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On low-dimensional models at NMR line shape analysis in nanomaterial systems

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Abstract. We present a model of localized spin dynamics at room temperature for the low-dimensional solid-state spin system, which contains small ensembles of magnetic nuclei ($N \sim 40$). The standard spin Hamiltonian (XXZ model) is the sum of the Zeeman term in a strong external magnetic field and the magnetic dipole interaction secular term. The ^{19}F spins in a single crystal of fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] have often been used to approximate a one-dimensional spin system. If the constant external field is parallel to the c axis, the 3D ^{19}F system may be treated as a collection of many identical spin chains. When considering the longitudinal part of the secular term, we suggest that transverse component of a spin in a certain site rotates in a constant local magnetic field. This field changes if the spin jumps to another site. On return, this spin continues to rotate in the former field. Then we expand the density matrix in a set of eigenoperators of the Zeeman Hamiltonian. A system of coupled differential equations for the expansion coefficients then solved by straightforward numerical methods, and the fluorine NMR line shapes of fluorapatite for different chain lengths are calculated.

1. Introduction

Our work is devoted to possibilities of one-dimensional models in the statistical theory of shape of the NMR absorption line. Recently, considerable progress has been made in studies on mechanisms responsible for the wings of a magnetic resonance line [1], but in absence of isolated groups of magnetic nuclei, a problem ‘as old as NMR’ of calculating the shape of the NMR absorption line is still one of the most difficult problems of solid state radiospectroscopy. The difficulties of the theory are compounded by the clear lack of experimental data: the absence of fine structure of the spectra makes them insufficiently critical in comparing theory and experiment. Therefore, considerable interest is associated with the experimental data obtained on the samples, in which the magnetic nuclei form low-dimensional lattice. Non-ergodic quasi-equilibria was also observed in the linear spin $\frac{1}{2}$ chains [2].

We consider a system of N particles of spins $\frac{1}{2}$ in a sample of volume V . The Hamiltonian for such a system in the rotating frame can be written as

$$H_{\text{R}} = H_{0,\text{R}} + \sum_{i \neq j}^N H^{(i,j)}. \quad (1)$$



Here the double sum is taken over all N spins i and j forming a regular lattice. For like spins the unperturbed Zeeman Hamiltonian $H_{0,R}$ is given by

$$H_{0,R} = \sum_{i=1} (\Omega_i - \omega_{\text{rf}}) S_i^z = \Delta\Omega \sum_{i=1} S_i^z. \quad (2)$$

For the case of like spins, one can eliminate $\Delta\Omega$ by performing the transformation into the interaction representation.

The shape of the absorption line plays an important role in NMR theory. However, in its calculation, in view of the absence of an explicit small parameter and the many-particle nature of the problem, it is necessary to make approximations based on the simplest estimates and physical intuition. One of such approaches [3–5] is based on the non-equivalence of interactions between longitudinal and transverse spin components in a truncated dipole Hamiltonian, obtained for $\xi = 1/2$ from a general Hamiltonian

$$H_R^{(ij)} = H^{(ij)} = \gamma^2 \hbar \frac{1 - 3\cos^2 \theta_{ij}}{r_{ij}^3} (S_i^z S_j^z - \xi S_i^+ S_j^-), \quad (3)$$

where r_{ij} is the distance between the i th and j th spins, θ_{ij} is the orientation of the vector \vec{r}_{ij} , connecting the two spins with respect to the main magnetic field, $\xi = 1/2$ – magnetic anisotropy. Here we consider the high-field approximation and retain only the first term of the dipolar Hamiltonian. This separation follows from the axial symmetry of the Hamiltonian, by which the longitudinal component of the total spin moment of the system is conserved, and the transverse damped to zero. This leads to a difference several times between the dephasing time (T_2) of the transverse spin components and the slow variation of the longitudinal components (spectral diffusion). With increasing magnetic anisotropy ($\xi \rightarrow 0$), these differences are amplified.

