The pseudopure state in homonuclear dipolar coupling spin systems

The pseudopure state in homonuclear dipolar coupling spin systems

G B Furman

Department of Physics, Ben Gurion University, Beer Sheva 84105, Israel and Ohalo College, Qatzrin, 12900, Israel

E-mail: gregoryf@bgu.ac.il

Abstract
Preparation of the pseudopure states in homonuclear systems of dipolar coupling spins is closely examined. An extremely important role of the non-diagonal part of zeroth-order coherence in the construction of the pseudopure state has been shown. Simulations of the preparation process of pseudopure states with the real molecular structures (a rectangular (1-chloro-4-nitrobenzene molecule), a chain (hydroxyapatite molecule), a ring (benzene molecule) and a double ring (cyclopentane molecule)) open the way to experimental NMR testing of the obtained results. The proposed method could be considered as a fruitful technology for quantum computation.

PACS numbers: 03.67.Lx, 82.56.−b, 76.60.−k

1. Introduction

Coherent control of multiple coupled quantum systems is expected to lead to profound insights in physics as well as to novel applications, such as quantum computation, quantum communication and quantum amplification. Such coherent control is an essential goal in various fields of quantum physics, but many of the advanced theoretical and experimental results are coming from one of the oldest areas of quantum physics: nuclear magnetic resonance (NMR). One of such results is a so-called pseudopure state, which was originally proposed for nuclear magnetic resonance quantum computing [1, 2].

Conveniently, the quantum algorithms start with a pure ground state where populations of all states except the ground state are equal to zero. In NMR however because of the small energy gaps, it is not possible to realize a pure state, where in the whole population is in one energy level, since it requires very low temperatures as well as very high magnetic fields. However, an alternative solution that was discovered to overcome this problem is a so-called pseudopure state [1, 2]. The density matrix of the spin system in this state can be partitioned into two parts. The first part of the matrix is a scaled unit matrix, but the second

part corresponds to a pure state. Such a pseudopure state imitates the pure ground states. The scaled unit matrix does not contribute to observables and is not changed by unitary evolution transformations. Therefore, the behaviour of a system in a pseudopure state is exactly the same as it would be in the pure state.

Recently, an elegant method of creating pseudopure states starting from an equilibrium state was proposed, which does not require a resolved equilibrium spectrum [3]. It is based on multiple-quantum (MQ) dynamics with filtering of the highest order multiple-quantum coherence (HOMQC). The HOMQC is constructed of just two states, $|\uparrow\rangle$ and $|\downarrow\rangle$, where $|\uparrow\rangle$ is the state with all spins up and $|\downarrow\rangle$ is the state with all spins down. The method has been used to prepare a pseudopure state in a six-ring homonuclear cluster of seven- and twelve-heteronuclear dipolar-coupled spins: single and fully labelled ^{13}C benzene in liquid-crystalline solvent [4, 5]. However, using the double-quantum effective Hamiltonian [6, 7] the HOMQC can be excited only in clusters of $(2 + 4n)$-coupled indentical spins ($n = 0, 1, 2, 3, \ldots$) [7, 8]. Furthermore, as we will show, a component critical to the operation of the method reduces to zero the intensity of the non-diagonal part of the zero quantum ($0Q$) coherence.

In the present paper, the technique of preparation of the pseudopure states by using MQ NMR will be extended to clusters of various even numbers of coupling homonuclear spins. A comprehensive study of the pseudopure state preparation process and the results of simulations for one-dimensional (1D) spin clusters with up to ten spins are presented.

