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# Evolution of spin entanglement and an entanglement witness in multiple-quantum NMR experiments

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We investigate the evolution of entanglement in multiple-quantum (MQ) NMR experiments in crystals with pairs of close nuclear spins-1/2. The initial thermodynamic equilibrium state of the system in a strong external magnetic field evolves under the non-secular part of the dipolar Hamiltonian. As a result, MQ coherences of the zeroth and plus/minus second orders appear. A simple condition for the emergence of entanglement is obtained. We show that the measure of the spin pair entanglement, concurrence, coincides qualitatively with the intensity of MQ coherences of the plus/minus second order and hence the entanglement can be studied with MQ NMR methods. We introduce an Entanglement Witness using MQ NMR coherences of the plus/minus second order.

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**1. Introduction.** Entanglement [1] is the key concept in Quantum Information Theory. It has played a crucial role in experiments on quantum computing and quantum teleportation. This resulted in intensive interest to the physics of entanglement from both theorists and experimentalists [2 – 5].

Entanglement is detected with the help of a so-called Entanglement Witness (EW). By definition, EW is an observable which has a positive expectation value for separable states and negative for some entangled states [6]. In particular, internal energy [7] and magnetic susceptibility [8] were used as EW in some cases. In this paper we propose a new type of an Entanglement Witness, the intensity of multiple quantum coherences in spin systems. This quantity is accessible in NMR experiments and thus opens a new approach to probing entanglement with highly advanced NMR techniques. A lot of NMR methods have been suggested in order to solve different problems of quantum information theory [9]. However, no entanglement is present in these approaches at all or, at least, room temperatures [10, 11]. In fact, entangled states emerge only at very low microkelvin temperatures in NMR experiments [12]. We suggest an multiple-quantum (MQ) NMR experiment in which entangled states appear at comparatively high millikelvin temperatures.

In the present work we focus on the simplest relevant system, a pair of spins $s = 1/2$ coupled by the dipole-dipole interaction in the conditions of the MQ NMR experiment [13]. Here the initial thermodynamic density matrix describing the interaction of the spins with the strong external magnetic field is subjected to the irradiation by the specially tailored sequence of resonance rf-pulses. The anisotropic dipolar Hamiltonian oscillates rapidly when the period of the sequence is less than the inverse dipolar frequency. The spin dynamics of the system is described by the averaged Hamiltonian which is responsible for the emergence of the MQ coherences of the zeroth and plus/minus second orders [14]. It is evident that the initial state of the system is separable. However we show with the Wootters criterion [15] that the entangled state emerges when the intensity of the MQ coherence of order 2 $(-2)$ exceeds the exactly calculated threshold depending on the external magnetic field and the temperature. Thus the intensity of the MQ coherence of the second order, which is the observable in MQ NMR experiments, serves as EW for spin systems.

**2. MQ dynamics of a dipolar coupled spin pair at low temperatures.** We consider a two-spin system in a strong external magnetic field $\mathbf{H}_0$. The thermodynamic equilibrium density matrix, $\rho_0$, of the system is

$$\rho_0 = \exp\left(\frac{\hbar\omega_0}{kT} I_z\right) \Big/ Z, \qquad (1)$$

where $\omega_0 = \gamma H_0$ ($\gamma$ is the gyromagnetic ratio), $T$ is the temperature, $I_\alpha = I_{1\alpha} + I_{2\alpha}$, and $I_{j\alpha} (j = 1, 2; \alpha = x, y, z)$ is the projection of the angular spin momentum operator of spin $j$ on the axis $\alpha$, and $Z$ is the partition function.

