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Abstract
An approach to creating the highest-order multiple-quantum coherences is developed. The method is based on using the multiple-quantum NMR technique and various initial conditions and can be considered as supplemental to earlier developed methods. Using the dipolar ordered state as the initial one, it is demonstrated that in a cluster of four and eight dipolar-coupled nuclear spins the highest-order multiple-quantum coherences can be created.

Multiple-quantum NMR spectroscopy has been developed to excite and detect multiple-quantum (MQ) coherences in solids with strong homonuclear dipole–dipole interactions [1, 2]. The growth of multiple-spin coherences and correlations is induced while the spin system is irradiated by multiple-pulse radio-frequency sequences. There are many radio-frequency pulse sequences exciting MQ coherences in a spin system. For a dipolar-coupled spin system, the multipulse sequence with an eight-pulse cycle [1, 2] is known to be very efficient. The MQ phenomena involve various multiple-spin transitions between the Zeeman energy levels and MQ coherence is formed at time $t > \omega_d^{-1}$, where ω_d is the characteristic frequency of dipole–dipole interaction (DDI) [1, 2]. Hence, $\omega_d t > 1$ is not a small parameter, which does not allow one to use perturbation methods to study MQ dynamics. Indeed only simple exactly solvable models of a spin system such as two and three dipolar coupling spins 1/2 [3, 4] or one-dimensional linear chains of spins [5, 6] have been analysed theoretically. The last achievement in this direction is the model with identical DDI coupling constants for all spin pairs [7–9]. Note that the simplified calculations essential for the case of identical DDI coupling constants have already been mentioned [10]. This model only describes zero- and second-order coherences, but in real solids DDI is characterized by the different coupling constants. In order to obtain important information on the molecular structure and spin dynamics of these systems, the evolution of a large number of modes of MQ coherence has to be analysed. Another important purpose of the study of MQ coherence is the field of quantum information processing [11–13]. Recently, the method based on MQ spin dynamics [14] of creating pseudopure spin states in large clusters of coupled spins has been proposed. The method used filtering multiple-quantum coherence [2] of the highest order, followed by a time-reversal period and partial

saturation. The preparation of the pseudopure spin state was experimentally demonstrated for a cluster of six dipolar-coupled proton spins of a benzene molecule in a liquid crystalline matrix. However, using the double-quantum effective Hamiltonian [2] the highest-order multiple-quantum (HOMQ) coherence can be excited only in clusters of $2 + 4n$ coupled identical spins, where $n = 0, 1, 2, 3 \ldots$ [2, 15].

In this paper we study MQ spin dynamics for a one-dimensional finite ring of nuclear spins $1/2$. For this system we proposed an approach of creating the HOMQ coherences that would be realized in solids with dipolar-coupled spins by means of the multiple-quantum NMR technique. The method is based on using various initial conditions and can be considered as supplemental to earlier developed methods to create MQ coherences. Using the dipolar ordered (DO) state as the initial one, it is demonstrated that in a cluster of four and eight dipolar-coupled nuclear spins the HOMQ coherences can be created. Nuclear dipolar order is characterized by a state with nuclear spins oriented along an internal local field generated by the dipole–dipole interactions (DDIs) [16]. Another very interesting and important initial condition is a pseudopure state (PS) [11–13]. It was obtained that in a chain of four spins coupled by dipole–dipole interactions a time evolution of the MQ coherences created using the DO and the PS states shows a very similar time dependence which can be used for preparation of the PS in a spin system.