2. Dynamics of zeroth-order quantum coherences

We shall consider the MQ dynamics of the spin-half ($I = 1/2$) system in an external magnetic field $\vec{H}_0$ with the Hamiltonian

$$H = H_0 + H_d, \tag{1}$$

where H_0 is the Zeeman interaction Hamiltonian,

$$H_0 = \omega_0 I_z, \tag{2}$$

where $\omega_0 = \gamma |\vec{H}_0|$ is the Larmor frequency ($\hbar = 1$), γ is the gyromagnetic ratio and I_j^z is the angular momentum operators in the Z direction. The secular part of the dipolar Hamiltonian in a high magnetic field for indentical nuclei is

$$H_{dd} = \sum_{j<k} D_{jk} \left[I_j^z I_k^z - \frac{1}{4} \left(I_j^+ I_k^+ + I_j^- I_k^- \right) \right], \tag{3}$$

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, r_{jk} is the distance between spins j and k, θ_{jk} is the angle between the internuclear vector $\vec{r}_{jk}$ and the external magnetic field $\vec{H}_0$. I_j^+ and I_j^- are the raising and lowering spin angular momentum operators of spin j.

The typical scheme of the MQNMR experiment is as follows: a spin system at an equilibrium state in a strong constant magnetic field acts upon in time t by the multiple-pulse sequence with an eight-pulse cycle [6, 7], called the preparatory period. The spin system undergoes next, for a time t_1, a free evolution which is driven by dipole–dipole interactions (DDI). Because the MQ coherences do not generate a magnetization, they are not directly measurable. Hence a detecting multiple-pulse 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 [7]

$$H_{\text{av}} = -\frac{1}{2} \sum_{j<k} D_{jk} \left(I_j^+ I_k^+ + I_j^- I_k^- \right). \tag{4}$$

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

$$\rho(t) = \text{e}^{-\text{i}H_{av}t} \rho(0) \, \text{e}^{\text{i}H_{av}t}, \tag{5}$$

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

$$J_{kQ}(t) = \frac{1}{Tr I_z^2} \sum_{p,q} \rho_{p,q}^2(t) \qquad \text{for} \quad k = m_{zp} - m_{zq}, \tag{6}$$

where m_{zp} and m_{zq} are the eigenvalues of I_z. 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 $\rho_{\text{eq}}(0) = I_z$ [6, 7], we shall also consider a mixture of two states:

$$\rho_{\text{int}}(0) = \pm|\uparrow\rangle\langle\uparrow| \mp |\downarrow\rangle\langle\downarrow| \tag{7}$$

as an initial condition [9]. The state $\rho_{\text{int}}(0)$ can be considered as an intermediate state. To transform the intermediate state (7) to the pseudopure one a non-unitary operation, such as a partial saturation, is needed, which redistributes, for example, the over population of the state $|\uparrow\rangle\langle\uparrow|$ among other states but does not change the population of the state $|\downarrow\rangle\langle\downarrow|$ [3].

In the spin-1/2 system, the equilibrium density matrix for an ensemble soaking in the strong magnetic field, $\vec{H}_0$, has only diagonal elements. The presence of these elements is said to represent the zeroth-order quantum coherence ($0Q$) [6, 7]. The zeroth-order quantum coherence can be defined according to equation (6) with $k = 0$. In the general case, not only the diagonal element of the density matrix ($\rho_{p,p}(t)$) satisfies this equation with $k = 0$, but also non-diagonal elements ($\rho_{p,q}(t)$ with $p \neq q$) have the same properties [10]. For our consideration, it is very convenient to divide contributions for $0Q$ intensity which comes from the diagonal ($D0Q$) $\left(J_{0Q_{\text{diag}}} \right)$ and non-diagonal ($ND0Q$) $\left(J_{0Q_{\text{non-diag}}} \right)$ matrix elements of the density matrix at time t. On the one hand, both coherences, $D0Q$ and $ND0Q$, have the same symmetry properties but their dynamics are very different.

