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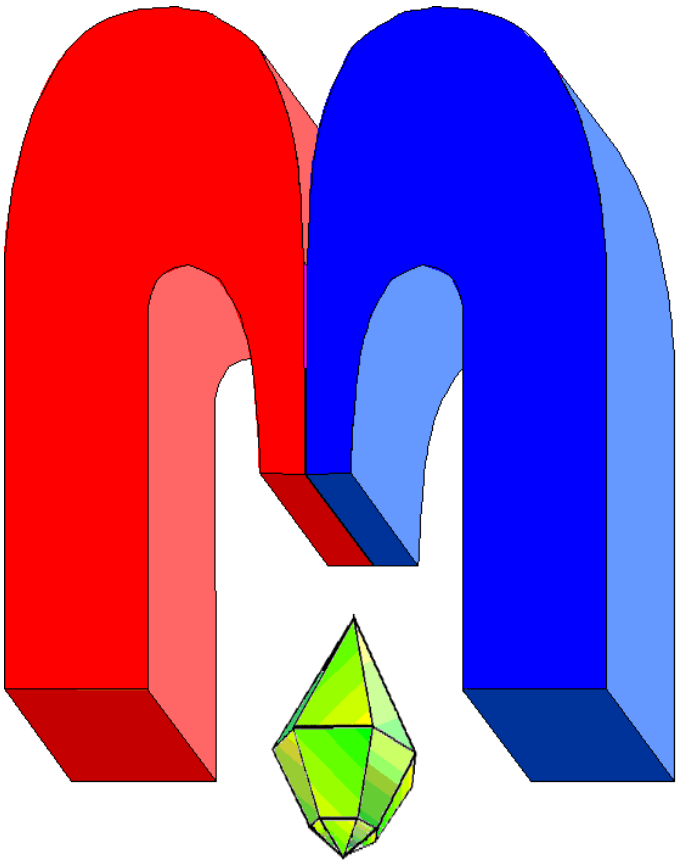

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Multiple quantum NMR of interacting equivalent spins.

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A theory of multiple quantum (MQ) NMR dynamics is developed for systems of interacting equivalent spins (s = 1/2). The theory can be applied for the interpretation of both MQ NMR spectra of bullvalene molecules dissolved in nematic liquid crystal solution and MQ NMR of nanopores in an external magnetic field. Numerical realization of the developed approach allows us to investigate MQ NMR dynamics in systems consisting of several hundred spins. The dependence of the MQ NMR coherence intensities on their orders (the profile of MQ coherence) is investigated in many-spin systems. It is shown that the profile is exponential in such systems. We discuss the information which can be extracted from MQ NMR spectra of systems of interacting equivalent spins.

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1. Introduction

Multiple quantum (MQ) NMR dynamics is the basis of MQ NMR spectroscopy [1] which, in turn, is a powerful tool to study nuclear spin distributions in different systems. Theoretical description of MQ NMR dynamics is a very difficult task because this problem is a many-spin and multiple-quantum one. A consistent quantum-mechanical theory has not been developed up to now except for one-dimensional systems [2-4]. The theory [2-4] leads to the conclusion that, starting with a thermodynamic equilibrium state, only zero and double quantum coherences are produced in the case of the nearest neighbour double-quantum Hamiltonian. Next-nearest couplings and other distant interactions lead to higher order coherences in MQ NMR spectra. However, the effect of these interactions is beyond the theory [2-4]. Numerical supercomputer calculations allow us to study MQ NMR dynamics of a spin chain consisting of no more than fifteen spins [5] which is insufficient to investigate the dependence of the MQ coherence intensities on their orders (the profile of MQ coherences [6]). In our recent article [7] we have worked out the approach to MQ NMR dynamics of systems of interacting spins when the dipole-dipole interactions (DDI) can be characterized by only one coupling constant. The developed approach [7] allows us to investigate MQ NMR dynamics in systems consisting of several hundred spins.