We shall consider a ring of a small number of spins $1/2$ in an external magnetic field $\vec{H}_0$ perpendicular to the plane of the ring. The essential interaction in solids for a system of nuclear spin $I = 1/2$ is the DDI. The secular part of the dipolar Hamiltonian in a high magnetic field for identical nuclei is

$$H_{dd} = \sum_{j<k} D_{jk}[I_j^z I_k^z - \tfrac{1}{4}(I_j^+ I_k^+ + I_j^- I_k^-)] \tag{1}$$

where $D_{jk} = \frac{\gamma^2 \hbar}{2r_{jk}^3}(1 - 3\cos^2 \theta_{jk})$ is the coupling constant between spins j and k, which can be presented as $D_{jk} = D_{max}\left[\frac{\sin \frac{\pi}{N}}{\sin \frac{\pi(k-j)}{N}}\right]^3$, $D_{max} = D_{12}$ is the coupling constant between nearest-neighbour spins, N is the number of spins in a ring, γ is the gyromagnetic ratio, r_{jk} is the distance between spins j and k and θ_{jk} is the angle between the internuclear vector $\vec{r}_{jk}$ and the external magnetic field. I_j^z is the angular momentum operator in the Z direction and I_j^+ and I_j^- are the raising and lowering spin angular momentum operators of spin j.

The typical scheme of the MQ NMR experiment is the following: a spin system at equilibrium state in a strong constant magnetic field is acted upon for a time t by the multipulse sequence with an eight-pulse cycle [1, 2], called the preparatory period. The system undergoes next, for a time t_1, a free evolution driven by DDI. Because the MQ coherences do not generate a magnetization, they are not directly measurable. Hence a detecting multipulse sequence is then applied, followed by the action of a 90° pulse, and the transverse magnetization is measured. In a rotating frame the average Hamiltonian describing the multiple-quantum dynamics at the preparatory period can be written in the form [2]
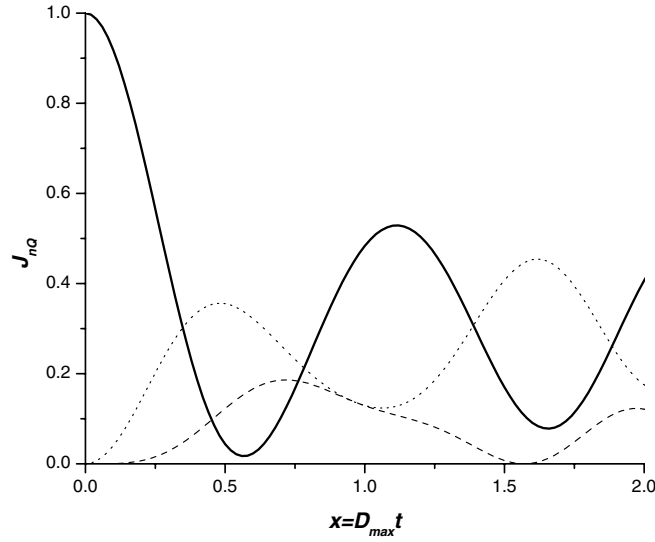
$$H = -\tfrac{1}{2}\sum_{j<k} D_{jk}(I_j^+ I_k^+ + I_j^- I_k^-). \tag{2}$$

The effect of the sequence of irradiating pulses on the spin system can be represented by the following equation:

$$\rho(t) = e^{-iHt}\rho(0)e^{iHt} \tag{3}$$

where $\rho(0)$ is the initial density matrix of the spin system. The experimentally observed values are the intensities of multiple-quantum coherences $J_{nQ}(t)$:

$$J_{nQ}(t) = \frac{1}{\mathrm{Tr}\, I_z^2}\sum_{p,q} \rho_{pq}^2(t) \qquad \text{for } n = m_{zp} - m_{zq} \tag{4}$$

Figure 1. Time dependences (in units of $\frac{1}{D_{max}}$) of the normalized intensities of 0Q and 2Q coherences in a ring of four nuclear spins 1/2 coupled by DDI with the thermal equilibrium initial state. Solid line and dashed lines are the zero-quantum intensity which comes from diagonal (J_{0Qdiag}) and non-diagonal ($J_{0Qnon\text{-}diag}$) matrix elements of the density matrix at time t, respectively; the dotted line is the two-quantum intensity J_{2Q}.

