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Multiple-pulse NQR dynamics of spin systems with strong heteronuclear coupling

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Abstract

The results are presented of a theoretical consideration of the nuclear quadrupole resonance (NQR) and spin–spin relaxation for a paramagnetic body containing nuclei of two different sorts coupled by the strong homonuclear and heteronuclear dipole–dipole interactions and influenced by an external multiple-pulse radiofrequency magnetic field acting only on nuclei of one sort. Kinetic equations were obtained giving the possibility of finding the time dependence of the magnetization of the body and the kinetic coefficients calculated as a function of the multiple-pulse field parameters. The possibilities of using the results in question for molecular structure and molecular dynamics investigations are briefly surveyed.

1. Introduction

It is well known that by means of studies of different kinds of paramagnetic resonance and relaxation a great deal of important information concerning inner molecular structure, interactions, and motion may be obtained. To get such information for some concrete molecules, the proper choice of paramagnetic body and of its magnetization time dependence is necessary. This choice is usually of the following kind (for example see Refs. [1–3]): as the body in question, a nuclear paramagnetic containing nuclei of two different sorts and influenced by an external magnetic field $\vec{H}(t) = \vec{H}_0 + \vec{H}_1$ with the radiofrequency (r.f.) part $\vec{H}_1(t)$ of the $\vec{H}(t)$ acting on the nuclei of two sorts; and as the magnetization time dependence, the NMR and nuclear magnetic spin–spin relaxation.

In addition to the "NMR scheme" described above, an analogous "NQR scheme" could be constructed which would be profitable in the sense that such a scheme would make it possible to eliminate the influence of the constant part $\vec{H}_0$ of $\vec{H}(t)$ on the inner molecular structure and the dynamics to be obtained and the r.f. part $\vec{H}_1$ acting only on nuclei of one sort.

This paper is aimed at presentation of the results of a theoretical consideration of some problems of NQR spin dynamics (see the Abstract); it is hoped that these results can be used for construction of the NQR scheme mentioned above.

2. Hamiltonian of the system

Let us consider a spin system of $I \geqslant 1$ and $S = 1/2$ spins and retain only those terms in the Hamiltonian $\mathcal{H}(t)$ which are necessary for

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description of dynamics of the spin system with homonuclear and heteronuclear interactions during the time intervals $t \ll T_1$, T_1 being the spin-lattice relaxation time. The evolution of the spin system influenced by the external multiple-pulse r.f. magnetic field acting only on I spins can be described by the state operator $\rho(t)$ which is a solution of the von Neumann equation ($\hbar = 1$)

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

with Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_Q + \mathcal{H}_{\mathrm{dd}} + \mathcal{H}_{\mathrm{r.f.}}(t) \tag{2}$$

Here

$$\mathcal{H}_Q = \sum_i \frac{eQq_{zz}}{4I(2I-1)}\left[3I_z^{i2} - \vec{I}^{i2} + \frac{\eta}{2}(I_+^{i2} + I_-^{i2})\right] \tag{3}$$

represents the interaction of the I-spin system with the electric field gradient,

$$\mathcal{H}_{\mathrm{dd}} = \mathcal{H}_{SS} + \sum_k \mathcal{H}_k \qquad k = IS \text{ and } II \tag{4}$$

where $\mathcal{H}_{SS}, \mathcal{H}_{IS}$ and $\mathcal{H}_{II}$ are the Hamiltonians of the dipole–dipole interactions between S–S, I–S, and I–I spins, respectively; $\mathcal{H}_{\mathrm{r.f.}}(t)$ gives the action of r.f. field on the I-spin system:

$$\mathcal{H}_{\mathrm{r.f.}}(t) = 2\sum_i \gamma \vec{I}^i \vec{H}_1 f(t)\cos(\omega t) \tag{5}$$

where $|\vec{H}_1|$ and ω are the r.f. field amplitude and frequency and $f(t)$ gives the times of appearance of the r.f. field pulses.