To show the difference in the evolution of the intensities of $D0Q$ coherence $\left(J_{0Q_{\text{diag}}} \right)$ and $ND0Q$ coherence $\left(J_{0Q_{\text{non-diag}}} \right)$ we shall consider rings of nuclear spins in an external magnetic field $\vec{H}_0$ perpendicular to the plane of the ring. We examine the evolution of $0Q$ coherences by letting the spin system evolve under a Hamiltonian (4) with the dipolar coupling constant $D_{jk} = D_1 \left[\frac{\sin \frac{\pi}{N}}{\sin(\frac{\pi}{N}(k-j))} \right]^3$; here D_1 is the coupling strength between the nearest spins. After calculating the evolution (equation (5)), we grouped the matrix elements in the density matrix $\rho_{p,q}(t)$ according to equation (6) with $k = 0$. The results of numerical simulations are presented in figure 1. For $t = 0$, the diagonal part determines completely the $0Q$ spectral intensity (figure 1(a)). Then, in the initial period of evolution, $0Q$ coherences arising from non-diagonal elements of the spin density operator appear (figure 1(b)). Despite a very different time evolution of the $J_{0Q_{\text{diag}}}$ and $J_{0Q_{\text{non-diag}}}$ intensities, it is impossible to separate them using the standard filtering technique [6, 7], which is based on the symmetry properties. This leaves us with only one possibility of separating the non-diagonal part of the $0Q$ coherences from the diagonal one, the evolution of the spin system under the influence
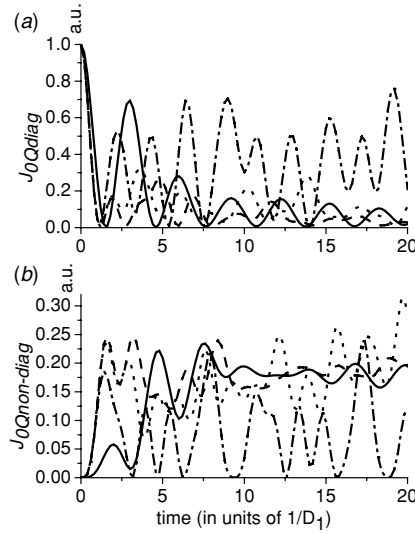
Figure 1. Time dependences (in units of $\frac{1}{D_1}$) of the normalized intensities of $0Q$ diagonal (*a*) and non-diagonal (*b*) parts in a ring of four (dash-dot line), six (dotted line), eight (dashed lines) and ten (solid line) nuclear spins 1/2 coupled by DDI with the thermal equilibrium initial state.

of the averaged Hamiltonian (4). During the evolution, the intensity of non-diagonal zeroth-order coherences $\left(J_{0Q_{\text{non-diag}}}\right)$ may reach its zero value. For example, in the four-spin ring the intensity of the non-diagonal part of the $0Q$ coherence reaches its zero value at times $t = 3.27$, 6.03 and 9.37 (figure 1(*b*)). One could anticipate that there exists a strong relation between the zeroth value of $J_{0Q_{\text{non-diag}}}$ intensities and preparation of the pseudopure state of a spin system.

