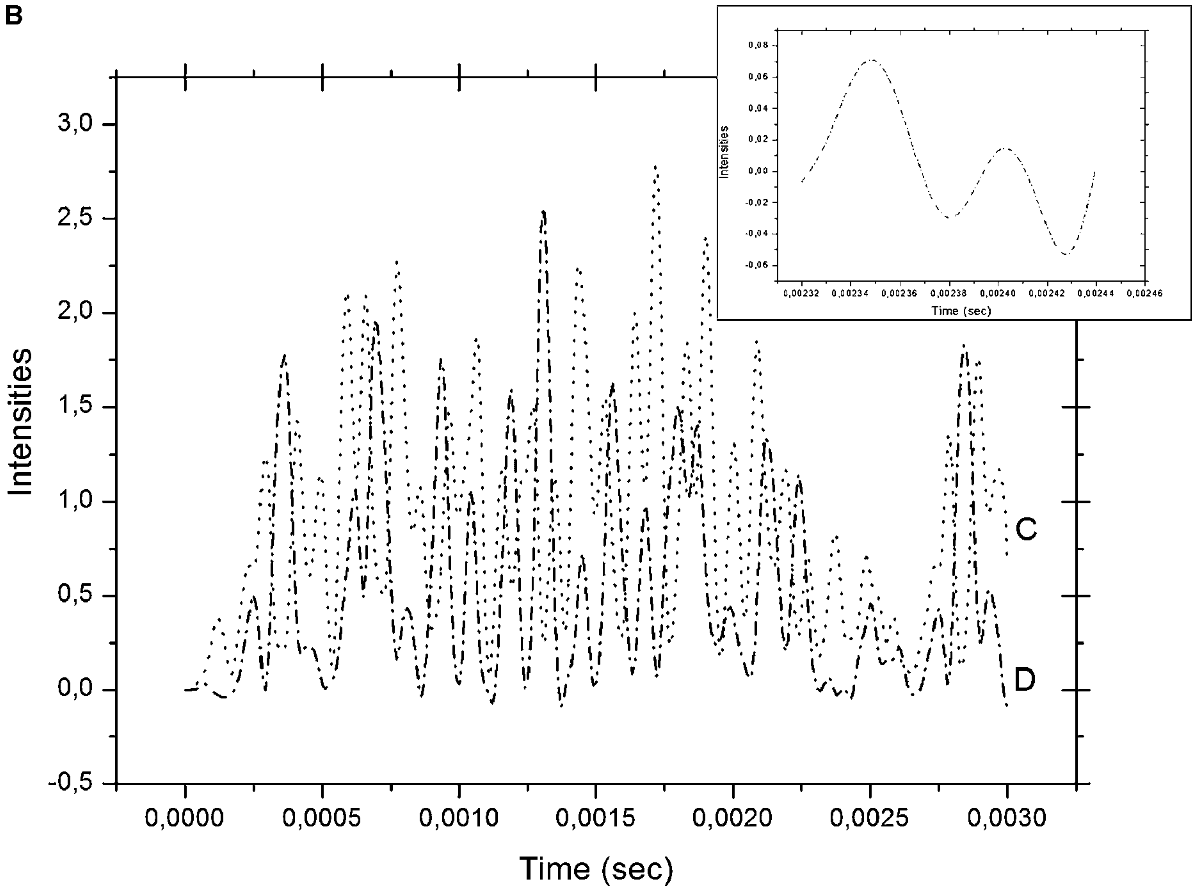

FIG. 3B. Time-course of MQ coherences for a spin ring of $N = 8$ spins at $\beta\omega_0 = 10$ (1 mK). MQ coherence of (C) $J_4(\tau) + J_{-4}(\tau)$ the fourth order (- - - - -), (D) $J_6(\tau) + J_{-6}(\tau)$ the sixth order (- · · · · -). The inset shows that the intensity of coherence of the sixth order can be negative.