where m_{zp} and m_{zq} are the eigenvalues of I_z; I_z is the projection of the total spin angular momentum on the I_z direction. Besides the typical initial equilibrium conditions usually used in the MQ NMR experiments, when the spin system is described in a high-temperature approximation by a density matrix $\rho(0) = I_z$, we shall also consider the following initial conditions: the spin system is initially in the dipolar ordered state and is described by a density matrix $\rho(0) = H_{dd}$ and the spin system is initially in a pure state with a density matrix $\rho(0) = |\uparrow\rangle\langle\uparrow|$, where $|\uparrow\rangle$ is the state with all spins up.

(a) Thermal equilibrium state. For our consideration it is very convenient to divide contributions for zero-quantum intensity which come from the diagonal (J_{0Qdiag}) and non-diagonal ($J_{0Qnon\text{-}diag}$) of the matrix elements of the density matrix at time t. The exact solution of equation (3) with the initial condition $\rho(0) = I_z$ gives the following expressions for the zero-quantum intensity with contribution only of diagonal matrix elements of the density matrix $\rho(t)$,

$$J_{0Qdiag} = \tfrac{1}{8}[1 + \cos(x\sqrt{2})][\cos(4x) + \tfrac{1}{4}\cos(8x) + \tfrac{3}{4}] + \tfrac{1}{4}[1 + \cos(x\sqrt{34})], \tag{5}$$

for zero-quantum intensity taking into account only non-diagonal matrix elements of $\rho(t)$

$$J_{0Qnon\text{-}diag} = \frac{\sin^2 2x}{4}\left[\frac{\sin^2(2x)}{2}(1 - 3\cos(x\sqrt{2})) - 1 + \cos(x\sqrt{2})\right], \tag{6}$$

and two-quantum intensity

$$J_{2Q} = -\tfrac{1}{4} + \tfrac{1}{8}\cos(x\sqrt{34}) + \tfrac{1}{16}\cos(2x\sqrt{2})\cos(16x) + \tfrac{1}{16}\cos(x\sqrt{2}), \tag{7}$$

where $x = D_{max}t$. Figure 1 shows the evolution of the normalized 0Q and 2Q coherences in the ring of four nuclear spins 1/2 coupled by DDI. We stress that the intensity of the four-quantum coherency is equal to zero.

$$J_{4Q} = 0. \tag{8}$$

Figure 1 simultaneously displays time dependences of the $J_{0Q\text{non-diag}}$, $J_{0Q\text{diag}}$ and J_{2Q} intensities for the thermal equilibrium initial state. The exact solutions (5)–(7) and computer simulation of the MQ coherences of the four-spin cluster have been obtained with a PC using the MATLAB package.

The impossibility of creating the eight-quantum coherence in a ring of eight spins can be demonstrated by numerical simulation. Figures 2(a) and (b) show all the possible coherences which can be created in this system obtained by numerical simulation with a PC using the MATLAB package.

(b) Dipolar ordered state. The dipolar ordered state can be creating by using the method consisting in performing an adiabatic demagnetization in the rotating frame [17]. Another method consists in transferring the Zeeman order of the spin system where all spins are oriented along an external field into a dipolar one where all spins are oriented along an internal local field, by a sequence of two pulses [16]. Then the multipulse sequence with an eight-pulse cycle [1, 2] is applied in order to excite the MQ coherences in the spin system at the dipolar ordered state. The exact solution of equation (3) with the initial condition $\rho(0) = H_{\text{dd}}$ gives the following expressions for zero-quantum, two-quantum, and four-quantum intensities in the ring of four spins:

$$J_{0Q\text{diag}} = \frac{1}{334\,084}\left[\left(\frac{2573}{142}\sqrt{2} - 1\right)4544\cos\left(\frac{\sqrt{34}x}{2}\right)\right.$$