3. Preparation of the pseudopure states

For the detailed testing of preparation of a pseudopure state, let us start with the simulation of the MQ dynamics in the four-spin cluster, which can be represented by spins of four hydrogen nuclei of 1-chloro-4-nitrobenzene molecule with the dipole–dipole coupling constants that are given by $D_1 = D_{12} = D_{34} = 1$, $D_{13} = D_{24} = 1/8$ and $D_{14} = D_{23} = \frac{1}{3\sqrt{3}}$. Figure 2(*a*) shows the intensity of the non-diagonal part of $0Q$ coherence starting from the equilibrium state, $\rho_{\text{eq}}(0)$, calculated according to equation (5) as a function of preparatory time, τ_1. One can see that $J_{0Q_{\text{non-diag}}}$ reaches its zero value at times $\tau_1 = 7.86$ and 12.61 (in units of $1/D_1$) (the arrows in figure 2(*a*) show these times). While, when the evolution starts with the initial condition (7), $\rho_{\text{int}}(0)$, the non-diagonal $0Q$ coherence does not excite, $J_{0Q_{\text{non-diag}}} = 0$ (figure 2(*b*)). Therefore, the strategy of preparation of a pseudopure state will consist of the following four operations: (i) excitation of MQ coherences starting from the equilibrium, $\rho_{\text{eq}}(0)$, and stopping the preparatory period at time when the intensity of $ND0QC$ is reduced to zero (at times $\tau_1 = 7.86$ or 12.61); (ii) the $2Q$ coherence is filtered; (iii) then the time reversal sequence during times $\tau_1 = 7.86$ or 12.61 is applied, and as a final stage, (iv) partial saturation is followed. Our simulation of the first three stages showed that the high mixed equilibrium state can be converted into the intermediate state (7) which consists of the mixture of only two states: $|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|$ with $\tau_1 = 7.86$ and $\tau_2 = 7.86$ (figure 3(*a*)) and $-|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|$ with $\tau_1 = 12.61$, $\tau_2 = 7.86$ (figure 3(*b*)).
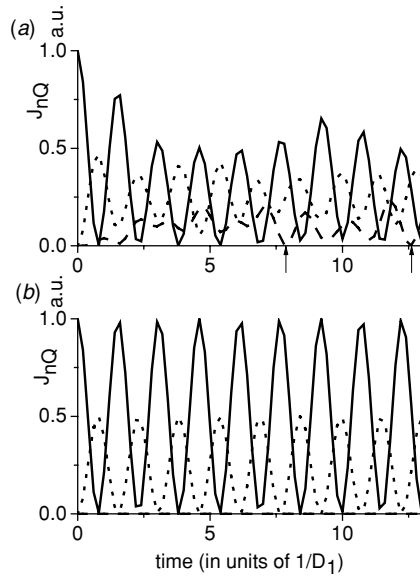
Figure 2. The normalized intensities of diagonal (solid line) and non-diagonal (dashed line) parts of 0Q coherences and 2Q coherence (dotted line) in a cluster of four nuclear spins 1/2 coupled by DDI (1-chloro-4-nitrobenzene) with the initial states: (a) $\rho(0) = I_z$, (b) $\rho(0) = -e_{1,1} + e_{16,16}$. The intensity of 4Q coherence is equal to zero.
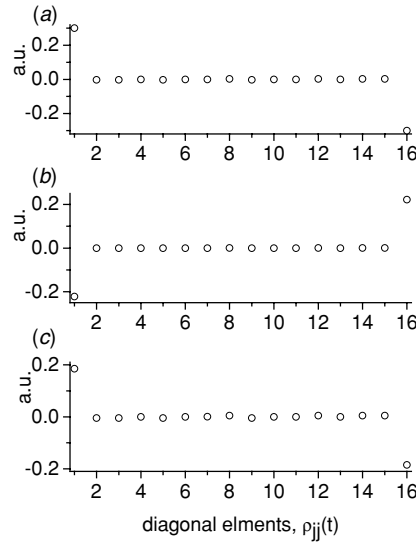

Figure 3. The diagonal elements of the density matrix at various combination of the time duration of the excitation (τ_1) and reversal (τ_2) periods in a cluster of four nuclear spins 1/2 coupled by DDI (1-chloro-4-nitrobenzene) with (a) $\tau_1 = 7.86$, and $\tau_2 = 7.86$, (b) $\tau_1 = 12.61$, $\tau_2 = 7.86$ and (c) numerical simulation in a linear chain consisting of four spin, $\tau_1 = 84.82$ and $\tau_2 = 84.82$.

The simulation with the spin chain was performed by using the Hamiltonian (4) with the dipolar coupling constants $D_{jk} = \frac{D_1}{(j-k)^3}$. Figure 3(c) shows the results of the simulation
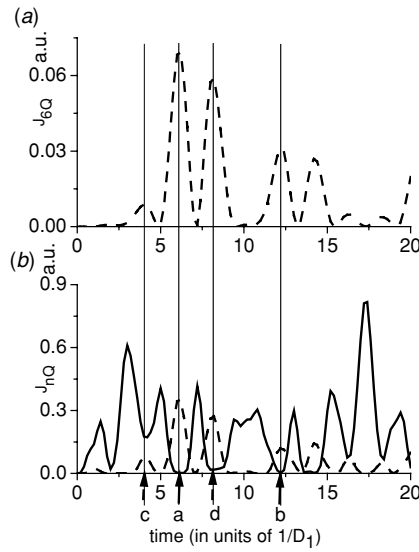
Figure 4. The intensity of the $6Q$ coherence in a ring of six spins with the thermal-equilibrium initial state, $\rho(0) = I_z$ (a) and the intensity of the $6Q$ coherence and the non-diagonal part of $0Q$ coherence with the initial state $\rho(0) = -e_{1,1} + e_{64,64}$ (b). The solid line is the $0Q$-quantum intensity which comes from the non-diagonal part of the density matrix ($J_{0Q_{\text{non-diag}}}$) and dashed is the six-quantum intensity J_{6Q}.