In the present paper we discuss physical realizations of the model [7] and describe numerical calculations of intensities of MQ NMR coherences in systems with 200-600 spins.

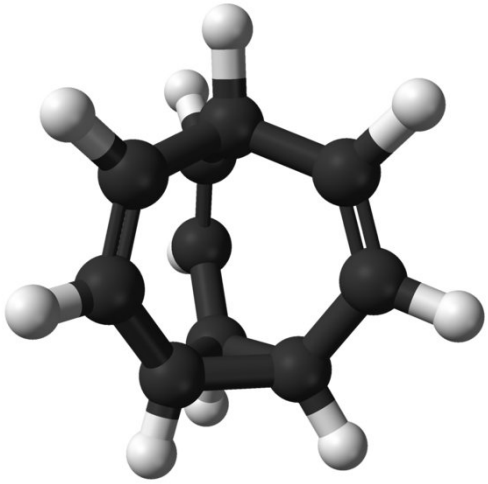

Figure 1 A molecule of bullvalene.

2. The systems of interacting equivalent spins

As examples of an application of the model [7] we consider two many-spin systems. The first system is bullvalene molecules, $C_{10}H_{10,}$ (Fig. 1) dissolved in nematic liquid crystal solution where 12

independent H-H dipolar couplings between the 10 protons in the static molecule are averaged to a single value because of rapid changes of molecular configurations.

The second example is a nanopore compound in a strong external magnetic field; the nanopores are filled with a gas of spin-carrying molecules (atoms) [8] (Fig. 2).

The DDI of spin carrying molecules (atoms) of a gas in the non-spherical nanopores in a strong external magnetic field are not averaged completely due to molecular diffusion [8, 9]. Then the residual averaged DDI are determined by only one coupling constant which is the same for all pairs of interacting spins [8, 9]. MQ NMR dynamics in nanopores is our main priority because it allows us to investigate the profile of intensities of MQ NMR coherences in an exactly solvable model.

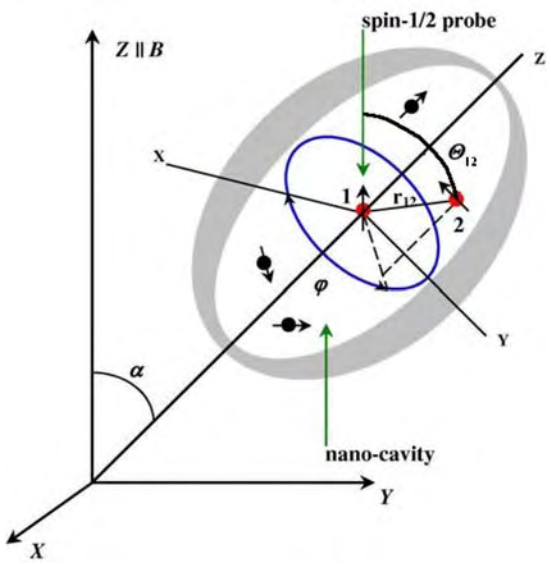

Figure 2 Spin-carrying molecules (atoms) in a nanopore in an external magnetic field.

3. MQ NMR dynamics in systems of interacting equivalent spins

The standard MQ NMR experiment consists of four distinct periods of time: preparation (τ), evolution (t_1), mixing (τ), and detection (t_2). MQ coherences are created by a multiple sequence consisting of eight-pulse cycles on the preparation period [1]. In the rotating reference frame [10], the averaged non-secular two-spin/two-quantum Hamiltonian, H_{MQ}, describing MQ dynamics of equivalent spins on the preparation period can be written as

$$H_{MQ} = -\frac{D}{2}\sum_{j<k}(I_j^+ I_k^+ + I_j^- I_k^-) = -\frac{D}{4}\left\{(I^+)^2 + (I^-)^2\right\}, \tag{1}$$

where D is the averaged dipolar coupling constant, I_j^+ and I_j^- are the raising and lowering operators of spin j, $I_j^+ = \sum_{j=1}^{N} I_j^{\pm}$ and N is the number of spins.