$$- \left(\frac{37}{48}\sqrt{2} + 1\right)10\,752\cos\left(\frac{3\sqrt{34}x}{2}\right) + 1047\,693\left(1 - \frac{6104}{20\,543}\sqrt{2}\right)$$

$$+ 277\,944\cos(\sqrt{34}x)\left(\tfrac{20\,252}{34\,743}\sqrt{2} + 1\right)$$

$$\left. + 109\,516\cos^2(\sqrt{34}x)\left(\tfrac{90}{131}\sqrt{2} + 1\right)\right], \tag{9}$$

$$J_{0Q\text{non-diag}} = \frac{23\,599}{167\,042}\left(1 - \frac{168\sqrt{2}}{23\,599}\right) + \frac{117\,638}{4259\,571}\cos^2(\sqrt{34}x)\left(1 + \frac{90}{131}\sqrt{2}\right)$$

$$+ \frac{3584}{1419\,857}\cos\left(\frac{2\sqrt{34}x}{2}\right)\left(1 + \frac{37}{48}\sqrt{2}\right)$$

$$+ \frac{4544}{4259\,571}\cos\left(\frac{\sqrt{34}x}{2}\right)\left(1 - \frac{2573}{142}\sqrt{2}\right)$$

$$- \tfrac{8260}{1419\,857}\cos(\sqrt{34}x)\left(1 - \tfrac{622}{6195}\sqrt{2}\right), \tag{10}$$

$$J_{2Q} = -\frac{704}{14\,739}\left[\sin^2\left(\frac{\sqrt{34}x}{2}\right)\left(1 + \frac{6}{11}\sqrt{2}\right) + \frac{131}{88}\sin^2(\sqrt{34}x)\left(1 + \frac{90}{131}\sqrt{2}\right)\right] \tag{11}$$

$$J_{4Q} = \frac{a^2}{1156}(5\sqrt{2} + 9)^2[\cos(\sqrt{34}x) - 1]^2. \tag{12}$$

Figure 3 simultaneously displays time dependences of the $J_{0Q\text{non-diag}}$, $J_{0Q\text{diag}}$, J_{2Q} and J_{4Q} intensities for the dipolar ordered initial state in a four-spin ring. One can see that at the evolution times when the 2Q and 4Q intensities reach their zero value, the intensities of the 0Q (both the diagonal and non-diagonal contributions) reach their major maxima. This time is shown by the arrow in figure 3.

In contrast to the initial equilibrium state, the dipolar one results in creation of non-zero HOMQ coherence. Figure 4 shown the time dependence of the 6Q and 8Q intensities obtained by numerical calculations for an eight-spin ring.

(c) Pseudopure state. The importance of preparation of the spin system in the pseudopure state consists in using this state as the initial one for quantum algorithms. The exact solution

(a)