of diagonal elements in a four-spin chain with $\tau_1 = 84.82$ and $\tau_2 = 84.82$. The quasi-one-dimensional clusters of uniformly spaced proton spins in hydroxyapatite, $Ca_5(OH)(PO_4)_3$ [11], can be used for the experimental realization of preparation of the pseudopure state in the spin chain.

The simulations show that the intermediate state (7) cannot be reached when the times of the first and the third periods do not coincide with the zero point of the non-diagonal part of $0Q$ coherences. It must be stressed that the HOMQC cannot be exited by using the double-quantum Hamiltonian in a four-spin system [8], and the pseudopure state is realized in the four-spin cluster without using the HOMQC.

The HOMQC state was used for preparation of the pseudopure state in the ring of six dipolar-coupled proton spins of a benzene molecule, C_6H_6, dissolved in a liquid crystal $ZLI1167$ [3]. As we shall see below the excitation of the HOMQC state is a necessary condition but insufficient for converting the mixed initial state to the state (7) in clusters with $(2 + 4n)$-coupled indentical spins. In order to confirm this point, we simulate the dynamics of the $0Q$ coherences, both arise from the diagonal and non-diagonal elements of the density matrix, in the ring of six spins by using the equilibrium state and mixture of two states (7) as initial states. Figure 4 gives the time dependences of the HOMQC ($6Q$ coherence) with an equilibrium initial state (figure 4(a)) and $6Q$ and $0Q$ (only the non-diagonal part) coherences in the ring of six nuclear spins coupled by the dipole–dipole interaction (figure 4(b)). To prepare the pseudopure state the preparatory period is stopped at time $\tau_1 = 6.08$, when the HOMQC intensity reaches one of its major maxima (this time is shown by the solid arrow a in figure 4(b)) and concurs with time when the intensity of non-diagonal $0Q$ coherence reduces to zero. Then, all MQ coherences are averaging out except the HOMQC [3]. After filtering the HOMQC the time-reversal period followed with the same duration, $\tau_2 = 6.08$, is applied. The numerical simulation results of the diagonal matrix elements of the density matrix are
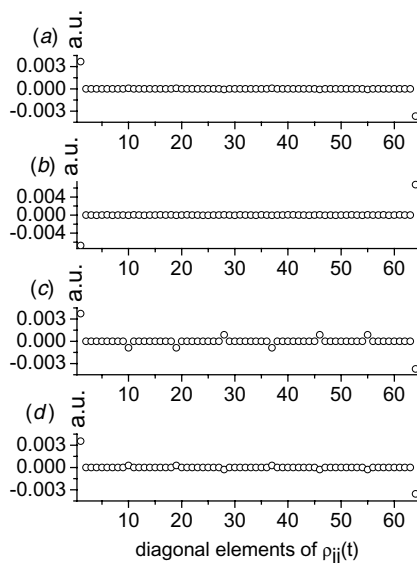
Figure 5. The diagonal elements of the intermediate density matrix in a ring of six spins at various combinations of the time durations of the excitation (τ_1) and reversal (τ_2) periods: (*a*) $\tau_1 = 6.08$, $\tau_2 = 6.08$; (*b*) $\tau_1 = 6.08$, $\tau_2 = 12.19$; (*c*) $\tau_1 = 6.08$, $\tau_2 = 4.02$; (*d*) $\tau_1 = 6.08$, $\tau_2 = 8.16$. These times are shown by the solid (a and b) and dashed (c and d) arrows in figure 4(*b*).