temperatures consists of coherences of the zeroth and ±second orders only. An analogous result was obtained earlier in Ref. (*7*) at $N \to \infty$. The term $\beta^{+}_{\frac{\pi}{2}}\beta_{\frac{\pi}{2}}$ appears in Eq. [17] for a linear chain with the odd number N. This term is diagonal and we should not transform it using the Bogolyubov transformation of Eq. [18]. Thus, we must exclude the index $k = \frac{\pi}{2}$ performing this transformation. Then Eq. [16] can be written in the form

$$J_n(\tau) = \frac{1}{Z}\mathrm{Tr}\big[\tilde{\rho}_n(\tau)e^{\beta\omega_0\sum_{k\neq\pi/2}\exp(-2i\epsilon_k\tau)\beta^{+}_{k}\beta_{\pi-k}+\beta\omega_0\beta^{+}_{\pi/2}\beta_{\pi/2}-\frac{1}{2}\beta\omega_0}\big]. \quad [23]$$

As a result, the MQ intensities have the form

$$J_0(\tau) = \frac{1}{2}\tanh\left(\frac{\beta\omega_0}{2}\right)\sum_{0<k<\pi}\cos^2(2\epsilon_k\tau),$$
$$J_{\pm 2}(\tau) = \frac{1}{4}\tanh\left(\frac{\beta\omega_0}{2}\right)\sum_{0<k<\pi}\sin^2(2\epsilon_k\tau). \quad [24]$$

The MQ intensities for rings with an odd number N of the spins can be found by the method described in Ref. (*7*). We use the high-temperature solution from Ref. (*11*). As a result, we obtain the MQ NMR spectral intensities (*7*)

$$J_0(\tau) = \frac{1}{2}\tanh\left(\frac{\beta\omega_0}{2}\right)\sum_{k}\cos^2(4b\tau\sin k),$$
$$J_{\pm 2}(\tau) = \frac{1}{4}\tanh\left(\frac{\beta\omega_0}{2}\right)\sum_{k}\sin^2(4b\tau\sin k), \quad [25]$$

with $k = \frac{2\pi m}{N}$, $m = 1, 2, \ldots, N$.

For a ring with an even number N of spins we used the constant of motion C:

$$C = e^{i\pi M}, \qquad \left(M = \frac{1}{2}N - I^z\right), \qquad [H, C] = 0. \quad [26]$$

Hence, the Hamiltonian of Eq. [2] consists of blocks corresponding to different eigenvalues of the operator $\exp(i\pi M)$ ($\exp(i\pi M) = \pm 1$). In order to diagonalize the density matrix operator $\rho_{\mathrm{ht}}(\tau)$ we use the expressions for its parts $\rho_n^{\mathrm{ht}}(\tau)$ for a ring from Ref. (*4*). Applying the same technique as for the linear chains one can find the expressions for the MQ coherences for