(b)
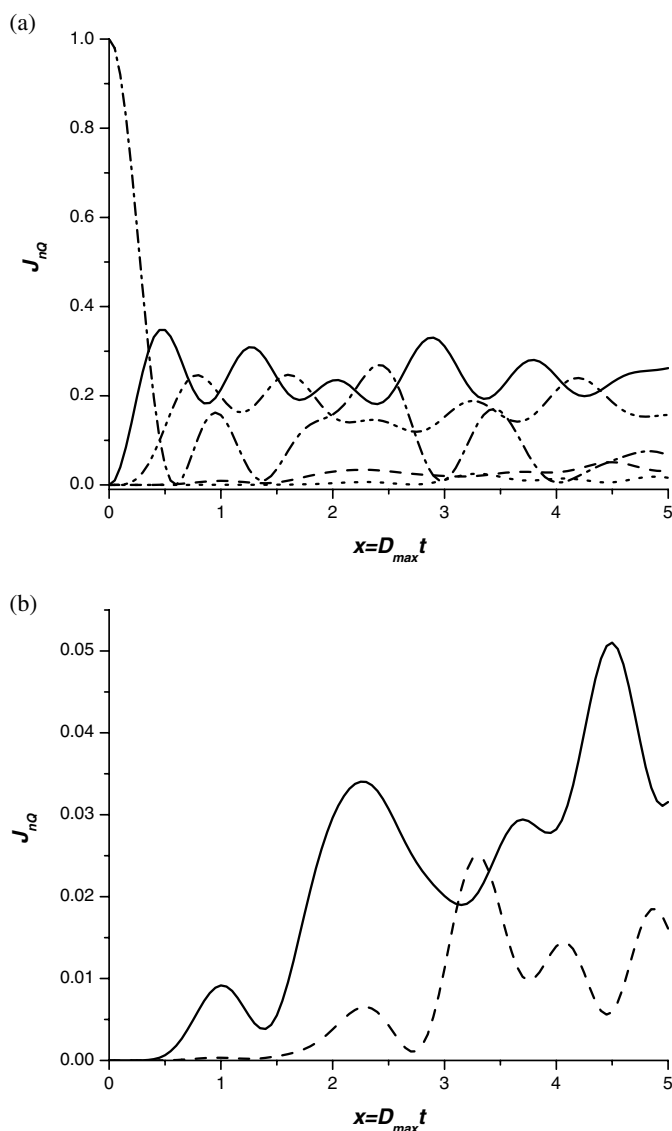
Figure 2. (a) The normalized intensities of 0Q, 2Q, 4Q and 6Q coherences in a ring of eight nuclear spins 1/2 coupled by DDI with the thermal equilibrium initial state. The dash–dot line and the dash–dot–dot lines are the zero-quantum intensity which comes from diagonal ($J_{0\text{Qdiag}}$) and non-diagonal ($J_{0\text{Qnon-diag}}$) matrix elements of the density matrix at time t, respectively; the solid line is the two-quantum intensity $J_{2\text{Q}}$, the dashed line is the four-quantum intensity $J_{4\text{Q}}$ and the dotted line is the six-quantum intensity $J_{6\text{Q}}$. Time is in units of $\frac{1}{D_{\max}}$. (b) The normalized intensities of only 4Q and 6Q coherences in a ring of eight nuclear spins 1/2 coupled by DDI with the thermal equilibrium initial state. The solid line is the four-quantum intensity $J_{4\text{Q}}$ and the dashed line is the six-quantum intensity $J_{6\text{Q}}$. Time is in units of $\frac{1}{D_{\max}}$.

of equation (3) with the initial condition $\rho(0) = |\uparrow\rangle\langle\uparrow|$ gives the following expressions for zero-quantum, two-quantum, and four-quantum intensities in the ring of four spin:

$$J_{0\text{Qdiag}} = \frac{209}{9248}\cos(2\sqrt{34}x) + \frac{947}{2312}\cos(\sqrt{34}x) + \frac{5251}{9248}, \tag{13}$$
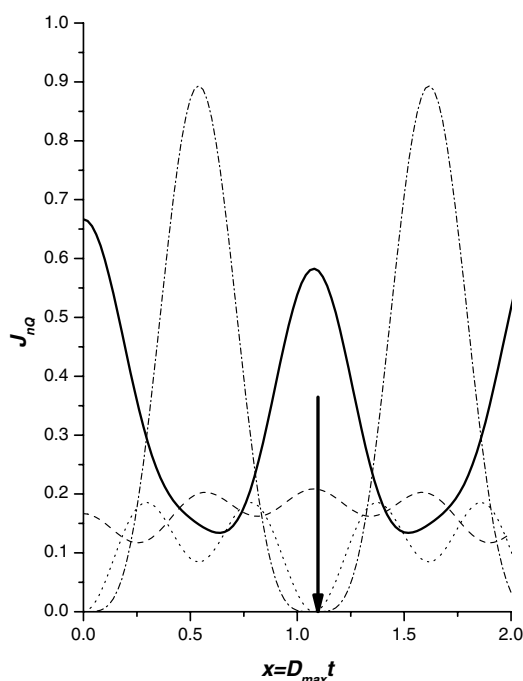
Figure 3. The normalized intensities of all possible coherences in a ring of four nuclear spins 1/2 coupled by DDI with the dipolar ordered initial state. The solid line and dashed lines are the zero-quantum intensity which comes from diagonal (J_{0Qdiag}) and non-diagonal ($J_{0Qnon-diag}$) matrix elements of the density matrix at time t, respectively; the dotted line is the two-quantum intensity J_{2Q} and the dash–dot line is the four-quantum intensity J_{4Q}. Time is in units of $\frac{1}{D_{max}}$.

