Relaxation Processes in NQR Multiple-Pulse Spin-Locking*

Radiospectroscopy Laboratory, Perm University, Perm, USSR

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A theory of the spin-lattice and spin-spin relaxation processes in quadrupole spin systems with
I > 1/2 in the situation of the multiple-pulse NQR spin locking is proposed for the pulse
sequence MW-4. The theory is based on the assumption that for i > T2 the change of the spin
system is a quasi-equilibrium process. Rate equations for inverse generalized temperatures are
obtained and the kinetic coefficients calculated for the case of exponential correlation functions.
The above assumption was confirmed for some substances containing the 35Cl and 123Sb, and the
time constant T1, characterizing the spin echo signal decay was investigated and compared with
the time constant T10 in the case of continuous spin locking.

Introduction

1. A theory of multiple-pulse excitation of quadrupole spin systems was proposed sometime ago
[1, 2] without taking into account any relaxation processes. In the present paper this theory is
generalized by considering relaxation processes due to both spin-lattice and spin-spin interactions in
the situation of multiple-pulse spin locking. The only
spin-lattice relaxation mechanism considered is the
thermal modulation of the electric field gradient.
The theory is developed for the pulse sequence
\[ \Phi_{0y} - (\tau - \Phi_{0y} - \tau) \] [3, 4] and for I > 1/2 (any other
pulse sequence could be considered as well) on
the supposition that during times later than ~ T2 after
the beginning of the pulse sequence the change of the spin system is slow enough to be considered as
a quasi-equilibrium process T2 ~ T1eq \equiv (\gamma H_{0E})^{-1}.
The linear rate equations for the inverse generalized
temperatures which enter the corresponding state operator were obtained by means of the usual
technique. The kinetic coefficients of these equations
were calculated for the exponential correlation functions.

2. To check the above supposition in a concrete
case, the following experiment was performed: the
nuclei 35Cl (I = 3/2) and 123Sb (I = 7/2) were
investigated in polycrystalline samples of SbCl3,
C2Cl6, and CCl3COOH at 77 K; the time constant T2

was found experimentally: for the pulse sequence
used and times T > T2 the signal decay was observed
with a time constant T1e > T2, which is considered
to confirm the supposition in question. Using the
same substances, some more experiments were done
aimed at the study of the time constant T1e and the
initial value M^eq (T2) of the quasi-equilibrium
magnetization in dependence on \( \tau \) and the resonance
offset \( \Delta \equiv \omega_0 - \omega_e \), and at a comparison of T1e
and the time constant T10 characterizing the continuous
spin locking situation.

Theory

1. In the operator representation used in [1, 2, 5]
the von Neumann equation of the quadrupole spin
system is (with \( \hbar = 1 \))

\[ i \frac{d\rho}{dt} = [\mathcal{H}(t), \rho(t)] \] (1)

with the Hamiltonian

\[ \mathcal{H}(t) = f(t) (aS) + \mathcal{H}^{SS}_0 + \mathcal{H}_{SL}(t). \] (2)

Here \( f(t) \) is the pulse function [1, 2], \( a \) the unit
vector of the effective field \( \omega_e \) [1, 2], \( S \) the effective
spin operator [1, 2], \( \mathcal{H}^{SS}_0 = \sum_m \mathcal{H}^{SS}_m \) with \( m = 0, \pm 1, \pm 2 \), the secular part of the dipole-dipole interaction
operator [2], and \( \mathcal{H}_{SL}(t) = \sum_q F_q(t) A_q \) the spin-lattice
interaction operator (see [6]), the only spin-lattice interaction mechanism considered being the
thermal modulation of the electric field gradient.

2. After the unitary transformation removing the
rapid (with respect to T2) part of \( g(t) \) (see [7-9]),

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Reprint requests to Prof. Dr. I. Shaposhnikov, Radiospectroscopy Laboratory, Perm University, Bukirev St. 15, Perm 614005, USSR.

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the evolution of the slow part \( \tilde{q}(t) \) of \( q(t) \) is given by the von Neumann equation

\[
\frac{d\tilde{q}}{dt} = [\mathcal{H}(t), \tilde{q}(t)]
\]

with the Hamiltonian

\[
\mathcal{H}(t) = -\omega_e (aS) + \mathcal{H}_{dd}^0 + \sum_{kr} (e^{ik\pi t/\tau} R_k^t + e^{-ik\pi t/\tau} R_k^t) + \mathcal{H}_{SL}(t).
\]

Here \( \mathcal{H}_{dd}^0 \) is the part of the operator \( \mathcal{H}_{dd}^0 \) commuting with the operator \( a \cdot S \), and the operators \( R_k^t \) characterize the interaction between the dipole-dipole system and the r.f. field, each \( R_k^t \) being effective on condition \( k\pi/\tau = r\omega_e \), where \( 2\tau \) is the interval between pulses.