The averaged DDI coupling constant, D, can be calculated for nanopores of different forms[9]. For ellipsoidal nanovoids it is

$$D(\Omega,\theta) = \frac{\gamma^2\hbar}{2}(3\cos^2\theta - 1)\frac{f(a/b)}{\Omega}, \tag{2}$$

where Ω is the nanovoide volume, $f(a/b)$ is the form-factor which depends on the ratio of the axes of the ellipsoidal nanocavity, and θ is the angle between the long axis of the ellipsoid and the external magnetic field.

Since the square of the total spin angular momentum $\hat{I}^2$ commutes with projections of I on an arbitrary direction, we have from Eq. (1) that

$$\left[H_{MQ}, \hat{I}^2\right] = 0. \tag{3}$$

The theory [7] uses the basis consisting of the common eigenstates of $\hat{I}^2$ and its projection I_z on the

direction of the external magnetic field. Since there are no transitions changing $\hat{I}^2$ in the MQ NMR experiments the problem splits into a set of simpler problems for different values of $\hat{I}^2$ and it is possible to avoid the problem of the exponential growth of the Hilbert space dimension with an increase of the number of spins. Such problem is inevitable in the basis of eigenstates of I_z (the multiplicative basis) [5].

In the new basis consisting of the common eigenstates $\hat{I}^2$ and I_z the Hamiltonian H_{MQ} contains the different blocks H_{MQ}^S corresponding to the different values of the total spin angular momentum S ($S^2 = S(S+1)$, $S = N/2, N/2 - 1, N/2 - 2, N/2 - [N/2]$; $[i]$ is an integer part of i):

$$H_{MQ} = \mathrm{diag}\{H_{MQ}^{N/2}, H_{MQ}^{N/2-1}, ..., H_{MQ}^{N/2-[N/2]}\}. \tag{4}$$

The density matrix $\rho(\tau)$ has the same block structure consisting of the blocks $\rho^S(\tau)$ ($S = N/2$, $N/2$ - 1, $N/2 - [N/2]$) as well. If we denote as $\rho_k^S(\tau)$ the contribution to $\rho^S(\tau)$ from MQ coherence of order k, then $J_{k,S}(\tau)$ ($-N \le k \le N$, $S = I, I-1, N/2 - [N/2]$) is the contribution to the intensity of MQ NMR coherence of the k-th order to the observable intensity $J_k(\tau)$**.** Then observable intensities of MQ NMR coherences $J_k(\tau)$ ($-N \le k \le N$) can be expressed as

$$J_k(\tau) = \sum_S n_N(S) J_{k,S}(\tau), \tag{5}$$

where $n_N(S)$ is the multiplicity of the intensities $J_{k,S}$ which is [11]

$$n_N(S) = \frac{N!(2S+1)}{\left(\frac{N}{2}+S+1\right)!\left(\frac{N}{2}-S\right)!}, \; 0 \le S \le \frac{N}{2}. \tag{6}$$

The method of the calculation of the intensities $J_{k,S}(\tau)$ is presented in Ref. 7.

4.Numerical calculations of MQ NMR dynamics of a system of equivalent spins

The intensities of MQ NMR coherences are oscillating functions even at very long times. As an example of such behaviour one can see the dependencies of intensities J_0, J_2, J_{20}, and J_{22} of the MQ coherences on the dimensionless time $t = D\tau$ which are shown in Fig. 3 for a system consisting of $N = 201$ spins in a nanopore [7]. The minimal frequency of these oscillations is of the order D and the minimal positive eigenvalue of the Hamiltonian H_{MQ} obtained from numerical calculations is $\left|\lambda^{(\min)}\right| = \frac{\sqrt{3}}{2} D$.