$$J_{0Qnon-diag} = \frac{449}{4624} \sin^4\left(\frac{\sqrt{34}x}{2}\right), \tag{14}$$

$$J_{2Q} = \frac{1}{4}\left[\cos^4\left(\frac{\sqrt{34}x}{2}\right) - 1\right], \tag{15}$$

$$J_{4Q} = \frac{1}{16} \sin^4\left(\frac{\sqrt{34}x}{2}\right). \tag{16}$$

Figure 5 simultaneously displays time dependences of the $J_{0Qnon-diag}$, J_{0Qdiag}, J_{2Q} and J_{4Q} intensities for the initial pure state. One can see that at the evolution times when the 2Q and 4Q intensities reach their zero value the intensities of the 0Q (only the diagonal contributions) reach their major maxima (this is shown by the arrow in figure 5). That time dependence coincides with the time evolution of MQ coherences of case (b) for the four-spin ring, where the dipolar ordered state was used as the initial one. Figures 6(a) and (b) give the time dependence of all the possible coherences which were created in the eight-spin ring where the pure state was used as the initial one.

There is a fundamental connection between the high order MQ and the formation of networks of correlated spins in solids. Excitation of the high orders of MQ coherences provides important information in the determination of coupling constants and molecular structure. As seen in figure 1, for the thermal equilibrium initial state MQ NMR spectra have only 0Q and 2Q quantum coherence orders in the four-spin system and 0Q, 2Q, 4Q and 6Q quantum coherences in the eight-spin system, while excitation of MQ coherences in the spin system
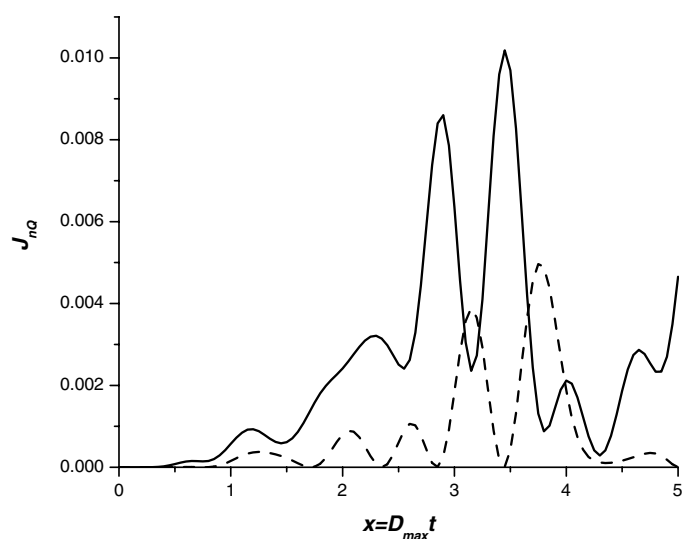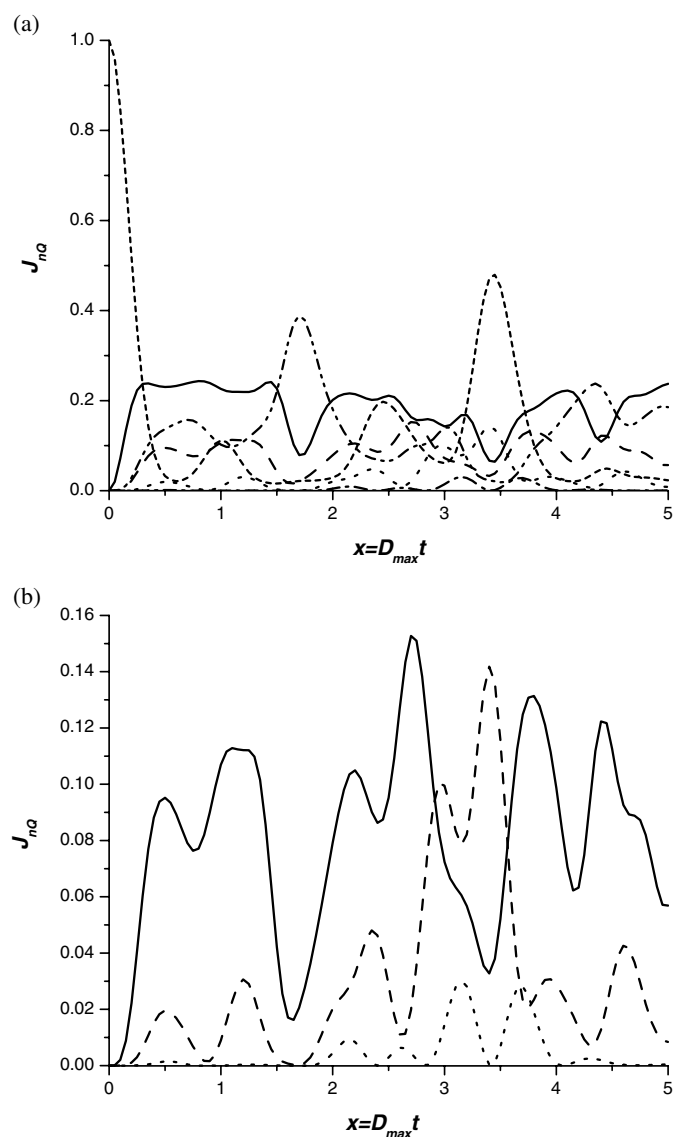
Figure 4. The normalized intensities of 6Q and 8Q coherences in a ring of eight nuclear spins 1/2 coupled by DDI with the dipolar ordered initial state. The solid line is the six-quantum intensity J_{6Q} and the dashed line is the eight-quantum intensity J_{8Q}. Time is in units of $\frac{1}{D_{max}}$.
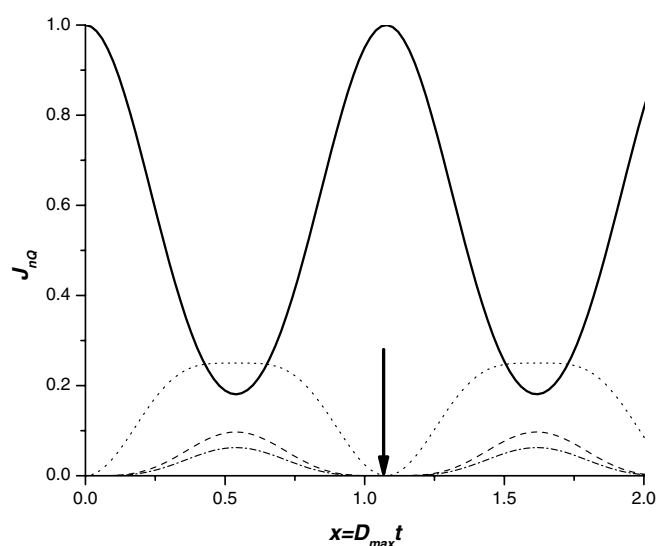
Figure 5. The normalized intensities of 0Q, 2Q and 4Q coherences in a ring of four nuclear spins 1/2 coupled by DDI with the pseudopure initial state. The solid line and dashed lines are the zero-quantum intensity which comes from diagonal (J_{0Qdiag}) and ($J_{0Qnon\text{-}diag}$) non-diagonal matrix elements of the density matrix at time t, respectively; the dotted line is the two-quantum intensity J_{2Q} and the dash–dot line is the four-quantum intensity J_{4Q}. Time is in units of $\frac{1}{D_{max}}$.

