

# Dynamics of off-diagonal coherence in multi-quantum NMR Fourier spectroscopy

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An analysis is made of the evolution of off-diagonal elements of the density matrix in multi-quantum NMR Fourier spectroscopy. Under certain conditions this evolution can be regarded as a random Markov process. An equation describing the dynamics of off-diagonal elements is derived. The dependence of the intensities of  $n$ -quantum resonances on the duration of a preliminary pulse sequence (the preparation sequence) agrees well with the available experimental results.

The methods of multi-quantum (MQ) NMR Fourier spectroscopy developed recently<sup>1-4</sup> make it possible to observe transitions in systems of  $N$  coupled spins subject to the selection rules applicable to the Zeeman quantum number  $\Delta m = 0, \pm 1, \pm 2, \dots, \pm N$ . Usually, MQ spectra are better resolved and easier to interpret than conventional spectra arising from  $\Delta m = \pm 1$  transitions. In particular, in a system of  $N$  coupled  $1/2$  spins the frequency of an  $N$ -quantum transition is independent of the dipole-dipole interaction, but is governed solely by the Zeeman frequency and by the magnitude of the chemical shift. Investigations of  $(N-1)$  and  $(N-2)$  quantum spectra usually make it possible to determine all the dipole constants.<sup>2</sup> These characteristics of MQ spectroscopy make it very attractive in studies of the structure of complex organic compounds. Applications of MQ Fourier spectroscopy methods to solids have been reported recently.<sup>5,6</sup> A satisfactory theoretical description of the relevant range of topics is still lacking. An attempt to provide such a description will be made below.

The following MQ experimental procedure is the one most frequently employed. A spin system, which is in a state of equilibrium in a strong static field is, subjected for a time  $\tau$  to a sequence of pulses (called a preparation sequence) and then the system evolves freely for a time  $t$  as described by the spin-spin interaction Hamiltonian. Then another sequence of pulses (called a detection sequence) is applied. At the end of this sequence and after a  $90^\circ$  pulse, the transverse magnetization is measured. This experiment is repeated for different values of  $t$  and then the resultant dependence of the transverse magnetization on the time  $t$  is Fourier-transformed. In a rotating coordinate system it is described by the expression

$$\begin{aligned} \langle I_x(t) \rangle = & \text{Tr} \{ I_x \exp(-i\pi I_y/2) V \exp(-iH_d t) U \rho(0) \\ & \cdot U^{-1} \exp(iH_d t) V^{-1} \\ & \cdot \exp(i\pi I_y/2) \} = \text{Tr} \{ V^{-1} I_x V \exp(-iH_d t) U \rho(0) \\ & \cdot U^{-1} \exp(iH_d t) \}, \end{aligned} \quad (1)$$

where  $U$  and  $V$  are the evolution operators describing the action of the pulse sequences on the spin system,  $H_d^z$  is the secular part of the dipole-dipole interaction, and

$$\rho(0) = (1 - a I_z) / \text{Tr}(1). \quad (2)$$

In Ref. 6 the phases of the rf pulses of the detection

sequence are shifted, compared with the corresponding phases of the preparation sequence, by an amount  $\Delta\varphi$  proportional to the time  $t$  ( $\Delta\varphi = \Delta\omega t$ ) and, moreover, the pulses in the detection sequence act in the reverse order, i.e., the evolution operator  $V$  can be represented in the form

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

Then, Eq. (1) can be rewritten as follows:

$$\langle I_x(t) \rangle = \text{Tr} \{ U I_z U^{-1} e^{-iH t} U \rho(0) U^{-1} e^{iH t} \}, \quad (3)$$

where

$$H = \Delta\omega I_z + H_d^z. \quad (4)$$

If we calculate the trace in Eq. (3) in the representation of the eigenfunctions of the Hamiltonian (4):

$$I_z |k, \alpha\rangle = k |k, \alpha\rangle, \quad H_d^z |k, \alpha\rangle = \omega_\alpha |k, \alpha\rangle,$$

where  $k$  is the Zeeman quantum number and  $\alpha$  is the dipole quantum number (this is possible because the parallel magnetization satisfies the condition  $[I_z, H_d^z] = 0$ ), and if we consider the Fourier transform, we obtain

$$\begin{aligned} \langle I_x \rangle_\omega = & \sum_{k, \alpha, l, \beta} \langle k, \alpha | U I_z U^{-1} | l, \beta \rangle \langle l, \beta | U \rho(0) U^{-1} | k, \alpha \rangle \\ & \cdot \delta[\omega - (k-l)\Delta\omega - \omega_\alpha + \omega_\beta]. \end{aligned} \quad (5)$$

Equation (5) shows that the spectrum consists of a series of lines corresponding to transitions accompanied by the absorption of  $n$  quanta of the rf field ( $n = k - l$ ). In the case of nonzero transitions ( $n \neq 0$ ), we find from Eq. (5) [subject to Eq. (2)] that the intensity of an  $n$ -quantum transition is described by

$$\begin{aligned} I_n \propto & \sum_{k, \alpha, \beta} |\langle k, \alpha | U \rho(0) U^{-1} | k+n, \beta \rangle|^2 \\ = & \sum_{k, \alpha, \beta} |\langle k, \alpha | \rho(\tau) | k+n, \beta \rangle|^2. \end{aligned} \quad (6)$$

