

Dynamics of multiple-quantum coherences in NMR spectroscopy of solids

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(Submitted 14 November 1995)

Zh. Éksp. Teor. Fiz. **109**, 2173–2178 (June 1996)

Development of multiple-quantum coherences in solids has been analyzed using an exact solution for the zz -model. Simple analytical expressions which are in good agreement with experimental data have been obtained for intensities of multiple-quantum coherences.

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1. INTRODUCTION

Multiple-quantum NMR spectroscopy¹ is a version of multiple-pulse Fourier spectroscopy. Whereas a conventional (single-quantum) NMR absorption spectrum can be expressed as a Fourier transform of a time correlation function of a single-spin operator (magnetization), multiple-quantum spectra are Fourier transforms of time correlators of more complex multiple-spin operators. Usually an experiment consists of the following stages: a preparation period in which an initial density operator that describes a system of polarized nuclear spins is transformed by a nonsecular Hamiltonian to a new state $\rho(\tau) = U(\tau)\rho(0)$; an evolution period during which the system is transformed by another Hamiltonian; a mixing period during which the density operator is refocused by the inverse evolution operator $U^{-1}(\tau)$ to a state characterized by a measurable magnetization; finally, the detection period in which the magnetization is measured.

If the system has been acted upon by a fairly complicated operator during the preparation period, the density operator $\rho(\tau)$ is a sum of a large number (infinite in an infinite system) of various multiple-spin operators. These operators can be grouped according to their symmetry under rotation about the quantization axis z :

$$\rho(\tau) = \sum_n \rho_n, \quad (1)$$

where

$$\exp(it\Delta S_z)\rho_n \exp(-it\Delta S_z) = \exp(itn\Delta)\rho_n, \quad (2)$$

and $S_z = \sum_i S_{iz}$ is the total z -component of the magnetization. The operator ρ_n is called a multiple-quantum coherence of order n . Let the initial density operator $\rho(0)$ describe a high-temperature state in which spins are polarized along the z -axis:

$$\rho(0) = (1 + \alpha S_z) / \text{Tr } 1,$$

and let the ultimately observed quantity be the z -component of the magnetization. Assume that the only interaction during the evolution period is the offset field Δ . Owing to this field, coherences of different orders gain different phase shifts [Eq. (2)], hence they can be separated. (In real experiment it is usually done by sequences of pulses with phase shifts proportional to time.¹) The unit operator in Eq. (2) can be omitted because it is invariant, and the initial

condition can be taken as $\rho(0) = S_z$. Then the final magnetization can be expressed with due account of Eqs. (1) and (2), as

$$\begin{aligned} \langle S_z(2\tau+t) \rangle &= \text{Tr}(S_z U^{-1}(\tau) U_\Delta(t) U(\tau) S_z) \\ &= \text{Tr} \left(\rho(\tau) \sum_n \rho_n \exp(itn\Delta) \right) \\ &= \sum_n \text{Tr}(\rho_n \rho_{-n}) \exp(itn\Delta). \end{aligned} \quad (3)$$

In deriving this equation, we have used the fact that $\text{Tr}(\rho_n \rho_{-n})$ is nonzero only when $n = -m$ (this follows from the invariance of the trace under unitary transformations; to prove this it is sufficient to consider rotations about the z -axis). Taking the Fourier transform with respect to time, we obtain the intensities of multiple-quantum coherences:

$$g_n = \text{Tr}(\rho_n \rho_{-n}). \quad (4)$$

We can see that the spectrum is a sum of δ -functions with intensities given by Eq. (4). If the Hamiltonian acting during the evolution period is more complicated, each δ -function should be replaced with a corresponding multiple-quantum spectrum, the total intensity of each spectrum being determined by Eq. (4). Note two obvious properties of intensities of multiple-quantum coherences: $g_n = -g_{-n}$, which follows from the fact that the operators commute under the trace, and $\sum_n g_n = \text{const}$, which follows from the invariance of $\text{Tr } \rho^2$ with respect to the evolution operator.

By investigating the evolution of multiple-quantum coherences, we can obtain a physical picture of the evolution of a complex many-particle system to its equilibrium state in terms of the emergence of coherences of successively higher order. On the other hand, it is clear that a theoretical description of such a process is more complicated than, for example, calculation of any given correlator. Therefore, in previously used theoretical approaches, the real dynamics has been replaced with random-walk models in abstract spaces.¹⁻³ An alternative approach is to simplify the spin Hamiltonian and to try to obtain an exact solution of the dynamic problem. This approach is described in the paper.

2. HAMILTONIAN

The simplest technique for generating multiple-quantum coherences⁴ is to act on a system of nuclear spins interacting through the secular dipolar Hamiltonian

$$\mathcal{H}_{Dz} = \sum_{i < j} b_{ij} \left(S_{iz} S_{jz} - \frac{1}{3} S_i S_j \right) \quad (5)$$

by a sequence of two pulses: $(\pi/2)_y - \tau - (-\pi/2)_y$. If we omit the exchange term and only retain the interaction of z -components of spins, we obtain the Hamiltonian

$$\mathcal{H}_{zz} = \sum_{i < j} b_{ij} S_{iz} S_{jz}, \quad (6)$$

which gives much simpler spin dynamics. For example, the calculation of NMR line shape (the correlator $\langle S_x(t) S_x(0) \rangle$) with this Hamiltonian becomes trivial. The intensities of multiple-quantum coherences with this Hamiltonian will be calculated in the next section.