3. It is our aim to obtain the time dependence \( A(t) \) of the amplitude of the quadrupole spin echo signal due to the spin-lattice and spin-spin interactions and to the action of the r.f. field. This will be done on the supposition that the change of the spin system state may be considered as a quasi-equilibrium process for \( t \gtrsim T_2 \sim \omega_{loc}^{-1} = (\gamma H_{loc})^{-1} \), where \( H_{loc} \) is the average characteristic of the inner magnetic field owing to the spin-spin interaction; if the Bloch equation is valid, \( T_2 \) has the order of magnitude of the transverse relaxation time entering this equation and characterizes the spin echo signal decay if the pulse sequence \( \Phi_{\omega_0} - (\tau - \Phi_{\omega_0} - \tau)^N \) is used (that is the sequences from the introduction in the particular case \( \psi = \varphi_0 \)).

4. In the framework of the customary “spin temperature approach”, the quasi-equilibrium process mentioned may be described, in the high temperature approximation, by the state operator

\[
\tilde{q}^{eq}(t) = Z^{-1} [1 - \beta_e^{eq}(t) \omega_e (aS) - \beta_d^{eq}(t) \mathcal{H}_{dd}^0 - \sum_m P_m^{eq}(t) \epsilon_{mm}],
\]

where \( \epsilon_{mm} \) are the projection operators introduced in [10], and the indices in the last term on the right hand side number the points of the spectrum of the main part of the Hamiltonian (see [5]), the dash denoting the omission of those influenced by the r.f. field.

5. To calculate \( A(t) \), we are in need of the inverse generalized temperatures \( \beta_e^{eq}(t), \beta_d^{eq}(t), P_m^{eq}(t) \). The corresponding rate equations may be obtained by the usual procedure (see [6]); they are (eq and \( t \) being omitted):

\[
\frac{d\beta_e}{dt} = -\sum_k W_k^e \left( \beta_e - \frac{\omega_k^e}{\omega_e} \beta_d \right) - T_1^e (\beta_e - \beta_d^e),
\]

\[
\frac{d\beta_d}{dt} = \sum_k W_k^d \left( \frac{\omega_k^d}{\omega_d} \beta_e - \beta_d \right) - T_1^d (\beta_d - \beta_d^e),
\]

\[
\frac{dP_m}{dt} = T_1^e (\beta_e - \beta_d^e) - \sum_m W_m (P_m - P_n),
\]

where \( \omega_k^e = \omega_e - k\pi/\tau r \) and \( \beta_d^e \) is the lattice inverse temperature. The expressions of the kinetic coefficients of (6)–(8) being very complicated, they are not given here. The dependence of the kinetic coefficients on the pulse sequence parameters and the lattice motion characteristics is given by the functions

\[
f^{eq}(\omega_{mn} - l\omega_e) = \sum_k \frac{\omega_{mn} - k\pi/\tau - l\omega_e}{(2k\pi + l\Theta)^2},
\]

where \( l = 0, \pm 1/2, \pm 1, \Theta = 2\pi\omega_e, \frac{\omega}{\omega} \) are the spectral densities of the lattice motion (see [6]), and \( \omega_{mn} \) the transition frequencies of the main part of the Hamiltonian.

The initial values \( \beta_e^{eq}(T_2), \beta_d^{eq}(T_2), P_m^{eq}(T_2) \), which are necessary to get the concrete solution of the rate equations (6)–(8), are to be obtained using the condition of the quasi-conservation of the corresponding quantities during the interval \( \sim T_2 \), namely: \( \text{Sp} \tilde{q}_+ (0) Q = \text{Sp} \tilde{q}^{eq} Q \) with \( Q \equiv \omega_e aS, \mathcal{H}_{dd}^0, \sum_m \lambda_0^m \epsilon_{mm} \), where \( \tilde{q}_+ (0) = q_+ (0) \) is the state operator immediately after the first pulse, and \( \lambda_0^m \) are the eigenvalues of the Hamiltonian’s main part.

6. To calculate the kinetic coefficients using (9), one has to know the correlators \( g_{qq'} \) of the lattice motion (see [6]). In the case of exponential correlators [11]

\[
g_{qq'}(\tau) = \langle F^{(q)}(t) F^{(q')}(-\tau) \rangle = \delta_{qq'} \langle F^{(q^2)}(0) \rangle \exp \left(-\frac{\tau}{\tau_q} \right),
\]
the functions $f^{(q)}$ are

$$f^{(q)}(\omega_{mn} - \omega_q = \langle F_q^2(0) \rangle \tau_q. $$

$$
\begin{aligned}
&\frac{1}{1 + \tau_q^2 \omega_{mn}^2} \frac{\omega_{mn} \tau_q \sin(\theta)}{\tau \left(1 + \frac{\omega_{mn} \tau_q \sin(\theta)}{2 \tau} \right)} - \frac{\tau_q}{2 \tau} \left[1 - \cos(\theta)\right] \\
&\left(1 - \frac{\omega_{mn} \tau_q}{\tau} \right) \frac{\text{sh} \left(\frac{2 \tau}{\tau_q}\right) + 2 \frac{\omega_{mn} \tau_q}{\tau} \sin(2 \tau \omega_{mn} - \theta)}{\left(1 + \frac{\omega_{mn} \tau_q}{\tau} \right)^2} \frac{1}{\cos(2 \tau \omega_{mn} - \theta)}
\end{aligned}

