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A CONTRIBUTION TO THE THEORY OF MULTIPLE-PULSE NARROWING OF NQR LINES

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ABSTRACT

A theory of the high resolution NQR spectroscopy experiments is developed in the framework of an average Hamiltonian approach analogous to that used in the theory of the NMR line pulse narrowing in solids. A specially constructed unitary operator is found making it possible to treat r. f. excitation of spin systems with nonequidistant spectra, spin and EFG asymmetry parameter being arbitrary. Time averaging is used to get an average Hamiltonian appropriate to dealing with arbitrary periodic multiple-pulse sequences. Relations between the sequence parameters are found ensuring realization of the averaging above mentioned in different cases of interest. The theoretical results obtained are consistent with available data on NQR multiple-pulse experiments.

INTRODUCTION

The high resolution NMR spectroscopy in solids emerged owing to the elaboration of the multiple-pulse narrowing technique and the developing of the mean Hamiltonian theory (see ref.1-3). Later on, more complicated systems were studied (ref.4-6) and more general theories proposed (ref.7-9 and ref.IO-11).

As to the high resolution problem in the NQR spectroscopy, only the case of the spin I = 1 was treated using different theoretical approaches analogous to those above mentioned (ref.12-14 and ref.15-17). In the paper presented a new theory is suggested making it possible to deal with quadrupole spin systems consisting of indentical nuclei with arbitrary spin influenced by an arbitrary multiple-pulse and -frequency r.f. field. Hereafter the main points of this theory are described and then an example of its application is considered.

RESULTS

General theory

The von Neumann equation for the state operator $\rho(t)$ of the

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system in question is (with $\hbar = 1$)

$$i\dot{\rho}(t) = \left[H(t), \rho(t)\right], \tag{1}$$

with Hamiltonian

$$H(t) = H_Q + H_1 + H_{r.f.}(t) ; \tag{2}$$

here

$$H_Q = \sum_j \frac{eQq^{\circ}_{zz}}{4I(2I-1)} \left[3I_z^{j2} - \vec{I}^{j2} + \frac{\eta}{2}\left(I_+^{j2} + I_-^{j2}\right)\right] \tag{3}$$

represents the interaction of the spin system with the spatially averaged electric field gradient (EFG) (the notations are conventional, the summation extends over the nuclei), H_1 takes into account the space inhomogeneity of the EFG and the interactions of the nuclei with one another (direct and indirect spin-spin interactions), and $H_{r.f.}(t)$ gives the action of the r.f. field on the spin system:

$$H_{r.f.}(t) = \sum_j \sum_p 2\gamma \vec{I}^j \vec{H}_p \cos(\omega_p t + f_p^{\varphi}(t)) f_p(t) ; \tag{4}$$

here H_p, ω_p are the r.f. amplitudes and frequencies and $f_p(t)$, $f_p^{\varphi}(t)$ usual and phase pulse functions respectively. Using the projection operators e^j_{mn} (see ref.18) defined by their matrix elements in the H_Q^j representations ($H_Q = \sum_j H_Q^j$, see Eq.(3)), the following expression of $H(t)$ may be obtained:

$$H(t) = (2I+1)^{-1} \sum_j \sum_{mn} \omega^{\circ}_{mn} e^j_{mm} + \sum_j \sum_{mn} G^j_{mn} e^j_{mn} + \sum_j \sum_{mn} \sum_{m'n'} D^{ij}_{mnm'n'} e^i_{m'n'} e^j_{mn} + \sum_j \sum_p \sum_{mn} 2\gamma H_p I^p_{mn} f_p(t) \cos(\omega_p t + f_p^{\Phi}(t)) e^j_{mn} , \tag{5}$$

where ω°_{mn} are the eigenfrequencies of H_Q and G^j_{mn}, $D^{ij}_{mnm'n'}$, I^p_{mn} are the matrix elements (in the representations above mentioned) of the "inhomogeneity part" of H_1, "spin-spin part" of H_1, and the operator $\vec{I}_p \cdot \vec{I}_{tot}$ (where $\vec{I}_{tot}$ is the total spin and $\vec{I}_p$ the unit vector of $\vec{H}_p$) respectively.