The action of a pulse sequence on a spin system can be described in two ways. One may assume that the pulses either act on the density operator or change the Hamiltonian (passive or active frames). In the second case the density operator remains unchanged, $\rho(0) = S_z$, and the Hamiltonian defined by Eq. (6) is transformed, e.g., by the sequence of two pulses described above to an effective Hamiltonian \mathcal{H}_{xx} . In selective multiple-pulse experiments,¹ they often use the pulse sequences which transform the dipolar Hamiltonian in Eq. (5) to the effective Hamiltonian

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_{Dx} - \mathcal{H}_{Dy} = \mathcal{H}_{xx} - \mathcal{H}_{yy}. \quad (7)$$

Thus we may consider the Hamiltonian \mathcal{H}_{zz} (\mathcal{H}_{xx}) as a model of the dipolar Hamiltonian in Eq. (5) for a two-pulse excitation or of the effective Hamiltonian in Eq. (7) in multiple-pulse experiments.

3. CALCULATION OF INTENSITIES OF MULTIPLE-QUANTUM COHERENCES

In the case of a translationally invariant system, it is sufficient to consider the initial condition $\rho(0) = S_{0z}$, where the index 0 denotes a selected spin. The solution of the equation of motion

$$\frac{d\rho(t)}{dt} = [\mathcal{H}_{xx}, \rho(t)] \quad (8)$$

with this initial condition can be rewritten in a compact form:

$$\begin{aligned} \rho(t) &= \exp(-i\tau\mathcal{H}_{xx}) S_{0z} \exp(i\tau\mathcal{H}_{xx}) \\ &= S_{0z} \cos(\tau A) - S_{0y} \sin(\tau A), \end{aligned} \quad (9)$$

where

$$A = \sum_j b_j S_{jx}, \quad b_j \equiv b_{0j}. \quad (10)$$

In order to separate the terms corresponding to multiple-quantum coherences of different orders in the density operator determined by Eq. (9), it should be subjected to a rotation

about the z -axis. In other words, imagine that a resonance detuning $\Delta \equiv 1$ is acting during the evolution period:

$$\rho(t + \tau) = \exp(itS_z) \rho(\tau) \exp(-itS_z). \quad (11)$$

By substituting Eqs. (9) and (10) into Eq. (11) and using the algebra of spin $S = 1/2$ operators (Pauli matrices), we obtain the following expression for the density operator at time $t + \tau$:

$$\begin{aligned} \rho(t + \tau) &= (1/2) S_{0z} \left\{ \prod_j (1_j \cos \alpha_j + iB_j \sin \alpha_j) \right. \\ &\quad \left. + \prod_j (1_j \cos \alpha_j - iB_j \sin \alpha_j) \right\} \\ &\quad + (i/2) (S_{0y} \cos t - S_{0x} \sin t) \\ &\quad \times \left\{ \prod_j (1_j \cos \alpha_j + iB_j \sin \alpha_j) \right. \\ &\quad \left. - \prod_j (1_j \cos \alpha_j - iB_j \sin \alpha_j) \right\}, \end{aligned} \quad (12)$$

where $\alpha_j = b_j \tau / 2$ and

$$B_j = \begin{pmatrix} 0 & \exp(it) \\ \exp(-it) & 0 \end{pmatrix}_j. \quad (13)$$

It is evident that the first line on the right of Eq. (12) is nonzero only when the number of multipliers with B_j is even (the terms with the odd numbers of multipliers with B_j have opposite signs). In the second line, only the terms with an odd numbers of multipliers contribute, and since the factors with $\sin t$ and $\cos t$ change the coherence order by ± 1 . So the right-hand side of Eq. (12) is nonzero only in the case of coherences of an even order.

It follows from the definition of the n -quantum coherence, Eq. (2), that

$$\rho_n = (1/2\pi) \int_{-\pi}^{\pi} \rho(\tau + t) \exp(-int) dt, \quad (14)$$

so the intensity of an n -quantum coherence, Eq. (4), can be expressed as

$$\begin{aligned} g_n &= (1/4\pi^2) \text{Tr} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} dt dt' \rho(\tau + t) \rho(\tau + t') \\ &\quad \times \exp(in(t - t')). \end{aligned} \quad (15)$$

After substituting Eqs. (12) and (13) into Eq. (15) and taking into account that only the terms quadratic in the operators 1_j and B_j for each spin have nonzero traces, we obtain the following equation for the intensities of multiple-quantum coherences of even orders:

$$\begin{aligned} g_n &= (1/\pi) \int_0^{\pi} dt \prod_j (\cos^2 \alpha_j - \cos t \sin^2 \alpha_j) \\ &\quad \times \{ \cos nt - (1/2) \cos[(n+1)t] - (1/2) \cos[(n-1)t] \}. \end{aligned} \quad (16)$$