A special case of the open chain is when we consider only the so-called “nearest-neighbour couplings”; there are $N - 1$ of them, all with $b = \frac{1 - 3\cos^2 \theta_{i,i+1}}{r_{i,i+1}^3}$. The Hamiltonian above then simplifies

to what we will refer to as our 1D NN model. The 1D NN case is known to be integrable (i.e. it has an exact analytical solution) via an algebraic method known as the Bethe Ansatz [6]. It is fair to say that in one dimension it is always important to consider boundaries, since physical systems only contain finite chains even in the absence of doping [7]. This is especially also true for artificially created spin chains using surface structures [8, 9], ion-traps [10], or ultra-cold gases [11–13] as quantum simulators, where measurements of spin correlations are in principle possible.

2. Theory and calculation

2.1. 1D dipolar model

Following direct-product formalism for calculating magnetic resonance signals [14], we seek the solution of the density matrix equation in the form

$$\rho(t) = \sum_{\{\varepsilon\}} g_{\{\varepsilon\}}(t) E_{\{\varepsilon\}}, \quad (4)$$

where the coefficients $g_{\{\varepsilon\}}(t)$ are functions of time, and the $E_{\{\varepsilon\}}$ are a set of basis operators with numbering scheme (ε), such that $H_{0,R} E_{\varepsilon} = [H_{0,R}, E_{\varepsilon}] = \mu \Delta\Omega E_{\varepsilon}$, where $H_{0,R}$ is the Zeeman energy, μ is the difference between the number of operators S^+ and S^- in an eigenoperator $E_{\{\varepsilon\}}$, and $\Delta\Omega$ is the resonant frequency offset of spectral packet with respect to the oscillating rf magnetic field ω_{rf} . These eigenoperators are linearly independent and orthonormal.

$$\text{Tr}(E_{\{\varepsilon\}}^\dagger E_{\{\varepsilon'\}}) = \delta_{\{\varepsilon\}, \{\varepsilon'\}}, \quad (5)$$

For a system of N particles of spin $1/2$, operators $E_{\{\varepsilon\}}$ can be written as a direct product of N spin operators corresponding to different particles

$$E_{\{\varepsilon\}} = \prod_{i=1}^N S_i^{(\varepsilon_i)}, \quad (6)$$

where $\varepsilon_i = \alpha, \beta, +, \text{ or } -$. S^+ and S^- are conventional raising and lowering spin operators and the polarization operators S^α and S^β . By using the above orthogonality property of the basis operators, one obtains a system of equations which couple the FID (free induction decay) components $g_{\{\varepsilon\}}(t)$. That is

$$\frac{\partial \rho_{\{\varepsilon\}}(t)}{\partial t} = -i \sum_{i \neq j}^N C_{\{\varepsilon\}\{\varepsilon'\}}^{(ij)} F(\vec{r}_{ij}) g_{\{\varepsilon'\}}(t). \quad (7)$$

The matrix $C^{(ij)}$ is defined by

$$C_{\{\varepsilon\}\{\varepsilon'\}}^{(ij)} F(\vec{r}_{ij}) = \text{Tr} \left(E_{\{\varepsilon\}}^\dagger \left[H^{(ij)}, E_{\{\varepsilon'\}} \right] \right), \quad (8)$$

where the dagger \dagger denotes the Hermitian conjugate. The explicit form of $C^{(ij)}$ clearly depends on the commutation relations between the basis operators and the Hamiltonian describing the interaction among the spin particles. In the case of the dipolar interaction, one obtains the following commutation properties for different types of pairwise combinations $S_i^{(\varepsilon_i)} S_j^{(\varepsilon_j)}$

$$\begin{aligned} \left[H^{(ij)}, S_i^+ \right] &= F(\vec{r}_{ij}) \left(S_j^z S_i^+ + \xi S_i^z S_j^+ \right), \\ \left[H^{(ij)}, S_i^+ S_j^z \right] &= \frac{1}{2} \xi F(\vec{r}_{ij}) \left(S_i^+ + \xi S_j^+ \right), \text{ etc.} \end{aligned} \quad (9)$$

where $F(\vec{r}_{ij}) \equiv \frac{1-3\cos^2\theta_{ij}}{r_{ij}^3}$. Let's move on to assessing the effect of localization on the spectra. Denoting

local field on site i as b , we get so-called the spin-isochromatic components [14]:

$$\begin{aligned} E(b) &= 2\sqrt{2} (2s+1)^{-N/2} N^{-1/2} \sum_i S_{i-1}^\alpha S_i^+ S_{i+1}^\alpha, \\ E(0) &= 2(2s+1)^{-N/2} N^{-1/2} \sum_i \left(S_{i-1}^\alpha S_i^+ S_{i+1}^\beta + S_{i-1}^\beta S_i^+ S_{i+1}^\alpha \right), \\ E(-b) &= 2\sqrt{2} (2s+1)^{-N/2} N^{-1/2} \sum_i S_{i-1}^\beta S_i^+ S_{i+1}^\beta, \end{aligned} \quad (10)$$

as well as new components which are ‘‘boundary terms’’ that need to be considered for return to the previous site:

$$\begin{aligned} E(b/2) &= 2\sqrt{2} (2s+1)^{-N/2} N^{-1/2} \sum_i \left(S_i^+ S_{i+1}^\alpha S_{i+2}^z + S_{i-2}^z S_{i-1}^\alpha S_i^+ \right), \\ E(-b/2) &= 2\sqrt{2} (2s+1)^{-N/2} N^{-1/2} \sum_i \left(S_{i-1}^+ S_i^\beta S_{i+1}^z + S_{i-1}^z S_i^\beta S_{i+1}^+ \right). \end{aligned} \quad (11)$$

Having applied an identity substitution

$$S_{i-2}^\alpha S_{i-1}^\alpha S_i^+ + S_i^+ S_{i+1}^\alpha S_{i+2}^\alpha = S_{i-2}^z S_{i-1}^\alpha S_i^+ + S_i^+ S_{i+1}^\alpha S_{i+2}^z + S_{i-1}^\alpha S_i^+ S_{i+1}^\alpha + \frac{1}{2} \left(S_{i-1}^\alpha S_i^+ S_{i+1}^\beta + S_{i-1}^\beta S_i^+ S_{i+1}^\alpha \right), \quad (12)$$

we get from the equation of motion for the many-body density matrix,

$$-i \left[H^{(ij)}, E(b) \right] \rightarrow b \left[\left(1 + \frac{1}{2} \xi \right) E(b) + \frac{1}{2} \xi E(b/2) + \frac{1}{2\sqrt{2}} \xi E(0) \right], \quad (13)$$

where boundary term is an eigenoperator $E(b/2)$, linearly independent and orthonormal. From the solution of the density matrix equation, it follows

$$\rho(t) = g_1(t)E(b) + g_2(t)E(b/2) + g_3(t)E(0) + g_4(t)E(-b/2) + g_5(t)E(-b), \quad (14)$$

which implies the equations for the components $g_{\{s\}}(t)$: $\frac{\partial \vec{g}(t)}{\partial t} = -i\mathbf{b}\mathbf{C}\vec{g}$, for short.

After the nonselective $(\pi/2)_x$ pulse the first no constant term of the density matrix $\rho(t)$ is given by

$$\rho_1(0) = -2^{-N} \frac{\hbar\Omega}{kT} \sum_{i=1}^N S_i^+ = 2^{-N/2} q [E(b) + \sqrt{2}E(0) + E(-b)], \quad (15)$$

where $q = \frac{\hbar\Omega\sqrt{N/2}}{2kT}$. The vector of initial values from equation (14) is $\vec{g}(0) = (1, \sqrt{2}, 1, 0, 0)$ that yields 5 possible spectral components. The amplitudes of individual spectral lines were determined by eigenvectors and eigenvalues of matrix \mathbf{C} .

Finally, the separation Δ between line shape components in fluorapatite was found 3.50 Oe (the experimental value 3.64 ± 0.20 Oe [15]). This estimation demonstrates the strong influence of the localization on the NMR absorption line shape. Fluorapatite spin dynamics involves the orthonormal states such as, for example, $E(b)$ and $E(b/2)$, and constructs the actual eigenvectors of spin system as a linear superposition of the eigenvectors representing the two structures. As both structures have different energy, they are not equal contributors to the overall structure – the superposition is a weighted average, or a 0.959:0.267 linear combination of $E(b)$ and $E(b/2)$. When more contributing structures are included, the eigenvectors become more accurate and more excited states can be derived from different combinations of the contributing structures.

The final results, frequencies and intensities (squared amplitudes), are given in Table I.