(11)

These expressions give the dependence of the kinetic coefficients on the correlation times $\tau_q$ and the pulse sequence parameters $\tau$ and $\theta$.

7. In the particular case of the equidistant spectrum of the main part of the Hamiltonian, the expressions (11) coincide with those obtained in [12–14].

Experimental

1. Formerly experimental investigations in the domain of the NQR multiple-pulse spectroscopy were performed only on substances containing $^{14}$N nuclei ($I = 1$) [15, 16]. In this paper the results of experiments made on the substances indicated in the Introduction are presented.

2. Some experiments were made to verify the supposition of the quasi-equilibrium character of the spin locking decay of the spin echo signal amplitude for $t \gtrsim T_2$. In Fig. 1 the echo signals for the $^{123}$Sb nuclei in SbCl$_3$ are shown vs $t$ for the pulse sequences

$$\left(\frac{\pi}{2}\right)_0 - \left(\tau - \frac{\pi}{2} - \tau\right)^N$$

and

$$\left(\frac{\pi}{2}\right)_0 - \left(\tau - \pi_0 - \tau\right)^N$$

(upper and lower parts of the figure, respectively). Figure 2 shows the envelope of the signals represented in the upper part of Figure 1. The same envelope for the $^{35}$Cl nuclei in CCl$_3$COOH is shown in Figure 3. These results may be considered as confirming the supposition in question in the case of the substances investigated.

Fig. 1. The oscillograms of the echo signals of $^{123}$Sb in polycrystalline SbCl$_3$ as functions of the pulse sequences $\left(\frac{\pi}{2}\right)_0 - \left(\tau - \frac{\pi}{2} - \tau\right)^N$ and $\left(\frac{\pi}{2}\right)_0 - \left(\tau - \pi_0 - \tau\right)^N$ (upper and lower parts of the figure, respectively), frequency is 39.118 MHz.

Fig. 2. The oscillogram of the envelope of the signals represented in the upper part of Figure 1.

Fig. 3. The oscillograms of the same envelope as in Fig. 2 but for $^{35}$Cl in polycrystalline CCl$_3$COOH and free induction decay in the same sample (upper and lower curves respectively), frequency is 39.969 MHz.
Some more experiments were performed aimed at a study of the $\tau$-dependence of $T_{1e}$ (see Fig. 4) and the quasi-equilibrium magnetization $M^{eq}(t)$, at the resonance offset $\Delta$ (it was found that for $\Delta \neq 0$ and arbitrary $\tau$ the time dependence of $M^{eq}$ was essentially non-exponential), and at a comparison between $T_{1e}$ and the time constant $T_{1e}$ [17] characterizing the continuous spin locking situation (it was noticed that near the resonance, $T_{1e}$ increased when noticed that near the resonance, $T_{1e}$ increased when $\tau$ decreased but always $T_{1e}$ remained smaller than $T_{10}$).

Conclusions

1. The theoretical approach to problems of the quadrupole spin system dynamics developed in this paper is more general than the former approaches because in the framework of this approach the spectrum of the main part of the quadrupole Hamiltonian, the electric field gradient symmetry, and the applied r.f. field pulse sequence may be arbitrary. Due to this general character, our approach makes it possible to perform investigations important for the solid state physics (for example, to study the slow motions of molecules and molecular fragments in molecular crystals) in a greater number of interesting cases than before.

2. On the other hand, the approach developed shares with the earlier ones a considerable limitation: it is fit only for cases of quasi-equilibrium processes in the spin systems considered. From the more general point of view, limitations of this kind are the inherent features of almost all the practically used theories of the non-equilibrium processes (for example, the so-called "spin temperature theories", see [18]). This fact is closely connected with the almost generally held but nevertheless erroneous view that the quantities and methods of thermodynamics are suited only for the study of the equilibrium states and quasi-equilibrium processes. This conception prevents, without any reasonable motivation, the use of thermodynamics in the investigations of the non-equilibrium processes which are not slow enough to be considered as sequences of equilibrium states. General theories free from these limitations, and their applications to different kinetic problems exist, see e.g. [19, 20]. It is planned to use the ideas and methods of such theories in the NQR resonance and relaxation investigations.

References