Dynamics of off-diagonal coherence in spin systems with restricted spectra

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The evolution of off-diagonal elements of the density matrix under the influence of a pulse train is considered for spin systems with restricted spectra. It is shown that this process can be regarded approximately as diffusion in frequency space. An equation is derived describing the dynamics of the off-diagonal elements that determine the intensity of the multiquantum transitions. The obtained dependences of these intensities on the pulse-train duration are in good agreement with the available experimental data.

The methods of multiquantum (MQ) NMR Fourier spectroscopy that have been vigorously developed in the last years make it possible to increase the resolution substantially by detecting transitions in systems of N interacting $\frac{1}{2}$-spins subject to the selection rules $\Delta m = 0, \pm 1, \pm 2, \ldots, \pm N$ (Refs. 1–4). In the theoretical interpretation of the corresponding experiments one encounters the problem of describing the dynamics of the off-diagonal elements of the density matrix under the action of various pulse trains. These off-diagonal elements are directly connected with the intensity $I_n(\tau)$ of n-quantum transitions (τ is the time of action of the pulse train, and $n = \Delta m$). We have previously[5] developed a theoretical approach based on an approximate treatment of the evolution as diffusion in frequency space. This approach has made possible a correct description of MQ experiments in solids,[6,7] where there are many coupled spins and the spectrum is practically unlimited. The obtained behavior of $I_n(\tau)$ agreed with experiment and it was shown that $I_n(\tau) \to 0$ as $\tau \to \infty$.

From the experimental standpoint, great interest attaches to the study of MQ spectra in systems consisting of a finite number of spins and having therefore a restricted spectrum, such as large organic molecules. Experiment has shown[8] that in such systems we have $I_n \to \exp(-n^2/N)$ as $\tau \to \infty$, where N is the number of spins. An attempt to describe such problems theoretically was undertaken in Ref. 9, where the exact Liouville equation was replaced by a system of linear differential equations, and this system was solved numerically. Notwithstanding the good agreement with experiment, the derivation of the system of equations is in no way physically grounded, and the region of its applicability is not clear.

At the same time, the simple diffusion model proposed in Ref. 5 can be used also in the case of spin systems with restricted spectra. This is the purpose of the present paper.

We consider N 1/2-spins coupled by a dipole–dipole (d–d) interaction. The typical scheme of the MQ experiment is the following: a spin system at equilibrium in a strong constant field and described by a density matrix

$$\rho(0)=(1-aI_n)/\mathrm{Sp}(1), \tag{1}$$

is acted upon in a time τ by a pulse train, called preparatory; the system undergoes next, for a time t, a free evolution determined by the d–d interaction; a (detecting) pulse train is then again applied, followed by the action of a 90-degree pulse, and the transverse magnetization is measured.

In a rotating coordinate frame we have

$$\begin{aligned}\langle I_x(t)\rangle &= \mathrm{Sp}[I_x \exp({}^1/{}_2 i\pi I_y)\, V \exp(-iH_d{}^z t)\\ &\quad\times U\rho(0)\,U^{-1} \exp(iH_d{}^z t)\, V^{-1} \exp({}^1/{}_2 i\pi I_y)]\\ &= \mathrm{Sp}[V^{-1} I_z V \exp(-iH_d{}^z t)\, U\rho(0)\,U^{-1} \exp(iH_d{}^z t)],\end{aligned} \tag{2}$$

where U and V are the evolution operators that determine the action of the preparatory and detecting pulse trains, and $H_d{}^z$ is the secular part of the d–d interaction. The detecting train is usually such that the following condition is satisfied[7]:

$$V=\exp(i\Delta\omega I_z t)\, U^{-1} \exp(-i\Delta\omega I_z t), \tag{3}$$

where $\Delta\omega$ is a frequency detuning introduced artificially to distinguish between transitions having different selection rules.