The MQ NMR experiment consists of four distinct periods of time: preparation, evolution, mixing, and detection [13]. MQ coherences are created by the multipulse sequence consisting of eight-pulse cycles on

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the preparation period [13]. In the rotating reference frame [16], the average Hamiltonian, $H_{MQ}$, for the two-spin system describing the MQ dynamics at the preparation period can be written as [13]

$$H_{MQ} = b\left(I_1^+ I_2^+ + I_1^- I_2^-\right) \tag{2}$$

where $b = (\gamma^2\hbar/\{2r_{12}^3\})(1 - 3\cos^2\theta_{12})$ is the coupling constant between spins 1 and 2, $r_{12}$ is the distance between spins 1 and 2, and $\theta_{12}$ is the angle between the internuclear vector $\vec{r}_{12}$ and the external magnetic field $\mathbf{H}_0$; $I_j^+$ and $I_j^-$ $(j = 1, 2)$ are the rasing and lowering operators of spin $j$.

The two-spin Hamiltonian $H_{MQ}$ can be diagonalized with the transformation (in the standard basis $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$)

$$U = \begin{pmatrix} 0 & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}, \tag{3}$$

and the density matrix, $\rho(\tau)$, at the end of the preparation period is

$$\rho(\tau) = e^{-iH_{MQ}\tau}\rho_0 e^{iH_{MQ}\tau} = \frac{1}{2(1+\cosh\beta)} \times$$
$$\times \begin{pmatrix} \cosh\beta+\cos(2b\tau)\sinh\beta & 0 & 0 & i\sin(2b\tau)\sinh\beta \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -i\sin(2b\tau)\sinh\beta & 0 & 0 & \cosh\beta-\cos(2b\tau)\sinh\beta \end{pmatrix}, \tag{4}$$

where $\beta = \hbar\omega_0/kT$. The diagonal part of the density matrix of Eq. (4), $\rho_{(0)}(\tau)$, is responsible for the MQ coherence of the zeroth order, and the non-diagonal parts, $\rho_{(2)}(\tau), \rho_{(-2)}(\tau)$, are responsible for the MQ coherences of the plus/minus second orders[13, 14]. The intensities of the MQ coherences of the zeroth, $G_0(\tau)$, and plus/minus second, $G_{\pm 2}(\tau)$, orders are[17]

$$G_0(\tau) = \mathrm{Tr}\left(\rho_{(0)}(\tau)\rho_{(0)}^{ht}(\tau)\right),$$
$$G_{\pm 2}(\tau) = \mathrm{Tr}\left(\rho_{(2)}(\tau)\rho_{(-2)}^{ht}(\tau)\right), \tag{5}$$

where $\rho_{(0)}^{ht}(\tau)$ is the diagonal part of

$$\rho^{ht}(\tau) = e^{-iH_{MQ}\tau} I_z e^{iH_{MQ}\tau} \tag{6}$$

and $\rho_{(2)}^{ht}(\tau), \rho_{(-2)}^{ht}(\tau)$ are the non-diagonal parts of the density matrix $\rho^{ht}(\tau)$. Using Eqs. (4)–(6) one can find that

$$G_0(\tau) = \tanh\frac{\beta}{2}\cos^2(2b\tau),$$
$$G_{\pm 2}(\tau) = \frac{1}{2}\tanh\frac{\beta}{2}\sin^2(2b\tau). \tag{7}$$

It is worth to emphasize that intensities of MQ coherences are observables in MQ NMR experiments. Eq. (7) shows that the intensities of the MQ coherences of the second order, $G_2(\tau)$, and the minus second order, $G_{-2}(\tau)$, are equal. However, in real experiment, certain errors are present and the experimental results for $G_2(\tau)$ and $G_{-2}(\tau)$ are not the same. Some of the errors can be compensated and the accuracy can be improved if one detects the sum of these coherences[18]. It is also worth to notice that the accuracy of the measurement of $G_2(\tau) + G_{-2}(\tau)$ is higher than for $G_0(\tau)$ [18]. Below we will use the sum of the MQ coherences of the plus/minus second order in order to introduce the entanglement witness.