Using the projection operators e^i_{mn} for the spins I, and p^i_{mn} for spins $S = 1/2$, defined by their matrix elements $\langle m|e^i_{m'n'}|n\rangle = \delta_{mm'}\delta_{nn'}$ and $\langle m|p^i_{m'n'}|n\rangle = \delta_{mm'}\delta_{nn'}$, and commutation relation:

$$[e^i_{mn}, p^j_{m'n'}] = 0 \tag{6}$$

$$[e^i_{mn}, e^j_{m'n'}] = \delta_{ij}(\delta_{nm'}e_{mn'} - \delta_{n'm}e_{m'n}) \tag{7}$$

the following expressions may be obtained:

$$\mathcal{H}_Q = (2I+1)^{-1}\sum_i\sum_{mn}\omega^0_m e^i_{mm} \tag{8}$$

$$\mathcal{H}_{SS} = \sum_{ij}\sum_{mnm'n'} F^{ij}_{mnm'n'} p^i_{mn} p^j_{m'n'} \tag{9}$$

$$\mathcal{H}_{IS} = \sum_{ij}\sum_{mnm'n'} D^{ij}_{mnm'n'} e^i_{mn} p^j_{m'n'} \tag{10}$$

$$\mathcal{H}_{II} = \sum_{ij}\sum_{mnm'n'} G^{ij}_{mnm'n'} e^i_{mn} e^j_{m'n'} \tag{11}$$

$$\mathcal{H}_{\mathrm{r.f.}}(t) = 2\sum_i\sum_{mn}\gamma H_1 I^i_{mn} f(t)\cos(\omega t) e^i_{mn} \tag{12}$$

where $\omega^0_{mn} = \lambda_m - \lambda_n$, λ_m are the eigenvalues of the operator $\mathcal{H}_Q$ and $F^{ij}_{mnm'n'}$, $D^{ij}_{mnm'n'}$, $G^{ij}_{mnm'n'}$, and I^i_{mn} are the matrix elements of the dipole–dipole Hamiltonians $\mathcal{H}_{SS}$, $\mathcal{H}_{IS}$, $\mathcal{H}_{II}$ and operator $\vec{l}\vec{I}^i$ (where $\vec{l}$ is the unit vector of $\vec{H}_1$), respectively.

It proves to be profitable to carry out the unitary transformation of the operators used by means of the operator $Q(t) = \exp(iAt)$ with

$$A = (2I+1)^{-1}\sum_i\sum_{mn}\omega_{mn} e^i_{mm} \tag{13}$$

where $\omega_{mn} = \omega$ if $\omega \approx \omega^0_{mn}$ and $\omega = \omega^0_{mn}$ otherwise. Substituting $\rho(t) = Q^+(t)\tilde{\rho}(t)Q(t)$ into (1) we obtain

$$i\frac{\mathrm{d}\tilde{\rho}(t)}{\mathrm{d}t} = [\tilde{\mathcal{H}}(t), \tilde{\rho}(t)] \tag{14}$$

where

$$\tilde{\mathcal{H}}(t) = \mathcal{H}_\Delta + \tilde{\mathcal{H}}_{\mathrm{dd}} + \tilde{\mathcal{H}}_{\mathrm{r.f.}}(t) \tag{15}$$

$$\mathcal{H}_\Delta = (2I+1)^{-1}\sum_i\sum_{mn}\Delta_{mn} e^i_{mm} \tag{16}$$

$$\tilde{\mathcal{H}}_{\mathrm{dd}} = \mathcal{H}_{SS} + \tilde{\mathcal{H}}_{IS} + \tilde{\mathcal{H}}_{II} \tag{17}$$

$$\tilde{\mathcal{H}}_{IS} = \sum_{ij}\sum_{mnm'n'} d^{ij}_{mnm'n'} e^i_{mn} p^j_{m'n'} \tag{18}$$

$$\tilde{\mathcal{H}}_{II} = \sum_{ij}\sum_{mnm'n'} g^{ij}_{mnm'n'} e^i_{mn} e^j_{m'n'} \tag{19}$$

$$\tilde{\mathcal{H}}_{\mathrm{r.f.}}(t) = \sum_i\sum_{mn}\gamma H_1 I^i_{mn} f(t)(\delta_{\omega,\omega_{mn}} + \delta_{\omega,\omega_{nm}}) e^i_{mn} \tag{20}$$