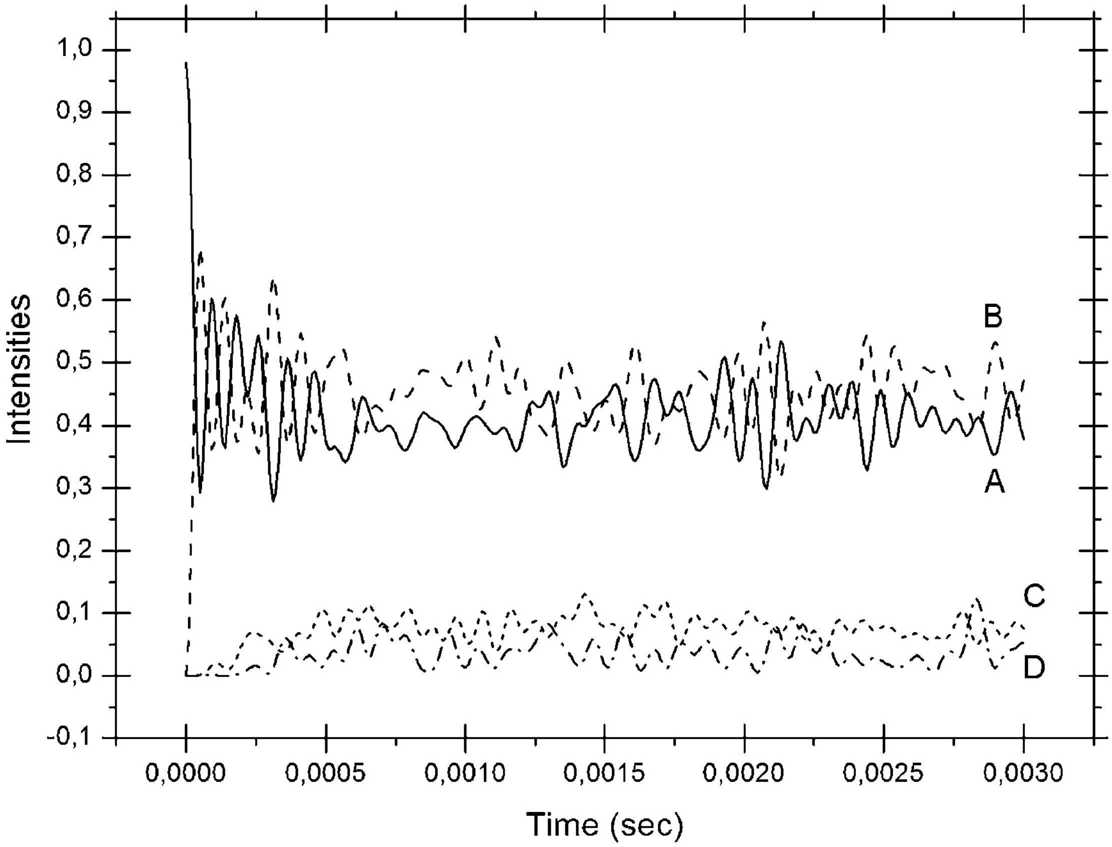

FIG. 4. Time-course of MQ coherences for a spin chain of $N = 8$ spins at $\beta\omega_0 = 0.5$ (20 mK). MQ coherence of (A) the zeroth $J_0(\tau)$ order(—), (B) $J_2(\tau) + J_{-2}(\tau)$ the second orders (— —), (C) $J_4(\tau) + J_{-4}(\tau)$ the fourth orders (- - - - -), (D) $J_6(\tau) + J_{-6}(\tau)$ the sixth orders (- · · · -).

a spin ring,

$$J_0(\tau) = \tanh\left(\frac{\beta\omega_0}{2}\right) \sum_{\substack{0<k<\pi \\ \alpha=o,e}} \cos^2\left(2\epsilon_k^\alpha \tau\right),$$
$$J_{\pm 2}(\tau) = \frac{1}{2} \tanh\left(\frac{\beta\omega_0}{2}\right) \sum_{\substack{0<k<\pi \\ \alpha=o,e}} \sin^2\left(2\epsilon_k^\alpha \tau\right), \qquad [27]$$

where α is the even (e) or odd (o) block of the Hamiltonian for $\exp(\mathrm{i}\pi M) = 1$ and $\exp(\mathrm{i}\pi M) = -1$, respectively, $\epsilon_k^o = D\cos k$ and $\epsilon_k^e = D\cos(k + \frac{\pi}{N})$ with $k = \frac{2\pi l}{N}$, $l = 1, 2, \ldots, N$.

As we see, the structure of the exact solutions for finite one-dimensional systems has the same form as for high-temperature regions. At the same time the strong temperature dependence of the MQ intensities is evident from the obtained results. It leads to new peculiarities of the MQ dynamics which will be discussed below.

4. THE TIME GROWTH OF MQ COHERENCES AT LOW TEMPERATURES

We demonstrate here the results of numerical calculations of the time growth of MQ coherences for short one-dimensional systems. We used the basic algorithm described in details in Ref. (*12*). In all calculations the value of the DDI constant of the nearest neighbors is assumed to be $D = 2\pi \cdot 2950\ \mathrm{s}^{-1}$ and the dipolar coupling constant between spins i and j, $D_{ij} = (D/2|i-j|^3)(3\cos^2\theta_{ij} - 1)$. At $\tau = 0$ the spin system is in thermal equilibrium and intensities of all coherences of the nonzeroth orders are equal to zero. In our calculations the parameter $\beta\omega_0$ which determines the temperature dependence of intensities of MQ coherences is chosen between $\frac{1}{2}$ and 10. It means that the temperature range for protons in the external magnetic field $H_0 = 5\mathrm{T}$ is an interval between 1 and 20 mK. For numerical calculations we used the modified formula of Eq. [8], which has the form,