shown in figure 5(*a*) and coincide with the experimental data [3]. Various combinations of the time duration of preparatory, τ_1, and time-reversal, τ_2, periods were used to prepare the intermediate state (7). Results of numerical calculations are presented in figure 5. One can see that when the preparatory period, τ_1, corresponds to one of the major maxima of the HOMQC intensity and this time coincides with the time when the $ND0QC$ is reduced to zero; the equilibrium state is practically ideally converted into the states $\pm|\uparrow\rangle\langle\uparrow| \mp |\downarrow\rangle\langle\downarrow|$ after the time-reversal period (figures 5(*a*) and (*b*)). Otherwise, when the preparatory period and time-reversal periods are not corresponded to the times when the intensity of $ND0QC$ reaches its zeroth value, the conversion is far from ideal. Comparison simulations obtained with times $\tau_2 = 4.02$ (figure 5(*c*)) and $\tau_2 = 8.16$ (figure 5(*d*)) (these times are shown by the dashed arrows c and d, respectively, in figure 4(*b*)) result that the deviation of the diagonal matrix elements from zero (except the two elements $\rho_{1,1}$ and $\rho_{64,64}$) is more than the values of the $ND0QC$ intensities that differ from zero.

This conclusion can be proved by simulating the multiple-quantum dynamics for a cluster consisting of ten spins. It is a complex system of dipolar coupled indentical spins with 1024 quantum states. As the modelling system consisting of ten spins, we shall consider spins of ten hydrogen atoms of a cyclopentane molecule with a chemical formula C_5H_{10} consisting of a ring of five carbon atoms each bonded with two hydrogen atoms above and below the ring plane. We take for the numerical simulations the high-temperature limits of the dipolar coupling constants: $D_{11'} = 1$, $D_{12} = -0.178$, $D_{12'} = -0.002$, $D_{13} = -0.093$ and $D_{13'} = -0.026$ [12]. Figure 6 gives time dependences of the $10Q$ and $0Q$ (only its non-diagonal part) coherences of a cluster that contains ten nuclear spins coupled by the dipole–dipole interaction. To prepare the pseudopure state by using the dynamics of HOMQC and ND0QC intensities, we will choose two characteristic times 6.59 and 9.04 (these times are shown by the dashed ($t = 6.59$) and solid ($t = 9.04$) arrows in figure 6), when the intensity
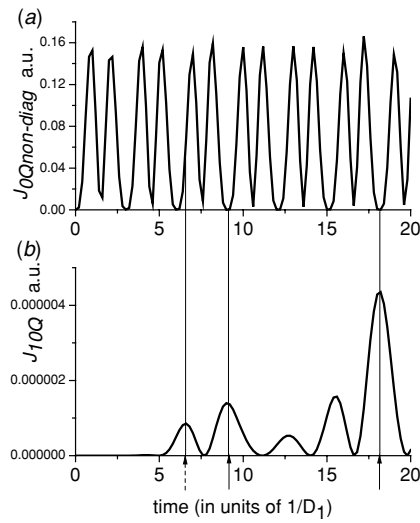
Figure 6. The normalized intensity of MQ coherences in cyclopentane: (*a*) non-diagonal part of $0Q$ coherences stating from the density matrix $\rho(0) = -e_{1,1} + e_{1024,1024}$ and (*b*) ten-quantum intensity with the equilibrium initial state, $\rho(0) = I_z$.
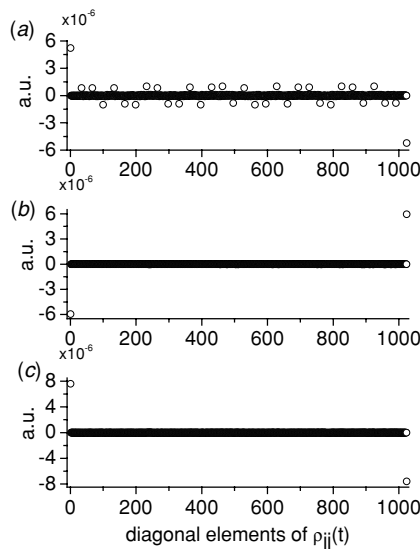