initially in the dipolar ordered state leads to emerging 4Q order in four- (figure 3) and 8Q order in eight-spin systems (figure 4). Thus, excitation of the MQ coherences in the dipolar ordered spin system by the very effective eight-pulse cycle multipulse sequence [1, 2] open a way to obtain important information on molecular structure and spin dynamics of these

Figure 6. (a) The normalized intensities of all possible coherences in a ring of eight nuclear spins 1/2 coupled by DDI with the dipolar ordered initial state. The short-dashed line and the dash–dot–dot lines are the zero-quantum intensity which comes from diagonal (J_{0Qdiag}) and non-diagonal ($J_{0Qnon-diag}$) matrix elements of the density matrix at time t, respectively; the solid line is the two-quantum intensity J_{2Q}, the dashed line is the four-quantum intensity J_{4Q}, the dotted line is the six-quantum intensity J_{6Q} and the dash–dot line is the eight-quantum intensity J_{8Q}. Time is in units of $\frac{1}{D_{max}}$. (b) The normalized intensities only of 4Q, 6Q and 8Q coherences in a ring of eight nuclear spins 1/2 coupled by DDI with the dipolar ordered initial state. The solid line is the four-quantum intensity J_{4Q}, the dashed line is the six-quantum intensity J_{6Q} and the dotted line is the eight-quantum intensity J_{8Q}. Time is in units of $\frac{1}{D_{max}}$.

systems. Using the double-quantum effective Hamiltonian [2] and the dipolar ordered initial state the HOMQ coherences can be excited in clusters of $4 + 4n$ coupled identical spins, where $n = 0, 1, 2, 3 \ldots$. Note that generation of the HOMQ coherences in clusters of $2 + 4n$ coupled

identical spins is forbidden for the dipolar ordered initial condition. A second reason for the importance of using the initially dipolar ordered state is that the evolution of the MQ intensities is very similar to that with the initial pseudopure state (figures 3 and 5). One can see from figures 3 and 5 that at the evolution time $t = 1.1D_{max}$ when the 2Q and 4Q intensities reach one of their minima, the intensities of the 0Q coherences, both from diagonal and non-diagonal elements of the density matrix, run up to their major maxima. The fact can be used to create the pseudopure state in the spin system consisting of identical nuclei. The method is based on filtering the 0Q coherence from the off-diagonal elements of the density matrix at time $t = 1.1D_{max}$ and on partial saturation. The efficiency of converting the dipolar ordered state into the pseudopure one is about 58%. The efficiency may be lower by a factor of two when the two pulse sequence is used to transfer the Zeeman order of the spin system into the dipolar one. This is because the two-pulse method is not an adiabatic process [18].

To conclude, we have modified the standard initial condition for excitation of the high orders of MQ coherences in a homonuclear spin system. Using the dipolar ordered state as an initial one, the 4Q and 8Q orders can be excited in the four- and eight-spin clusters. For the four-spin ring we found that the time dependence of the intensities of MQ coherences in the spin system initially in the dipolar ordered state is very similar to the time dependence of the MQ intensities with spin system initially in the pseudopure state. This fact can be used to prepare the spin system with homonuclear DDI to be in the pseudopure state. Starting with the thermal equilibrium initial state the Zeeman order of the spin system can be transferred into a dipolar one. Then the MQ coherences can be created by using the multiple pulse sequence. The last step is filtering the off-diagonal 0Q coherence and partial saturation. The relatively high efficiency of the proposed method gives the possibility to increase the size of systems consisting of identical spins with individually addressable quantum states.

Acknowledgments

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