**3. Concurrence and entanglement witness in MQ NMR experiments.** The initial state of the system determined by (1) is separable. Entanglement appears in the course of the preparation period of the MQ NMR experiment when the MQ coherence of the second order has a sufficiently large intensity. In order to estimate the entanglement quantitatively we apply the Wootters criterion [15]. According to [15], one needs to construct the spin-flip density matrix

$$\tilde{\rho}(\tau) = (\sigma_y \otimes \sigma_y)\rho^*(\tau)(\sigma_y \otimes \sigma_y) \tag{8}$$

where the asterisk denotes complex conjugation in the standard basis $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$ and the Pauli matrix $\sigma_y = 2I_y$. The concurrence of the two–spin system with the density matrix $\rho(\tau)$ is equal to [15]

$$C = \max\{0, 2\lambda - \lambda_1 - \lambda_2 - \lambda_3 - \lambda_4\},$$
$$\lambda = \max\{\lambda_1, \lambda_2, \lambda_3, \lambda_4\}, \tag{9}$$

where $\lambda_1$, $\lambda_2$, $\lambda_3$, and $\lambda_4$ are the square roots of the eigenvalues of the product $\rho(\tau)\tilde{\rho}(\tau)$. Using Eqs. (4), (8), (9) one obtains

$$\lambda_{1,2} = \frac{\sqrt{1+\sin^2(2b\tau)\sinh^2\beta} \pm |\sin(2b\tau)|\sinh\beta}{4\cosh^2(\beta/2)},$$

$$\lambda_{3,4} = \frac{1}{4\cosh^2(\beta/2)}. \tag{10}$$

As a result, the concurrence, $C$, is

$$C = \frac{|\sin(2b\tau)|\sinh\beta - 1}{2\cosh^2(\beta/2)}. \tag{11}$$

The entangled state can appear only at $\sinh\beta > 1$ when the intensity of the MQ coherence of the second order

has the maximal value. This condition means that the entanglement appears at temperatures

$$T < \frac{\hbar\omega_0}{k\ln(1+\sqrt{2})}. \qquad (12)$$

If one takes $\omega_0 = 2\pi 500 \cdot 10^6\,\mathrm{s}^{-1}$ the entangled state emerges at the temperature $T_E \approx 27\,\mathrm{mK}$. It is interesting to notice that in a linear chain of dipolar coupled nuclear spins in the thermodynamic equilibrium state, entanglement appears only at microkelvin temperatures [12].

The simple connection between the concurrence, $C$, and the intensities of the MQ coherences of the plus/minus second orders, $G_{\pm 2}(\tau)$, can be found from Eqs. (7), (9)–(11):

$$C = \sqrt{\tanh\frac{\beta}{2}[G_2(\tau)+G_{-2}(\tau)]} - \frac{1}{2\cosh^2(\beta/2)}. \qquad (13)$$

Thus, entanglement is possible only when

$$G_2(\tau)+G_{-2}(\tau) > \frac{1}{2\sinh\beta\cosh^2(\beta/2)}, \qquad (14)$$

and EW can be introduced as the following

$$\mathrm{EW} = \frac{1}{2\sinh\beta\cosh^2(\beta/2)} - \{G_2(\tau)+G_{-2}(\tau)\}. \qquad (15)$$

In the initial moment of time $G_2(0)+G_{-2}(0) = 0$, $\mathrm{EW} > 0$ and the considered system is in a separable state. In the course of the MQ NMR experiment the intensity of the MQ coherence of the second order grows and the entanglement witness, EW, changes its sign. It means that an entangled state appears. According to Eq. (7) the intensities of the MQ coherences periodically change in time. The sign of EW changes also periodically. Thus separable and entangled states change periodically in the considered system. The time evolutions of the MQ coherences of the zeroth and second orders together with the corresponding concurrence are represented in Fig.1 at $\beta = 3$.

One can see that the concurrence is close to the sum of the MQ coherences of the plus/minus second orders, $G_2(\tau)+G_{-2}(\tau)$, at almost all durations of the preparation period of the MQ NMR experiment. At large $\beta$ (small temperatures) the expression $[2\sinh\beta\cosh^2(\beta/2)]^{-1}$ tends to zero and the maximal value of $G_2(\tau)+G_{-2}(\tau)$ tends to one. This means that the concurrence coincides with the maximal value of $G_2(\tau)+G_{-2}(\tau)$ at small temperatures. The corresponding dependencies of the concurrence and the maximal value of the sum $G_2(\tau)+G_{-2}(\tau)$ on $\beta$ are given in Fig.2.