We introduce the eigenvalues of the operators $I_z = \Sigma_{i=1}^{N} I_i{}^z$ and $([H_d{}^z, I_z] = 0)$:

$$I_z|k\alpha\rangle = k|k\alpha\rangle, \quad H_d{}^z|k\alpha\rangle = \omega_\alpha|k\alpha\rangle. \tag{4}$$

Expression (1), following a Fourier transformation with respect to t, can then be written in the form

$$\begin{aligned}\langle I_x\rangle_\omega \sim \sum_{k\alpha,l\beta} &\langle k\alpha|UI_zU^{-1}|l\beta\rangle \langle l\beta|U\rho(0)\,U^{-1}|k\alpha\rangle\\ &\times \delta(\omega-(k-l)\Delta\omega-\omega_\alpha+\omega_\beta).\end{aligned} \tag{5}$$

Expressions (4) show that the spectrum consists of a number of lines corresponding to transitions with absorption of n quanta of the RF field ($n = k - l$). Just as in Ref. 5, we assume that the matrix elements in (5) do not depend on α or β. This is equivalent to assuming that the widths of the lines corresponding to various multispin processes are equal. From Eq. (5), with allowance for (2), we can then obtain for the intensity of the nonzero transitions

$$\begin{aligned}I_n &\sim \sum_k C_k C_{k+n} \langle k|U\rho(0)\,U^{-1}|k+n\rangle \langle k+n|U\rho(0)\,U^{-1}|k\rangle\\ &= \sum_{klm} C_k C_{k+n} \langle k|U|l\rangle \rho_{ll}(0) \langle l|U^{-1}|k+n\rangle \langle k+n|U|m\rangle\\ &\quad\times \rho_{mm} \langle m|U^{-1}|k\rangle.\end{aligned} \tag{6}$$

The matrix elements of the evolution operator can be represented as

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$$\langle k|U(\tau)|l\rangle=|U_{kl}(\tau)|\exp[i\Phi_{kl}(\tau)].$$

The characteristic time of change of the phase $\Phi_{kl}(\tau)$ for the pulse trains used in the experiment[7,8] is of the order of ω_d^{-1}, where ω_d^{-1} is the linewidth due to the *d–d* interaction. Since we shall consider only time intervals longer than ω_d^{-1}, we can assume that averaging takes place in (6) over the rapidly varying phases (the random-phase approximation). Expression (6) takes the form

$$I_n\sim\sum_{kl}C_kC_{k+n}C_l^2|\langle k|U(t)|l\rangle|^2\,|\langle k+n|U(t)|l\rangle|^2\,|\rho_{ll}(0)|^2. \tag{7}$$

Our main task is now to obtain a diffusion-type equation for the matrix elements of the evolution operator, in analogy with what was done in Ref. 5. Since the evolution operator has the group property

$$U(t_3-t_1)=U(t_3-t_2)U(t_2-t_1),$$

we have in the matrix elements

$$U_{k\alpha,l\beta}(t_3-t_1)=\sum_{m,\gamma}U_{k\alpha,m\gamma}(t_3-t_2)\,U_{m\gamma,l\beta}(t_2-t_1),$$

or approximately

$$U_{kl}(t_3-t_1)=\sum_{m}C_mU_{km}(t_3-t_2)\,U_{ml}(t_2-t_1). \tag{8}$$

Using again random-phase approximation, we get

$$|\langle k|U(t_3-t_1)|l\rangle|^2$$
$$=\sum_{m}C_m^2|\langle k|U(t_3-t_2)|m\rangle|^2\,|\langle m|U(t_2-t_1)|l\rangle|^2. \tag{9}$$

We introduce the quantity

$$P_{x,y}(t)=C(x)C(y)|\langle x|U(t)|y\rangle|^2. \tag{10}$$

Changing in (9) from summation to integration we obtain the Smoluchowski equation for

$$P_{x,y}(t_3-t_1)=\int_{-N/2}^{N/2}dz\,P_{x,z}(t_3-t_2)P_{z,y}(t_2-t_1),$$

from which we can obtain in standard fashion[10,5] a diffusion equation for $P_{x,y}(t)$:

$$\partial P_{x,y}/\partial t=D\partial^2P_{x,y}/\partial y^2. \tag{11}$$

(See Ref. 5 concerning the calculation of the diffusion coefficient D. It is of the order of the *d–d* linewidth.) Since the evolution operator satisfies in our approximation the condition

$$\sum_{n}C_n|\langle m|U(0)|n\rangle|^2=1,$$

the initial condition for (11) takes the form

$$P_{x,y}=C(x)\delta(y-x). \tag{12}$$

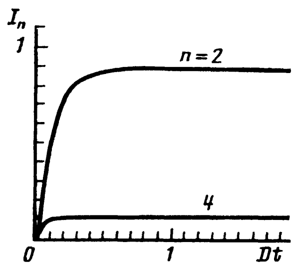

FIG. 1. Plot of intensity of n-quantum transitions in a system of $N=6$ $\frac{1}{2}$-spins.