$$J_n(\tau) = \mathrm{Tr}\left[\rho(\tau)\rho_n^{\mathrm{ht}}(\tau)\right] = \sum_{M_i - M_j = n} \rho_{ij}(\tau)\rho_{ji}^{\mathrm{ht}}(\tau), \qquad [28]$$

where M_i, M_j are the projections of the total spin momentum on the z axis. Figure 2 shows the time evolution of MQ coherences for the eight-spin ring at 20 mK and the analogous results at 1 mK are presented in Figs. 3A, 3B. It is worth noticing that at small times $t < 10^{-5}$ s the numerical results of Figs. 2, 3A, and 3B coincide with the analytical ones described by Eq. [27]. At short times MQ dynamics can be described by an exchange

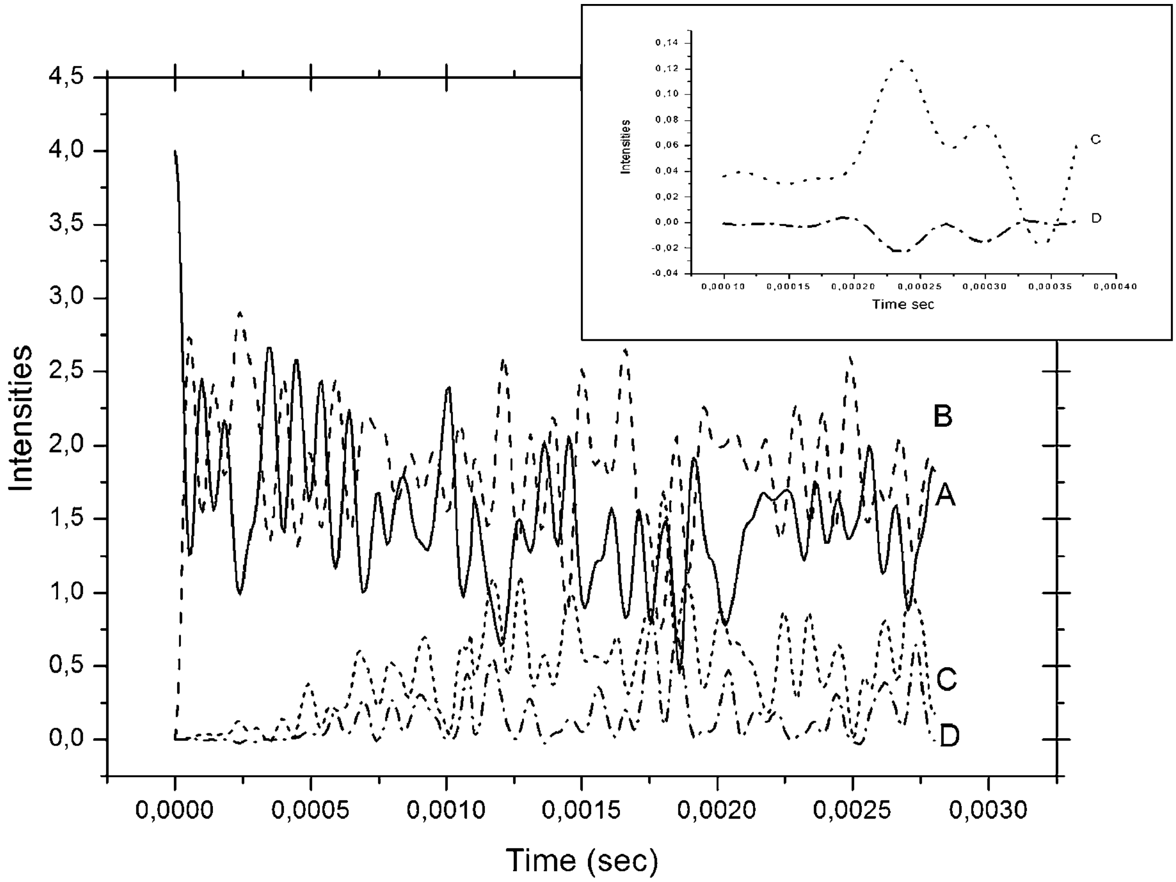

FIG. 5. Time-course of MQ coherences for a spin chain of $N = 8$ spins at $\beta\omega_0 = 10$ (1 mK). MQ coherence of (A) the zeroth $J_0(\tau)$ order(—), (B) $J_2(\tau) + J_{-2}(\tau)$ the second orders (— —), (C) $J_4(\tau) + J_{-4}(\tau)$ the fourth orders (- - - - -), (D) $J_6(\tau) + J_{-6}(\tau)$ the sixth orders (- · · · -). The inset shows that the intensities of coherences of the fourth and sixth orders can be negative.