It proves to be profitable to carry out the unitary transformation of the operators used by means of the transformation operator $U(t) = \exp(iAt)$ with (ref.19, 20)

$$A = (2I + 1)^{-1} \sum_{j} \sum_{mn} \omega_{mn} e^{j}_{mm} \tag{6}$$

where $\omega_{mn} = \omega_p$ if $\omega^{o}_{mn} \simeq \omega_p$ and $\omega_{mm} = \omega^{o}_{mn}$ otherwise (the performing of this transformations will be denoted by tilde). The result is this:

$$i \dot{\tilde{\rho}}(t) = \left[H^{*}, \tilde{\rho}(t)\right] \tag{7}$$

with

$$H^{*} \equiv H^{*}_{Q} + \tilde{H}_{1} + \tilde{H}_{r.f.} \tag{8}$$

where

$$H^{*}_{Q} = \tilde{H}_{Q} - A = (2I + 1)^{-1} \sum_{j} \sum_{mn} \Delta_{mn} e^{j}_{mm} \tag{9}$$

and $\Delta_{mn} = \omega^{o}_{mn} - \omega_{mn}$. As usual, we replace $\tilde{H}_1$ by its secular (with respect to H_Q) part H_1^{sec} and $\tilde{H}_{r.f.}$ by its part $H^{*}_{r.f.}$ containing no rapidly oscillating terms (refs. 1, 2). So we obtain

$$H^{*}(t) = H^{*}_{Q} + H_1^{sec} + H^{*}_{r.f.} \tag{10}$$

instead of Eq. (8).

In the farther development of the theory we confine ourselves to the case of one-frequency pulse sequences with $f^{\varphi}(t)$=const (no index p is necessary), to present the principal points of the theory without entering into technical details; the extension of the theory aimed at taking account of arbitrary pulse sequences is also done. It may be shown in the way analogous to that used in (ref.7) that in this case the sum $H^{*}_{Q} + H^{*}_{r.f.}$ in Eq. (10) may be replaced by the operator $\vec{\omega}_e \cdot \vec{S}$ without any change of the results obtainable by means of H^{*} if $\vec{\omega}_e = \omega_e \vec{a}$ and $\vec{S}$ are defined as follows: ω_e is the solution of the equation

$$\cos(\tfrac{t_c}{2}\omega_e) = \cos(\tfrac{\Phi}{2}) \cos(\tfrac{t_c}{2}\Delta^{\omega}) \ , \quad 0 \leqslant \tfrac{t_c}{2} \cdot \omega_e \leqslant 2\pi \tag{11}$$

and

$$a_1 = \sin(\tfrac{\Phi}{2}) \sin^{-1}(\tfrac{t_c}{2}\omega_e), \ a_2 = 0, \ a_3 = \cos(\tfrac{\Phi}{2}) \sin(\tfrac{t_c}{2}\Delta^{\omega}) \sin^{-1}(\tfrac{t_c}{2}\omega_e); \tag{12}$$

here $\Delta^{\omega} \equiv 4(2I+1)^{-1}\Delta$, t_c is the pulse sequence period, $\Phi \equiv 2\varphi\sqrt{KK^* + RR^*}$, φ is the pulse angular duration, and K, K^*, R, R^* are some known functions of the matrix elements of the operator $\vec{I}\cdot\vec{I}_{tot}$ mentioned after Eq. (5); as to the expressions of the components $S_{1,2,3}$ of $\vec{S}$, they are rather complicated and we confine ourselves to putting down their commutation laws: $[S_a, S_b] = iS_c$, a,b,c = 1,2,3 with cyclical permutations. It is possible and convenient to present H_1^{sec} as the sum $\sum_m H_1^m$, $m = 0, \pm 1/2, \pm 1, \pm 3/2, \pm 2$, the H_1^m obeying commutation laws $[(\vec{a}\cdot\vec{S}), H_1^m] = mH_1^m$. After doing that and using the approach analogous to that utilized in (ref.9), the following equation of motion may be obtained for $\bar{\rho}(t) = L^{-1}(t)\tilde{\rho}(t)L(t)$ with $L(t) = T\exp\{-i\int_0^t dt'[H_Q^* + H_{r.f.}^*(t')]\}$, T being the Dyson time ordering operator (ref. 1)