Here

$$\Delta_{mn} = \omega^0_{mn} - \omega_{mn} \tag{21}$$

$$d^{ij}_{mnm'n'} = D^{ij}_{mnm'n'}(\delta_{mn} + \delta_{m\bar{n}}) \tag{22}$$

$$g^{ij}_{mnm'n'} = G^{ij}_{mnm'n'}[(\delta_{mn} + \delta_{m'n'})(\delta_{m\bar{n}} + \delta_{m'\bar{n}'}) + (\delta_{mn'} + \delta_{m'n})(\delta_{m\bar{n}'} + \delta_{m'\bar{n}})] \tag{23}$$

and $\bar{m} = -m$, $\bar{n} = -n$. When obtaining Eqs. (18)–(20) the rapidly oscillating terms called non-secular were omitted.

3. Effective Hamiltonian (zeroth approximation)

The action of a periodic r.f. field pulse on a spin system consists of a preparatory pulse taking the spin system out of equilibrium and a multiple-pulse sequence. The state operator, $\rho_+(0)$, immediately after the end of the action of the preparatory pulse forms the initial condition for Eq. (14) which describes the evolution of the spin system under the influence of a multiple-pulse periodic action.

Eq. (14) has a solution

$$\tilde{\rho}(t) = U(t)\rho_+(0)U^+(t) \tag{24}$$

where $U(t)$ is the solution of the following equation:

$$i\frac{\mathrm{d}U(t)}{\mathrm{d}t} = \tilde{\mathcal{H}}(t)U(t) \tag{25}$$

with initial condition

$$U(0) = 1 \tag{26}$$

The periodicity of $\tilde{H}(t)$ allows us to write the evolution operator $U(t)$ in Floquet form [4] as

$$U(t) = P(t)e^{-itH} \tag{27}$$

where $P(t)$ has the same periodicity as $\tilde{H}(t)$ and H is the time-independent effective Hamiltonian.

In the multiple-pulse experiments t_c is usually chosen in such a manner that $\epsilon = \|\tilde{\mathcal{H}}_{dd}\| t_c \ll 1$ (here $\|\tilde{\mathcal{H}}_{dd}\|$ is the norm of the operator $\tilde{\mathcal{H}}_{dd}$), so we can expand the operators $P(t)$ and H as follows:

$$P(t) = \sum_{\mu=0}^{\infty} \epsilon^{\mu} P_{\mu}(t) \tag{28}$$

$$H = \sum_{\mu=0}^{\infty} \epsilon^{\mu} H^{(\mu)} \tag{29}$$

From Eq. (25) we have for $\mu = 0$

$$i\frac{\mathrm{d}U_0(t)}{\mathrm{d}t} = \tilde{\mathcal{H}}_0(t)U_0(t) \tag{30}$$

where $\tilde{\mathcal{H}}_0(t) = \mathcal{H}_\Delta + \tilde{\mathcal{H}}_{\mathrm{r.f.}}(t)$ and

$$U_0(t) = P_0(t)e^{-itH^{(0)}} \tag{31}$$

The operator $P_0(t)$ is the solution of the equation

$$i\frac{\mathrm{d}P_0(t)}{\mathrm{d}t} = [\mathcal{H}_\Delta + \tilde{\mathcal{H}}_{\mathrm{r.f.}}(t)]P_0(t) - P_0(t)H^{(0)} \tag{32}$$

with initial condition

$$P_0(0) = 1 \tag{33}$$

where $H^{(0)}$ is given by

$$\begin{aligned} H^{(0)} &= \frac{i}{t_c}\ln U_0(t_c) \\ &= \frac{i}{t_c}\ln\left(T\exp\left\{-i\int_0^{t_c}\mathrm{d}t[\mathcal{H}_\Delta + \tilde{\mathcal{H}}_{\mathrm{r.f.}}(t)]\right\}\right) \\ &= -\,\omega_e(\vec{a}\,\vec{\Sigma}) \end{aligned} \tag{34}$$