process between the zero-quantum and ±2-quantum coherence orders both at high temperatures and at low ones. At the same time, this process is symmetrical at high temperatures but it is asymmetrical at low temperatures. Asymmetry of the exchange process becomes brightly expressed at times $t > 10^{-5}$ s at temperatures lower than 10 mK. The effect can be explained if we consider the Taylor series for the density matrix operator $\rho(\tau)$, i.e.,

$$\rho(\tau) = e^{-\mathrm{i}H\tau}\frac{e^{\beta\omega_0 I^z}}{Z}e^{\mathrm{i}H\tau} = \frac{e^{\beta\omega_0 I^z}}{Z} + \mathrm{i}\tau\left[H, \frac{e^{\beta\omega_0 I^z}}{Z}\right] + \frac{\tau^2}{2}\left[H, \left[\frac{e^{\beta\omega_0 I^z}}{Z}, H\right]\right] - \cdots. \quad [29]$$

The main conclusion is the following. At low temperatures MQ coherences of high orders emerge faster than at high temperatures. Taking into account that the spin–lattice relaxation is slow at low temperatures one can measure intensities of MQ coherences of high orders without any distortions and compare them with the results of calculations presented here. Figures 4 and 5 show the time evolution of the MQ coherences for the eight-spin chain at 20 and 1 mK, respectively. One can see from the inset of Fig. 5 that the intensities of coherences of the fourth and sixth orders are negative at some preparation times τ. It can be explained in the following way. The density matrix operator $\rho(\tau)$ can be expressed through the complete system of high-temperature density operators $\rho_n^{\mathrm{ht}}(\tau)$ $(n = 0, \pm 2, \pm 4, \ldots)$

$$\rho(\tau) = \sum_n a_n(\tau, \beta)\rho_n^{\mathrm{ht}}(\tau). \quad [30]$$

One can obtain the intensities of MQ coherences substituting Eq. [30] in Eq. [8],

$$J_n(\tau, \beta) = \sum_m \mathrm{Tr}\left[a_m(\tau, \beta)\rho_m^{\mathrm{ht}}(\tau)\rho_n^{\mathrm{ht}}(\tau)\right] = a_n(\tau, \beta)J_n^{\mathrm{ht}}(\tau), \quad [31]$$

where $J_n^{\mathrm{ht}}(\tau)$ is the high-temperature MQ intensity of the order n. One can see from Eq. [31] that in the general case MQ intensities can be negative at some times and temperatures. The point is that MQ NMR experiments are modulation ones. The initial polarization which is 0Q coherence is transferred in the course of the MQ NMR experiment to a set of oscillating parts of the longitudinal magnetization and the frequencies of these oscillations are determined by the orders of the MQ coherences. In principle, the amplitudes of the oscillating parts of the longitudinal magnetization can have an arbitrary sign. At the same time, intensities of MQ coherences are always positive at high temperatures (*5, 6*).

The developed analytical methods of MQ dynamics are applied at very rigid restrictions (exactly equal spacing of the spins, only dipole–dipole nearest neighbor interactions, etc.). However, one can use methods of perturbation theory to take into account different special cases. The situation is strongly simplified at numerical investigations when one can consider an arbitrary one-dimensional spin system to investigate its MQ dynamics completely. In particular, the program used can be applied to systems with different spacing of spins, different chemical shifts for the different spins in the chain, and so on.

Multiple quantum NMR in solids remains an interesting and very hard problem for theoretical investigations. We have developed analytical and numerical methods for analyzing the MQ dynamics of one-dimensional systems at low temperatures. This theoretical investigation is a basis for an interpretation of the results of future MQ NMR experiments at low temperatures.

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