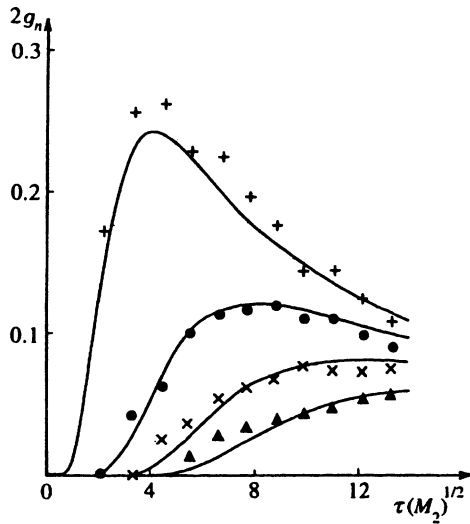


FIG. 1. Intensities g_n of multiple-quantum coherences for (crosses) $n=4$, (circles) $n=8$, (slanted crosses) $n=12$, and (triangles) $n=16$ versus time. The experimental points are data from Ref. 1, the curves are calculations by Eq. (20).

In most three-dimensional solid structures (except magnetically diluted systems and those with clearly defined spin clusters), each spin has many neighbors with close absolute values of the constants of dipolar interaction. In this case, an NMR line shape for the zz -model, e.g., can be described fairly accurately by a Gaussian curve. Using this property, we can simplify Eq. (16), considerably. The product over j contains a lot of cofactors with close values. This means that, when the product decays significantly, each cofactor is still close to unity, i.e., the condition $\alpha_j \ll 1$ holds for all α_j . After expanding each cofactor in powers of α_j and presenting it in an exponential form, we obtain the following expression:

$$g_n = \exp(-M_2 \tau^2) (1/\pi) \int_0^\pi dt \exp(M_2 \tau^2 \cos t) \{ \cos nt + (1/2) \cos[(n+1)t] + (1/2) \cos[(n-1)t] \}, \quad (17)$$

where

$$M_2 = \frac{1}{4} \sum_j b_j^2 \quad (18)$$

is the second moment of the Hamiltonian from Eq. (6). Using modified Bessel functions

$$I_n(x) = (1/\pi) \int_0^\pi dt \exp(x \cos t) \cos nt, \quad (19)$$

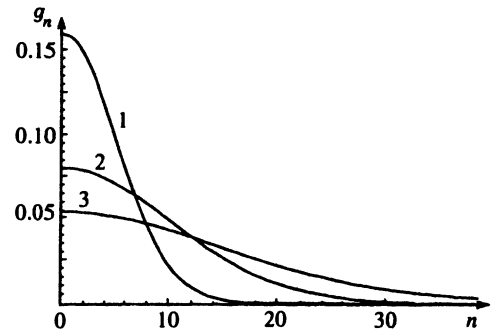


FIG. 2. Intensity distribution of multiple-quantum coherences versus their orders at (1) $\tau(M_2)^{1/2}=5$, (2) 10, and (3) 15.

we can express the final result in a more compact form:

$$g_n = \exp(-M_2 \tau^2) \{ I_n(M_2 \tau^2) + (1/2) I_{n+1}(M_2 \tau^2) + (1/2) I_{n-1}(M_2 \tau^2) \}. \quad (20)$$

Figure 1 shows the intensities g_n of multiple-quantum coherences for $n=4, 8, 12, 16$ calculated using Eq. (20). The calculations are compared to experimental data for polycrystalline hexamethylbenzene taken from Ref. 1 (the quantity $g_n + g_{-n} = 2g_n$ was measured). The numerical value $M_2^{-1/2} = 57 \mu\text{s}$ was selected to plot the experimental points. Given that the accuracy of these measurements is not high and the Hamiltonian is a model one, the agreement is fairly good.

Figure 2 illustrates the evolution of the coherence intensity versus its order (let us recall that only coherences of even orders are nonzero) by curves plotted for three moments of time: $\tau(M_2)^{1/2} = 5, 10$, and 15 . Then the intensities decay proportionally to τ^{-1} . This picture is consistent with the increase in the maximum order of the observed coherences: $n \propto \tau$.

The author is indebted to E. B. Fel'dman for fruitful discussions. The work was supported by Russian Foundation for Fundamental Research (grant No. 95-03-08645).

¹J. Baum, M. Munovitz, A. N. Garroway, and A. Pines, *J. Chem. Phys.* **83**, 2015 (1985).

²M. Munovitz, A. Pines, and M. Mehring, *J. Chem. Phys.* **86**, 3172 (1987).

³L. L. Buishvili, M. N. Gvilava, and M. G. Menabde, *Zh. Éksp. Teor. Fiz.* **95**, 1005 (1989) [*Sov. Phys. JETP* **68**, 578 (1989)].

⁴W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.* **64**, 2229 (1976).

Translation provided by the Russian Editorial office.