DIFFUSION IN NUCLEAR QUADRUPOLE RESONANCE

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With the aid of the method of random trajectories, formulas have been obtained for the first time for diffusion damping of the amplitudes of nuclear quadrupole spin echo signals because of molecular vibration-rotation in a two-frequency four-pulse program for spin 5/2 and zero asymmetry parameter. The formulas are similar to the result of Hahn for diffusion in NMR.

Nuclear diffusion in liquids in inhomogeneous magnetic fields in NMR was studied by Hahn by the spin-echo method [1]. Slichter [2] presented a simple derivation of the Hahn formula for diffusion damping of the magnetization at the time of an echo in a four-pulse program.

The aim of this paper is to obtain a formula for the diffusion damping of the echo signal for pulsed nuclear quadrupole resonance in solids, since such a formula has been lacking thus far.

In NMR a magnetization signal arises because of the existence of an electric-field gradient in the nucleus. If the vibration-rotations of the molecule produce a continuum of values of the gradient, then the resonance quadrupole frequency of the nuclei will vary with time, leading to an irreversible change in the amplitude of the quadrupole-echo signal.

The method of random trajectories is appropriate for the classical treatment of a lattice. This equation for an incomplete average density matrix has the form [3]

$$\frac{\partial}{\partial t} < \rho_s >_q = -iL_{sq} < \rho_s >_q + L_q < \rho_s >_q,$$

(1)

where $L_{sq} = \{H(s, q), \ldots\}$ is the Liouville operator, $s$ is the spin variable, and $q$ is the classical variable.

The form of the operator $L_q$ is found from the Einstein-Fokker (EF) equation

$$\frac{\partial P}{\partial t} = L_q P,$$

where $P$ is the density of the conditional probability of the variable $q$. If the operator $L_q$ has the form

$$L_q = -a \frac{\partial}{\partial q} + D \frac{\partial^2}{\partial q^2},$$

where \( a \) and \( D \) are constants, then Eq. (1) has the solution

\[
\langle \rho_s \rangle_q(t) = \exp\{-i L_{aq} t\} \exp\left\{-D \left[ \frac{\partial L_{zz}^2}{\partial t} \right] \frac{2q}{3} \right\} \langle \rho_s \rangle_{\varphi}(0),
\]  
(2)

with the condition

\[
D \frac{\partial^2 L_{zz}}{\partial q^2} = a \frac{\partial L_{zz}}{\partial q}.
\]

We take the quadrupole Hamiltonian in the form [4]

\[
H(s, q(t)) = \frac{cQ q_{zz}(t)}{4J(2J-1)} [3J - J(J+1)];
\]

\[
q_{zz}(t) = q_{zz}\left(1 - \frac{3}{2} \sin^2 \vartheta(t) \right) \simeq q_{zz}\left(1 - \frac{3}{2} \delta^2(t) \right).
\]

where \( q_{zz} \) is the z-th component of the electric-field-gradient tensor of the nucleus and \( \theta \) is the angle between the z axes of the moving and fixed coordinate systems of the gradient tensor.

Suppose that a molecule with a quadrupole nucleus executes vibrations and rotations in a parabolic noise well,

\[
\begin{align*}
\dot{\vartheta}(t) + \frac{3}{2} \{1 + \vartheta(t)\} \dot{\vartheta}(t) + \omega^2_0 \vartheta(t) + \epsilon_\vartheta \vartheta(t) \vartheta(t) & = 0, \\
\dot{\varphi}(t) + \frac{1}{2} \{1 - \varphi(t)\} \dot{\varphi}(t) + \omega^2_\varphi \varphi(t) & = 0,
\end{align*}
\]

(3)

where \( \zeta(t) \) and \( \xi(t) \) are independent complete delta-correlated Gaussian random processes, \( \omega_0 \) is the frequency of the vibration-rotations, and \( \zeta(0) = 0, \xi(0) = 0, \langle \zeta(t) \xi(t) + t' \rangle = \sigma_\zeta^2 \delta(t') \). We go over to the new variables \( u(t) \) and \( \varphi(t) \):

\[
\begin{align*}
\vartheta(t) & = \exp\{\zeta(t)\} \sin[\omega_0 t + \varphi(t)]; \\
\varphi(t) & = \exp\{\zeta(t)\} \cos[\omega_0 t + \varphi(t)],
\end{align*}
\]

(4)

When Eq. (4) is taken into account and averaging is carried out over the period \( T = 2\pi / \omega_0 \), Eq. (3) corresponds to the Einstein-Fokker equation

\[
\begin{align*}
\frac{dP}{dt} & = L_{\varphi} P = \frac{3}{2} \frac{\partial P}{\partial u} + \varphi \frac{\partial P}{\partial \varphi} = \frac{3}{4} \frac{\partial^2 P}{\partial u^2} + \frac{3}{2} \frac{\partial^2 P}{\partial u \partial \varphi} + \frac{1}{2} \frac{\partial^2 P}{\partial \varphi^2},
\end{align*}
\]

(5)

where \( P(u, \varphi) = \vartheta(u(t) - u) \varphi(\varphi(t) - \varphi) \) is the combined probability density of the processes \( u \) and \( \varphi \).

For simplicity we set \( \beta = 0 \) and \( \zeta(t) = 0 \), whereupon Eq. (5) coincides with the EF equation [5] and Eq. (1) becomes

\[
\begin{align*}
\frac{\partial}{\partial t} \langle \rho_s \rangle_{\varphi} & = \left[1 - \frac{3}{4} e^{iu} \right] L \langle \rho_s \rangle_{\varphi} + \frac{1}{2} \varphi_u \frac{\partial^2 \langle \rho_s \rangle_{\varphi}}{\partial u^2} - \varphi_u \frac{\partial \langle \rho_s \rangle_{\varphi}}{\partial u} + \varphi_{\varphi} \frac{\partial^2 \langle \rho_s \rangle_{\varphi}}{\partial \varphi^2},
\end{align*}
\]

(6)

where

\[
\varphi_u = \frac{aL_{zz}}{4}, \varphi_{\varphi} = \frac{aL_{zz}}{8}.
\]

Substituting \( \langle \rho_s \rangle_{\varphi} = \langle \rho_s \rangle_u < \rho_s >_u \) into Eq. (6), from Eq. (2) we get the solution

\[
\langle \rho_s \rangle_u(t) = \exp\left\{-i \left(1 - \frac{3}{4} e^{iu} \right) L t \right\} \exp\left\{-\frac{1}{2} \varphi_u \left(\frac{3}{2} e^{iu} \right)^2 \frac{L^2}{3} \right\} \langle \rho_s \rangle_{u_0}(0),
\]

(7)

where

\[
\exp\left\{-a^2 L^2 \right\} \ldots = \int_{-\infty}^{\infty} dx \exp\left\{-i x^2 - i2 \sqrt{\pi} x a L \right\} \ldots,
\]

\[
L^2 = [H, [H, \ldots]].
\]

Upon solving the dynamic problem during the action of pulses and using formula (7) in the interval between pulses for spin 5/2 and the asymmetry parameter \( \eta = 0 \) in the two-frequency four-pulse program [4] \( (\omega_2, \tau, \omega_1 \omega_2) \), we get a formula for the diffusion damping of six signals of a two-frequency quadrupole echo.