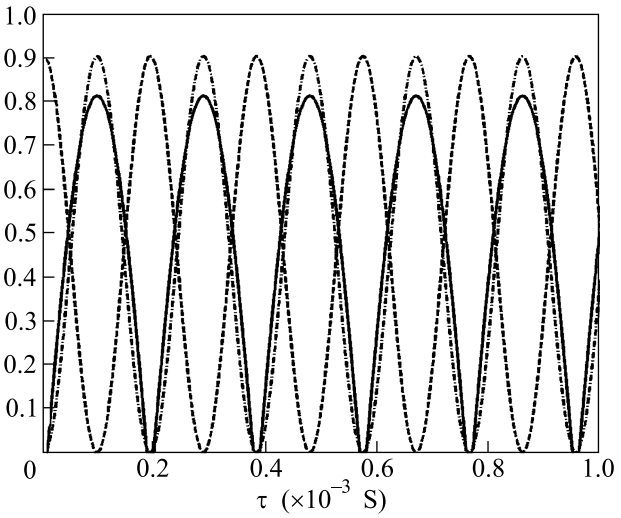


Fig.1. The dependencies of the MQ coherences and the concurrence on the time of the preparation period, $\tau$, of the MQ NMR experiment at $\beta = 3$. The coupling constant is equal to $b = 2\pi 1307\,\mathrm{s}^{-1}$; solid line – concurrence; dashed line – intensity of the MQ coherence of the zeroth order; dash-point line – $G_2(\tau)+G_{-2}(\tau)$ (see the text)

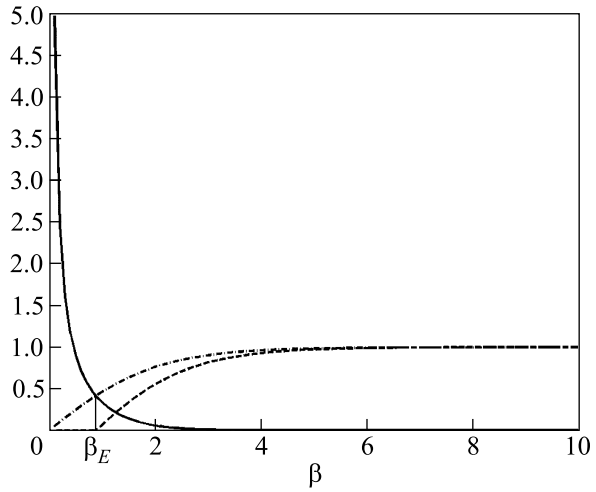


Fig.2. The dependence of the concurrence (dashed line) and the maximal value of $G_2(\tau)+G_{-2}(\tau)$ (dash-point line) on the parameter $\beta$. The solid line describes the function $[2\sinh\beta\cosh^2(\beta/2)]^{-1}$. Here the coupling constant is equal to $b = 2\pi 1307\,\mathrm{s}^{-1}$.The entangled state emerges at temperatures less than $T_E = \hbar\omega_0/(k\beta_E)$

We can conclude that the entangled states appear in MQ NMR experiments at sufficiently small temperatures. In contrast to Ref. [5] we study entanglement in a system of nuclear spins(not electron ones). Such systems are more robust to decoherence which causes the loss of the quantum information which was obtained during quantum computation. A problem, related to ours, was studied in Ref. [19]. That work focuses on

the high temperature regime in which entanglement is absent. The prediction of the existence of an entangled state at high temperatures [19] is an artifact of an incorrect choice of the initial density matrix.

**4. Conclusion.** MQ NMR experiments can be used for the analysis of entangled states in spin systems. We have introduced an Entanglement Witness using observable intensities of the MQ NMR coherences of the plus/minus second order and analyzed entanglement in term of the Wootters criterion. Entangled states emerge when the sum of intensities of the MQ coherences of the plus/minus second order exceeds an exactly calculated threshold depending on the external magnetic field and the temperature. MQ NMR can be considered as a new method for obtaining entangled states in spin systems.

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