Therefore, the intensity of an  $n$ -quantum transition is proportional to the sum of the squares of the absolute values of the corresponding off-diagonal elements of the density matrix. Finding how the intensity  $I_n$  depends on  $\tau$  is the main task of the theory of MQ spectroscopy. The following simple model was proposed in Ref. 6: a pulse sequence produces a

cluster of  $N$  spins and the number of spins  $N$  increases directly proportional to the time  $\tau$ . All transitions in such a system are regarded as equally probable and the intensity of an  $n$ -photon resonance is described simply by the corresponding number of possible transitions. However, this model does not predict the experimentally observed maxima in the dependence of  $I_n$  on  $\tau$ . Moreover, the model in question is insensitive to the structure of the pulse sequences used.

Our aim will be to obtain equations for off-diagonal elements of the density matrix  $\rho(\tau)$ , or equivalently, for matrix elements of the evolution operator  $U(\tau)$ . The main approximation which will be used here is the assumption of the Markov nature of the evolution of a spin system under the action of a pulse sequence.

The evolution operator is known to have the group property:

$$U(t_3-t_1) = U(t_3-t_2)U(t_2-t_1) \quad (7)$$

or, in terms of the matrix elements

$$U_{k\alpha;l\beta}(t_3-t_1) = \sum_{m\gamma} U_{k\alpha;m\gamma}(t_3-t_2)U_{m\gamma;l\beta}(t_2-t_1). \quad (8)$$

We shall introduce the probability of a transition from a state  $|k, \alpha\rangle$  to a state  $|l, \beta\rangle$ :

$$P_{k\alpha;l\beta}(\tau) = |U_{k\alpha;l\beta}(\tau)|^2. \quad (9)$$

Then, multiplying both sides of Eq. (8) by complex conjugates and assuming that summation of the right-hand side of Eq. (8) involves averaging over the phases of the matrix elements, we obtain

$$P_{k\alpha;l\beta}(t_3-t_1) = \sum_{m\gamma} P_{k\alpha;m\gamma}(t_3-t_2)P_{m\gamma;l\beta}(t_2-t_1). \quad (10)$$

We shall introduce the density of the number of states  $f(\omega)$  in the space of the eigenfunctions of the Hamiltonian (4):

$$H|\omega\rangle = \omega|\omega\rangle,$$

which gives the following expression if we pass from summation to integration in Eq. (8):

$$W(\omega_3, t_3 | \omega_1, t_1) = \int d\omega_2 W(\omega_3, t_3 | \omega_2, t_2) W(\omega_2, t_2 | \omega_1, t_1), \quad (11)$$

where

$$W(\omega_3, t_3 | \omega_1, t_1) = f^{i_3}(\omega_3) f^{i_1}(\omega_1) P_{\omega_3; \omega_1}(t_3-t_1). \quad (12)$$

Equation (11) has the form of the Smoluchowski equation for the transition probability. Hence, in the usual manner<sup>7</sup> we can readily obtain the Fokker-Planck equation

$$\frac{\partial W(\omega, \tau | \omega_0)}{\partial \tau} = -\frac{\partial}{\partial \omega} (AW) + \frac{\partial^2}{\partial \omega^2} (DW), \quad (13)$$

where

$$A(\omega) = \lim_{t \rightarrow 0} \frac{1}{t} \int d\omega' (\omega' - \omega) W(\omega', t | \omega), \quad (14)$$

$$D(\omega) = \lim_{t \rightarrow 0} \frac{1}{2t} \int d\omega' (\omega' - \omega)^2 W(\omega', t | \omega).$$

We calculate the transport coefficient  $D$  by going over to summation in Eq. (14):

$$D = \lim_{t \rightarrow 0} \frac{1}{2t} \sum_{k\alpha} (\omega_{k,\alpha} - \omega_{l,\beta})^2 |U_{k\alpha;l\beta}(t)|^2. \quad (15)$$

We can assume approximately that the expression  $|U_{k\alpha;l\beta}(t)|^2/t$ , which represents the probability of a transition per unit time, depends only on the difference  $k-l$ , and not on the initial state. Then, Eq. (15) can be represented in the form

$$D = \lim_{t \rightarrow 0} \frac{1}{2t \text{Tr}(1)} \sum_{k\alpha;l\beta} (\omega_{k,\alpha} - \omega_{l,\beta})^2 |U_{k\alpha;l\beta}(t)|^2. \quad (16)$$

We can easily see that in this approximation the coefficient  $A$  vanishes.

In calculating the transition probability  $|U_{k\alpha;l\beta}(t)|^2/t$  we note that, according to the averaging method of Ref. 8, slow evolution of the spin system under the action of a pulse train is governed by a time-independent effective Hamiltonian

$$H_{eff} = \bar{H} + \frac{1}{2} [\bar{H}, \bar{H}] + \dots,$$

where

$$\bar{H} = \frac{1}{t_c} \int_0^{t_c} dt H(t), \quad \bar{H} = i \int dt' [H(t') - \bar{H}],$$

and  $t_c$  is the period of a pulse sequence.