We seek the solution of (11) in the form of a Fourier series:

$$P_{x,y}(t)=\sum_{k}a_k(x,t)\exp\left(\frac{2ik\pi y}{N}\right). \tag{13}$$

Substituting (13) in (11) and taking the initial condition (12) into account we get

$$P_{x,y}(t)=C(x)\sum_{k}\exp\left(-\frac{4k^2\pi^2Dt}{N^2}\right)\exp\left[\frac{2ik\pi(y-x)}{N}\right]. \tag{14}$$

According to (6), the intensity of an n-quantum transition is

$$I_n\sim\int dx\,dy\,P_{x+n,y}(t)P_{x,y}(t). \tag{15}$$

Substituting here (14) and changing to summation, we get

$$I_n=A\sum_{l=0}^{N-n}C_lC_{l+n}\left[1+2\sum_{k=1}^{\infty}\exp\left(-\frac{8k^2\pi^2Dt}{N^2}\right)\cos\left(\frac{2k\pi n}{N}\right)\right], \tag{16}$$

where A is a normalization constant. The stationary value of $I_n(t)$ is obviously

$$I_n^{st}=A\sum_{l=0}^{N-n}C_lC_{l+n}$$
$$=A\sum_{l=0}^{N-n}(N!)^2[l!\,(n+l)!\,(N-l)!\,(N-l-n)!]^{-1}. \tag{17}$$

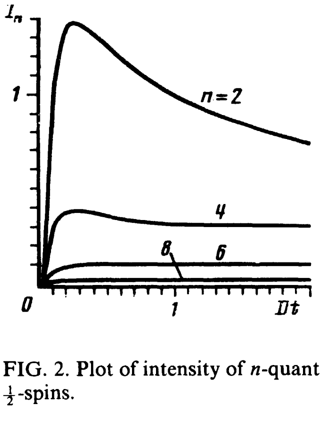

FIG. 2. Plot of intensity of n-quantum transitions in a system of $N=21$ $\frac{1}{2}$-spins.

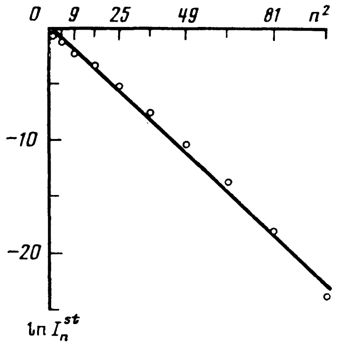

FIG. 3. Plot of I_n^{st} vs n at $N = 21$. The straight line was drawn at least squares.

It is convenient to define the constant A such that the following condition is met:

$$\sum_{n=1}^{N} I_n^{st} = 1.$$

We consider two specific cases corresponding to available experimental data,[8] $N = 6$ and $N = 21$. The results of the numerical calculations with the aid of (16) and (17) are shown in Figs. 1 and 2. This behavior of $I_n(t)$ agrees well with experiment.

Expression (17) for the stationary value of the magnetization at large N (in our case, at $N = 21$) is well approximated by a Gaussian curve (see Fig. 3):

$$I_n^{st} \propto \exp(-n^2/N). \tag{18}$$

This result agrees with the experimental data[8] and with the simple qualitative estimates of Ref. 7. The same result can be obtained from (17) analytically if it is noted that the main contribution to the sum in (17) is made by the terms with $l \approx N/2$. Putting $l = N/2 + k$, using the Stirling formula, retaining in the expansion only the terms quadratic in k, and changing from summation to integration, we obtain Eq. (18). As seen from (18), as $N \to \infty$ we have $I_n^{st} \to 0$, in agreement with the results of Ref. 5.

We see thus that the simple diffusion model previously proposed by us in Ref. 5 for spin system with unrestricted spectra is valid also in the case of a finite number of spins, and good agreement with experiment is observed already at $N = 6$.

The present results can be used in the planning and interpretation of experiments on NMR MQ spectroscopy.

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