Table 1. Calculated NMR spectrum for the linear three-spin chain model (relative to the Larmor frequency)¹.

Frequency (Oe)	Intensity
± 3.50	0.294
± 1.36	0.135
0	0.143

As expected, the next five-spin model transitions are grouped about the three-spin model transitions and after a Gaussian convolution, the line shapes from the two models would not differ significantly.

2.2. 3D dipolar model

The present work is essentially a computer simulation with identical, rigid spins. The first results justified our expectations [16]. They were obtained for 3D lattice structure of the single crystal CaF_2 . The following expression was obtained for the shape of the NMR line, which is the Fourier transform of the FID components $g_{\{s\}}(t)$:

$$g(\omega) = \text{Re} \frac{\Gamma_x(i\omega)}{1 - (\xi^2 + 2\xi)(i\omega\Gamma_x(i\omega) - 1) - \Gamma_x^2(i\omega)\xi^2\Delta_z^2(1 + \xi)^2}, \quad (16)$$

¹ For the largest ratio between the strongest intra- and cross- chain couplings.

where $\Delta_z^2 = \frac{1}{4} \sum_j b_{ij}^2$, and $\Gamma_x(i\omega)$ is connected by the Laplace transform with $\Gamma_x(t)$, correlation function of the total magnetic moment of the system. The difference was from contributions of cross-correlation functions in the expression for $F_x(t)$, autocorrelation function for the spin in one of the nodes, because we neglected the possibility of returning to the original node in the 3D CaF₂ spin system, which is strict for large-dimensional lattices if dimension $d \rightarrow \infty$. Under these assumptions, the following equation was obtained for $\Gamma_x(i\omega)$:

$$\Gamma_x(i\omega) = \int_0^{\infty} \exp\left\{-i\omega t - t\xi^2\Delta_z^2\Gamma_x(i\omega) - \frac{\Delta_z^2 t^2}{2}\right\} dt, \quad (17)$$

This result differs from the result of [3], in which not all the terms retained in the above approximation are considered. The fourth moment of the absorption line by formula (16) is less than the total value by 14%, and by the results of [3] without renormalization, by 19%. The value of the fourth moment for 1D fluorapatite is less than the total by only 10%, which confirms the applicability of our approximation.

3. Discussion

In the calculation of the spectra of correlation functions, we will follow an approximation proposed in [3–5]; in other words, we consider the longitudinal part of interaction in full while the transversal part is considered partly. Although the basic assumption about the constancy of fields is strict in the limit $\xi \rightarrow 0$, formula (16) qualitatively correctly describes the change in the form of the spectrum with a change in the magnetic anisotropy parameter ξ : the narrowing from Gaussian at 0 to the δ function at $\xi = -1$, and broadening for $\xi > 0$ too. We found a numerical solution of equation (17) for various values of the parameter ξ and calculated the atlas of the spectra using formula (17). For a truncated dipole Hamiltonian, a line with a flat top is obtained, somewhat flatter than in the experiment. The best agreement with experiment has spectra at lower values $|\xi|$. Similar expansion was obtained in the calculations of other authors [3, 5]. It was explained because of the difference in the action of close and distant spins on the spin. The inclusion of the processes discarded above, connected with the change in the longitudinal components of the spins, will act in the same direction.

In the formulas (16), (17) it is easy to include the heteronuclear interaction and inhomogeneous broadening of the Gaussian form. The mean square of the corresponding field Δ_H^2 is added to Δ_z^2 in the last term of the exponent in (17), and in the formula (16) in the denominator it is necessary to replace in the second term ξ by $\xi_1 = \xi\Delta_z^2 / (\Delta_z^2 + \Delta_H^2)$, and in the last term $\xi^2\Delta_z^2(1 + \xi)^2$ by $\xi_1^2(\Delta_z^2 + \Delta_H^2) + \xi^2\Delta_z^2(2\xi_1 + \xi_1^2)$. The calculation performed with the obtained formulas makes it possible to trace the approximation of the shape of the NMR line to the Gaussian line in such systems as the parameter increases.

In conclusion, we considered model of localized states in fluorine spin system of fluorapatite in comparison with 3D case. We have considered low-dimensional spin system and found strong dependence the absorption NMR line shape on spin localization.

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