Figure 7. The diagonal elements of the density matrix in a cyclopentane with ten spins at various combinations of the times of the preparation (τ_1) and time-reversal periods (τ_2): (*a*) $\tau_1 = 6.59$, $\tau_2 = 6.59$; (*b*) $\tau_1 = 6.59$, $\tau_2 = 9.04$; (*c*) $\tau_1 = 9.04$, $\tau_2 = 9.04$.

of the HOMQC reaches of its maxima and the intensity of $ND0QC$ reduces to zero (at time $t = 9.04$) and does not reaches its zero value ($t = 6.59$) (figures 6(*a*) and (*b*)). Simulations of the preparatory period with time $\tau_1 = 6.59$, where $J_{0Q_{\mathrm{non\text{-}diag}}} \neq 0$, and the time-reversal period with the same duration do not lead to the good conversion of the initial equilibrium state to the state $|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|$ (figure 7(*a*)). This result connects with the fact that the intensity

of $ND0QC$ does not reduce to zero. At the same time, the simulations with time-reversal duration period $\tau_2 = 9.04$, where $J_{0Q_{\text{non-diag}}} = 0$, result in a very good conversion of $\rho_{\text{eq}}(0)$ to the states $|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|$ for $\tau_1 = 6.59$ (figure 7(b)) and $-|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|$ for $\tau_1 = 9.04$ (figure 7(c)). It should be noted that the evolution of the total $0Q$ and $6Q$ coherences in a six-spin ring and $10Q$ in a ten-spin cluster with the Hamiltonian of equation (4) and the thermal-equilibrium initial state, has been simulated previously [13, 14]. The results of our simulations with the initial density matrix $\rho_{\text{eq}}(0)$ coincide with the dependences obtained in [13, 14].

4. Conclusion

In conclusion, we have shown that there exists a strong relation between the zeroth value of $J_{0Q_{\text{non-diag}}}$ intensities and preparation of the pseudopure state of a spin system. If the duration of the time-reversal period is not concurred with the times when the intensity of the non-diagonal part of $0Q$ coherences reduces to zero, then the state with only two non-zero diagonal elements cannot be reached. Our simulations of the preparation process of pseudopure states with the real molecular structures, such as a rectangular (1-chloro-4-nitrobenzene molecule), a chain (hydroxyapatite molecule), a ring (benzene molecule) and a double ring (cyclopentane molecule), confirm this conclusion and open the way to the experimental testing.

Acknowledgments

References

[1] Cory D G, Fahmy A F and Havel T F 1997 *Proc. Natl Acad. Sci. USA* **94** 1634
[2] Gershenfeld N and Chuang I L 1997 *Science* **275** 350
[3] Lee J-S and Khitrin A K 2004 *Phys. Rev.* A **70** 022330
[4] Lee J-S and Khitrin A K 2005 *Phys. Rev. Lett.* **94** 150504
[5] Lee J-S and Khitrin A K 2005 *J. Chem. Phys.* **122** 041101
[6] Murdoch J B, Warren W S, Weitekamp D P and Pines A 1984 *J. Magn. Reson.* **60** 205
[7] Baum J, Munovitz M, Garroway A N and Pines A 1985 *J. Chem. Phys.* **83** 2015
[8] Suter D, Liu S B, Baum J and Pines A 1987 *Chem. Phys.* **114** 103
[9] Furman G B and Goren S D 2005 *J. Phys.: Condens. Matter.* **17** 4501
[10] Fel'dman E B and Lacelle S 1997 *J. Chem. Phys.* **107** 7067
[11] Cho G and Yesinowski J P 1996 *J. Phys. Chem.* **100** 15716
[12] Poupko R, Luz Z and Zimmermann H 1982 *J. Am. Chem. Soc.* **104** 5307
[13] Doronin S I, Maksimov I I and Fel'dman E B 2000 *J. Exp. Theor. Phys.* **91** 597
[14] Lee J-S and Khitrin A K 2006 Private communication