Here T is the Dyson time-ordering operator, ω_e the effective frequency, and direction $\vec{a}$ of $\vec{\omega}_e$ can be obtained from equations

$$\cos(\omega_e t_c/2) = \cos(\phi/2)\cos(\Delta t_c/2) \tag{35}$$

$$a_1 = \frac{\sin(\phi/2)}{\sin(\omega_e t_c/2)} \qquad a_2 = 0$$

$$a_3 = \frac{\cos(\phi/2)\sin(\Delta t_c/2)}{\sin(\omega_e t_c/2)} \tag{36}$$

and $\vec{\Sigma}$ is the effective spin operator satisfying the commutation rule: $[\Sigma_1, \Sigma_2] = i\Sigma_3$ [5]. Using the unitary transformation

$$U^*(t) = P_0^+(t)U(t) \tag{37}$$

Eq. (25) may be written as follows:

$$i\frac{\mathrm{d}U^*(t)}{\mathrm{d}t} = [H^{(0)} + \mathcal{H}^*_{dd}(t)]U^*(t) \tag{38}$$

with initial condition

$$U^*(0) = 1 \tag{39}$$

where

$$\mathcal{H}^*_{dd}(t) = \mathcal{H}_{SS} + \sum_k \mathcal{H}^*_k(t) \tag{40}$$

$$\mathcal{H}^*_k(t) = P_0^+(t)\mathcal{H}_k P_0(t) \tag{41}$$

4. Quasi-equilibrium magnetization

Let us first consider the case where $\omega_e \approx \omega_{loc}^{SS} \approx \omega_{loc}^{IS} \approx \omega_{loc}^{II}$, where $\omega_{loc}^{k} = [Sp(\mathcal{H}_k^2)/Sp(\vec{a}\,\vec{\Sigma})^2]^{1/2}$, and $\omega_{loc}^{SS} = [Sp(\mathcal{H}_{SS}^2)/Sp(\gamma_S^2\Sigma_i S_z^{i2}]^{1/2}$ [6]. The solution of Eq. (25) can be expressed in terms of the operator

$$C(t) = P_0^+(t)P(t) = 1 + \sum_{\mu=1}^{\infty} \epsilon^{\mu} C_{\mu}(t) \tag{42}$$

and

$$C_k(0) = 0 \quad \text{for} \quad \mu \geqslant 1 \tag{43}$$

Using Eqs. (32) and (38) the equation for $C(t)$ can be obtained:

$$i\frac{dC(t)}{dt} = [H^{(0)}, C(t)] - C(t)(H - H^{(0)}) + \tilde{\mathcal{H}}^*_{dd}(t)C(t) \tag{44}$$

and $C(0) = 1$. In the first approximation with respect to ϵ we have from Eq. (44):

$$i\frac{dC_1(t)}{dt} = [H^{(0)}, C_1(t)] - H^{(1)} + \tilde{\mathcal{H}}^*_{dd}(t) \tag{45}$$

and $C_1(0) = 0$. Consider the Fourier series of the operators $C_1(t)$ and $\tilde{\mathcal{H}}^*_{dd}(t)$:

$$C_1(t) = \sum_{n=-\infty}^{\infty} B_n e^{-i(2\pi ni/i_c)} \tag{46}$$

$$\tilde{\mathcal{H}}^*_{dd}(t) = \mathcal{H}_{SS} + \sum_k \sum_{n=-\infty}^{\infty} \sum_{l_k} c^n_{l_k} \mathcal{H}^{l_k}_k e^{-i(2\pi ni/i_c)} \tag{47}$$

where

$$c^n_{l_k} = \frac{(-1)^n \sin\theta_{l_k}}{n\pi + \theta_{l_k}} \qquad \theta_{l_k} = l_k \omega_e t_c/2 \tag{48}$$

The operators $\mathcal{H}^{l_k}_k$ satisfy the following commutation rules:

$$[H^{(0)}, \mathcal{H}^{l_k}_k] = -\omega_e l_k \mathcal{H}^{l_k}_k \tag{49}$$

with

$$l_k = 0, \pm\tfrac{1}{2}, \pm 1 \quad \text{for} \quad k = IS$$

$$l_k = 0, \pm\tfrac{1}{2}, \pm 1, \pm\tfrac{3}{2}, \pm 2 \quad \text{for} \quad k = II \tag{50}$$