In order to investigate the profile of MQ NMR coherences the averaged intensities of MQ coherences over several periods $T = 2\pi D / \left|\lambda_{3/2}^{(\min)}\right|$ were calculated:

$$\overline{J} = \frac{1}{K_0 T} \int_{t_0}^{t_0 + K_0 T} J_k(\tau) d\tau. \tag{7}$$

Here K_0 is a some positive integer taken form the requirement that the increase in the averaging interval does not change $\overline{J}_k$. We have found that it is enough to take $K_0 = 2$.

The distribution of the intensities $\overline{J}_{2k}$ can be represented as follows:

$$\overline{J}_{2k} = \begin{cases} A_1(1 + 2a_1|k| + 4a_2k^2)\exp(-2\alpha_1|k|), & k = \pm 1, \pm 3, \ldots, \\ A_2 \exp(-2\alpha_2|k|), & k = \pm 2, \pm 4, \ldots \end{cases} \tag{8}$$

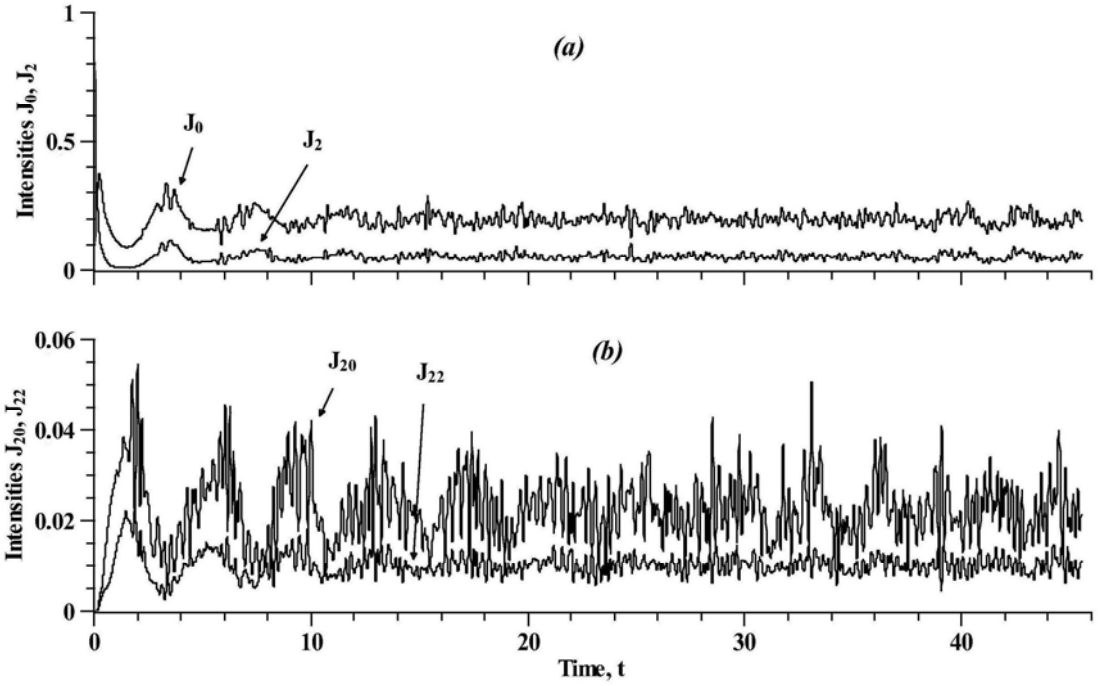

Figure 3 Oscillating dependencies of the intensities of MQ NMR coherences on the dimensionless time t in a system of $N = 201$ spins in a nanopore; a) J_0 and J_2; b) J_{20} and J_{22}.

Parameters A_i, a_i and α_i (i = 1, 2) have been found for N = 201, 401 and 601.The results of these approximations allows us to emphasize that the intensities of MQ coherences have exponential dependence on their orders.

The comparison of the theoretical and experimental data yields, for example, the information about the volume of nanopores, their form-factor and orientation with respect to the external magnetic field. The number of spin-carrying molecules in the nanopores can be also obtained.

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