$$i\dot{\bar{\rho}}(\bar{t}) = \varepsilon\Big[\sum_m \chi_m(\bar{t})\exp(-im\Theta\bar{t})\, V^m, \bar{\rho}(\bar{t})\Big], \tag{13}$$

where $\varepsilon \equiv \|H_1\| t_c$, $\bar{t} = t/t_c$, $\chi_m(\bar{t})$ are some known periodic functions with the unit period, $\Theta = t_c\omega_e$, and $V^m \equiv \|H_1\|^{-1} H_1^m$. In the multiple-pulse experiments one usually chooses t_c in such a manner that $\varepsilon \ll 1$ which makes it reasonable to apply the method analogous to that used in (ref.10,11) and to replace approximately (with respect to ε) the equation (13) by the following equation for $\bar{\rho}(\bar{t})$:

$$i\dot{\bar{\rho}}(\bar{t}) = \varepsilon[\bar{H}, \bar{\rho}(t)] \tag{14}$$

with the time-independent operator

$$\bar{H} = \chi_0^0 V^0 + \frac{\varepsilon}{2}\sum_{n=-\infty}^{\infty}\sum_m \frac{\check{\chi}_m^n \chi_{-m}^n}{2\pi n + m\Theta}[V^{-m}, V^m] \tag{15}$$

where χ_m^n are the Fourier coefficients of the functions $\chi_m(\bar{t})$.

The operator $\bar{H}$ being time-independent, one can treat different problems of the spin system dynamics, by means of the equation (14) much easier than by means of the equation (1) with time-dependent H(t). In particular, it conserns the problem of the NQR lines narrowing. An example of the approach to such problems based on the use of the operator H is considered below.

Example

It is well known that the NQR line spectrum may be obtained as the Fourier transform of the envelope of the echo signals. Consider the simple "model" case where the spectrum consists of only a single line. This line is narrower the flatter is the envelope - that is, the nearer to zero is the commutator $[\bar{H},\bar{\rho}_+(0)]$ where $\bar{\rho}_+(0)$ is $\bar{\rho}$ just after the first pulse. So the condition of the ideal narrowing is this:

$$[\bar{H},\bar{\rho}_+(0)] = 0 \qquad (16)$$

(note that this condition follows from the time-independence of $\bar{H}$!).

Consider now the concrete pulse sequence $\Phi^{\circ}_{\psi_0} - (\tau - \Phi_{\psi} - \tau)^N$ where ψ_0, $\Phi^{\circ}_{\psi_0}$ and ψ, Φ_{ψ} are the phase and angular duration of the first and all the next pulses respectively. Constructing $\bar{H}$ for this sequence, it may be shown (ref. 20) that in the case $\psi_0 - \psi = \pi/2$ Eq. (16) follows from the condition

$$tg(\frac{\Phi_{\psi}}{2})\ (tg\Phi^{\circ}_{\psi_0})^{-1} = \sin(\Delta^{\omega}\tau) \qquad (17)$$

which occurs for $\Delta = 0$ and arbitrary Φ_{ψ} if $\Phi^{\circ}_{\psi_0} = \pi/2$. The case $\Phi^{\circ}_{\psi_0} = \pi/2$, $\Delta = 0$, and $\psi_0 - \psi = \pi/2$ occured in the experiments (ref.13,14); in these experiments the echo signals were observed during a long time ~ 10 sec which means that the line was very narrow . This is an example of the agreement of our theoretical prediction and the experimental data.

Conclusion

The succes of NMR line narrowing theories makes it reasonable to apply the analogous theory to NQR. The theoretical approach to the study of the quadrupole spin system dynamics presented in this paper may be used : to find the pulse sequence parameters and the initial condition ensuring the line narrowing by means of the cut-off (one is used to call it "averaging") of some kind of interactions in the spin system; to study the weak interactions after cut-off of the strong ones; to analyse the results of the relaxation experiments aimed at the investigation of the slow motions of molecules and molecular fragments in crystals.

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