Inserting Eqs. (46) and (47) into (45) we obtain:

$$\sum_{n=-\infty}^{\infty} \frac{2\pi n}{t_c} B_n e^{-i(2\pi ni/i_c)} = \sum_{n=-\infty}^{\infty} [H^{(0)}, B_n] e^{-i(2\pi ni/i_c)} - H^{(1)} + \mathcal{H}_{SS} + \sum_k \mathcal{H}^{(0)}_k + \sum_k \sum_{n=-\infty}^{\infty} \sum_{l_k \neq 0} c^n_{l_k} \mathcal{H}^{l_k}_k e^{-i(2\pi ni/i_c)} \tag{51}$$

and for $n \neq 0$ Eq. (51) gives:

$$\frac{2\pi n}{t_c} B_n = [H^{(0)}, B_n] + \sum_k \sum_{l_k \neq 0} c^n_{l_k} \mathcal{H}^{l_k}_k \tag{52}$$

We shall look for the solution of Eq. (52) in the form

$$B_n = \sum_k \sum_{l_k \neq 0} b^n_{l_k} \mathcal{H}^{l_k}_k \tag{53}$$

Substitution of Eq. (53) into Eq. (52) gives:

$$b^n_{l_k} = \frac{c^n_{l_k} t_c}{2(n\pi + \theta_{l_k})} \tag{54}$$

Using the initial condition $C_1(0) = 0$ for B_0 we obtain the expression

$$B_0 = -\sum_{n \neq 0} B_n = -\frac{t_c}{2} \sum_k \sum_{l_k} \left(\cot\theta_{l_k} - \frac{\sin\theta_{l_k}}{\theta^2_{l_k}} \right) \mathcal{H}^{l_k}_k \tag{55}$$

For $n = 0$ Eq. (51) gives

$$H^{(1)} = [H^{(0)}, B_0] + \mathcal{H}_{SS} + \sum_k \mathcal{H}^0_k + \sum_k \sum_{l \neq 0} c^0_{l_k} \mathcal{H}^{l_k}_k \tag{56}$$

Inserting Eq. (55) into (56) and (46) and using relation (49) we obtain:

$$H^{(1)} = \mathcal{H}_{SS} + \sum_k \mathcal{H}^0_k + \sum_k \sum_{l_k \neq 0} \theta_{l_k} \cot\theta_{l_k} \mathcal{H}^{l_k}_k \tag{57}$$

$$C_1(t) = \frac{i_c}{2} \left[-\sum_k \sum_{l_k \neq 0} \left(\cot\theta_{l_k} - \frac{\sin\theta_{l_k}}{\theta^2_{l_k}} \right) \mathcal{H}^{l_k}_k + \sum_k \sum_{n \neq 0} \sum_{l_k \neq 0} \frac{(-1)_n \sin\theta_{l_k}}{(n\pi + \theta_{l_k})^2} \mathcal{H}^{l_k}_k e^{-(2i\pi ni/i_c)} \right] \tag{58}$$

Unitary transformation

$$U_1(t) = [1 + C_1(t)]^+ U^*(t) \tag{59}$$

of Eq. (38) gives

$$i\frac{dU_1(t)}{dt} = [H_{\text{eff}} - H^{(0)} C_1^2(t) + H^{(1)} C_1(t) - C_1(t) \tilde{\mathcal{H}}^*_{dd}(t)] U_1(t) \tag{60}$$

where

$$H_{\text{eff}} = H^{(0)} + H^{(1)} \tag{61}$$

The time-dependent part of the right-hand side of Eq. (60) is proportional to ϵ^2 and is taken into account by means of perturbation theory [3]. So it may be assumed that during the time $\approx T_2$ the spin system will reach a quasi-equilibrium state [3,7]:

$$\rho_{eq} = 1 - \alpha_{eq} H_{eff} \tag{62}$$

For the times $\approx T_2$ we may also neglect the absorption of r.f. field energy by the spin system and use the low energy conservation:

$$Sp[\rho_+(0)H_{eff}] = Sp(\rho_{eq} H_{eff}) \tag{63}$$

which gives:

$$\frac{M_{eq}}{M_0} = \left\{ 1 + 2\left[\sum_k \frac{Sp(H_k^0)^2}{Sp(H^{(0)})^2} + \sum_k \sum_{l_k \neq 0} (\theta_{l_k} \cot \theta_{l_k})^2 \frac{Sp(H_k^{l_k} H_k^{-l_k})}{Sp(H^{(0)})^2} + \frac{Sp(\mathcal{H}_{SS})^2}{Sp(H^{(0)})^2} \right] \right\}^{-1} \tag{64}$$

where M_{eq} is the quasi-equilibrium magnetization in the $\vec{a}$ axis direction and M_0 is the magnetization immediately after the first pulse. The expression (64) shows that the observed quasi-equilibrium magnetization decreases which means that for the times $\approx T_2(\approx 1/||\mathcal{H}_{dd}||)$ occurs with an energy exchange between I and S spin systems. The destruction of the I-spin magnetization may be large if $Sp\mathcal{H}_{SS}^2/Sp(H^{(0)})^2 \gg 1$.

Further evolution of the spin system leads to a decrease of the magnetization under the influence of the time-dependent perturbation.

5. Kinetic equation

In the case where $\omega_e \approx \omega_{loc}^{SS} \gg \omega_{loc}^{IS} \gg \omega_{loc}^{II}$, which can take place, for example, if $\gamma_S \gg \gamma_I$, the Hamiltonian in Eq. (38) can be divided into two parts:

$$\mathcal{H}(t) = \mathcal{H}_0 + V(t) \tag{65}$$

where

$$\mathcal{H}_0 = H^{(0)} + \mathcal{H}_{SS} \tag{66}$$

$$V(t) = V_0(t) + V_1(t) \tag{67}$$

The perturbation $V(t)$ consists of the time-independent part

$$V_0 = \sum_k \mathcal{H}_k^0 + \sum_k \sum_{l_k \neq 0} c_{l_k}^0 \mathcal{H}_k^{l_k} \tag{68}$$

$$V_1(t) = \sum_k \sum_{n \neq 0} \sum_{l_k \neq 0} c_{l_k}^n \mathcal{H}_k^{l_k} e^{-i(2\pi n/t_c)} \tag{69}$$

After the unitary transformed [7]

$$U_2(t) = \prod_{m \neq 0} \exp\left[i\frac{2\pi m}{t_c}(\vec{a}\vec{\Sigma}) \right] e^{-iA_m} \times \exp\left[-i\frac{2\pi m}{t_c}(\vec{a}\vec{\Sigma}) \right] U^*(t) \tag{70}$$

where

$$A_m = \frac{it_c}{2} \sum_k \sum_{l_k \neq 0} \frac{c_{l_k}^{-m}}{l_k(m\pi + \omega_e t_c/2)} \mathcal{H}_k^{l_k} \tag{71}$$

Eq. (38) gives

$$i\frac{dU_2(t)}{dt} = \left[H^{(0)} + \mathcal{H}_{SS} + \sum_k \mathcal{H}_k^0 + \sum_k \sum_{l_k \neq 0} c_{l_k}^n \mathcal{H}_k^{l_k} + V_2(t) \right] U_2(t) \tag{72}$$

where

$$V_2(t) = \sum_{mn} (e^{i(2\pi m/t_c)} R_m^n + e^{-(2\pi m/t_c)} R_m^{-n}) \tag{73}$$

The spin system can be characterized by the two integrals of motion $H^{(0)}$ and $\mathcal{H}_{SS}$, ($[H^{(0)}, \mathcal{H}_{SS}] = 0$), and on time $\approx T_2$ its state operator has the form [3,7]

$$\rho_{eq} = 1 - \alpha H^{(0)} - \beta \mathcal{H}_{SS} \tag{74}$$

In the course of the further evolution of the spin system two processes take place. At first, the perturbation V_0, which does not commute either with $H^{(0)}$ or with $\mathcal{H}_{SS}$ leads to the thermal equilibrium between I and S spin systems which is the reason for the magnetization decrease [6,8,9]. Secondly, $V_1(t)$ causes the resonance processes [3,7] where n I-spins absorb the r.f. field energy $n\omega_e$ and the S-spin system absorbs the r.f. field energy $\omega_n^m = 2m\pi/t_c - n\omega_e$. This second process also leads to a decrease of magnetization.