The pulse sequence

$$(\Delta/2 - 90_x - 2\Delta - 90_x - \Delta - 90_x - 2\Delta - 90_x - \Delta - 90_x - 2\Delta - 90_x - \Delta/2)^n,$$

was used in Ref. 6, where  $t_c = 12\Delta$  is the period of the sequence and  $90_{\pm x}$  are rf pulses rotating the magnetization by angles  $\pm 90^\circ$  about the  $x$  axis. For this sequence the first approximation for the effective Hamiltonian is

$$H_{eff} = H^2 + H^{-2}, \quad (17)$$

where

$$H^{\pm 2} = \frac{1}{2} \sum_{ij} a_{ij} I_i^{\pm} I_j^{\pm}. \quad (18)$$

Since the matrix elements of the evolution operator are calculated using the eigenfunctions of the Hamiltonian (4), we can assume that evolution of the spin system during the action of a pulse sequence is described by the Hamiltonian

$$H = H_0 + V(t),$$

$$H_0 = \Delta \omega I_z + H_d^z, \quad V(t) = H^2 \exp(2i\Delta\omega t) + H^{-2} \exp(-2i\Delta\omega t), \quad (19)$$

where  $H_0$  is the ground-state Hamiltonian and  $V(t)$  is the perturbation operator.

We can now readily calculate  $D$  using conventional perturbation theory:

$$D = \frac{1}{\text{Tr}(1)} \sum_{k\alpha;l\beta} (\omega_{k,\alpha} - \omega_{l,\beta})^2 \cdot 2\pi \langle k, \alpha | H^2 | l, \beta \rangle \langle l, \beta | H^{-2} | k, \alpha \rangle \cdot \delta(\omega_{k,\alpha} - \omega_{l,\beta} - 2\Delta\omega) = 4(\Delta\omega)^2 \int_{-\infty}^{\infty} dt \langle H^2(t) H^{-2} \rangle, \quad (20)$$

where

$$\langle H^2(t)H^{-2} \rangle = \text{Tr} [\exp(-iH_d t) H^2 \exp(iH_d t) H^{-2}] / \text{Tr}(1). \quad (21)$$

Employing the Gaussian approximation for the correlation function (21)

$$\langle H^2(t)H^{-2} \rangle = \langle H^2 H^{-2} \rangle \exp(-M_2 t^2 / 2),$$

where

$$M_2 = -\text{Tr} ([H_d^z, H^2][H_d^z, H^{-2}] / \text{Tr}(H^2 H^{-2}))$$

is the second moment, we obtain

$$D = 4(2\pi/M_2)^{1/2} (\Delta\omega)^2 \langle H^2 H^{-2} \rangle. \quad (22)$$

Therefore, Eq. (13) assumes the form of a conventional diffusion equation

$$\partial W / \partial \tau = D \partial^2 W / \partial \tau^2. \quad (23)$$

The initial condition for this equation can be determined as follows: since  $U(0) = 1$  and the matrix elements satisfy  $U_{k\alpha;l\beta}(0) = \delta_{kl} \delta_{\alpha\beta}$ , it follows that by going over to a continuous distribution, we obtain

$$W(\omega, 0 | \omega_0) = \delta(\omega - \omega_0).$$

The solution of Eq. (23) subject to this initial condition is well known:

$$W(\omega, \tau | \omega_0) = (4\pi D \tau)^{-1/2} \exp[-(\omega - \omega_0)^2 / 2D\tau]. \quad (24)$$

We can now readily determine the dependence of the intensity of an  $n$ -quantum resonance on  $\tau$ . Equation (6) can be rewritten in the form

$$I_n \propto \int_{-\infty}^{\infty} d\omega_0 W(\omega + n\Delta\omega; t | \omega_0) W(\omega, t | \omega_0) \\ \propto \tau^{-1/2} \exp[-n^2 (\Delta\omega)^2 / 4D\tau]. \quad (25)$$

The expression for  $I_n$  is independent of  $\Delta\omega$ , since the diffusion coefficient  $D$  of Eq. (22) is proportional to  $(\Delta\omega)^2$ . It is clear from Eq. (25) that the maximum value of the intensity of an  $n$ -quantum resonance is observed when

$$\tau_{max}^n = n^2 \tau_0, \quad (26)$$

where

$$\tau_0 = \frac{(M_2/2\pi)^{1/2}}{8\langle H^2 H^{-2} \rangle}.$$

It also follows from Eqs. (25) and (26) that the maximum intensity of an  $n$ -photon resonance falls as  $n$  increases, in accordance with the law

$$I_n^{max} \propto n^{-1}. \quad (27)$$

Equations (26) and (27) are in good agreement with the experimental results of Ref. 6.

The proposed method for calculating the intensities of  $n$ -quantum resonances can be used to find the optimal durations of pulse sequences used in MQ Fourier spectroscopy.

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