The equations that describe the time evolution of the quantities α and β from Eq. (74) may be obtained using a well known procedure [3,7]. The result is:

$$\frac{d\alpha}{dt} = -\sum_{mn} W_n^m \left(\alpha - \frac{\omega_n^m}{\omega_e}\beta\right) - T_{IS}^{-1}(\alpha - \beta)$$

$$\frac{d\beta}{dt} = \sum_{mn} W_n^m \frac{(\omega_n^m)^2}{(\omega_{loc}^{SS})^2}\left(\frac{\omega_e}{\omega_n^m}\alpha - \beta\right) + T_{IS}^{-1}(\alpha - \beta) \quad (75)$$

Here T_{IS}^{-1} is inverse cross-relaxation time:

$$T_{IS}^{-1} = \Gamma_{IS}\int_0^\infty d\tau \cos\omega_e\tau\xi(\tau) \quad (76)$$

where

$$\Gamma_{IS} = \sum_{l\neq 0} c_l^0 c_{-l}^0 l^2 Sp(\mathcal{H}_{IS}^l \mathcal{H}_{IS}^{-l})/Sp(\vec{a}\vec{\Sigma})^2$$

$$\text{for} \quad k = IS \quad (77)$$

$$\xi(\tau) = Sp\left\{\left[\sum_i\sum_{mn} d_{mn}^i p_{mn}^i\right]\left[\sum_i\sum_{mn} d_{mn}^i p_{mn}^i(\tau)\right]\right\}\Big/ \times Sp\left(\sum_i\sum_{mn} d_{mn}^i p_{mn}^i\right)^2 \quad (78)$$

$$p_{mn}^i(\tau) = \exp(i\mathcal{H}_{SS}\tau)p_{mn}^i\exp(-i\mathcal{H}_{SS}\tau) \quad (79)$$

W_n^m are the rates of relaxation transitions:

$$W_n^m = \sum_k\sum_{l=0} l_k^2\int_0^\infty d\tau[q_n^m(\tau)e^{il_k\omega_n^m\tau} + (79)]/Sp(\vec{a}\vec{\Sigma})^2 \quad (80)$$

where

$$q_n^m(\tau) = Sp[R_m^n R_m^{-n}(\tau)] \quad (81)$$

$$R_m^{-n}(\tau) = \exp(i\mathcal{H}_{SS}\tau)R_m^{-n}\exp(-i\mathcal{H}_{SS}\tau) \quad (82)$$

To calculate the kinetic coefficients (76) and (80) the correlation functions $\xi(\tau)$ [2,6] and $q_n^m(\tau)$ are needed. Coefficient Γ_{IS} is connected with the second moment of the quadrupole-resonance line of the I spins [6].

The dependence of the kinetic coefficient T_{IS}^{-1} on the pulse sequence parameters is

$$T_{IS}^{-1} \approx \frac{\sin^2\theta_l}{\theta_l^2} \quad (83)$$

For the W_n^m it is easy to calculate their dependence on the pulse period t_c [7]. For example, if $\Delta = 0$ and $\phi = \pi/2$, the main effect on the spin system dynamics is due to the term R_4^I, which leads to the time of magnetization decrease $\approx t_c^{-4}$ for homonuclear and $\approx t_c^{-8}$ for heteronuclear dipole–dipole interactions.

At last, let us consider a case where $\omega_e \gg \omega_{loc}^{SS}$, ω_{loc}^{IS}, ω_{loc}^{II}. This case is similar to the previously considered one, the difference being that the quasi-equilibrium state operator is:

$$\rho_{eq} = 1 - \alpha H^{(0)} - \beta\left(\mathcal{H}_{SS} + \sum_k \mathcal{H}_k^0 + \sum_k\sum_{l=0} c_{l_k}^0 \mathcal{H}_k^{l_k}\right) \quad (84)$$

In the case in question the kinetic equations for α and β are similar to those in Eq. (75) but without the last right hand side terms proportional to T_{IS}^{-1}.

6. Conclusion

The results presented in this paper show the multiple-pulse NQR method to be an effective means of molecular structure, interaction and motion investigations based on the use of nuclear resonance and relaxation data to obtain information about the strong heteronuclear dipole–dipole interactions.

7. References

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