INTERFERENCE EFFECT IN NUCLEAR MAGNETIC RELAXATION. III

By J. S. Blicharski

Institute of Physics, Jagellonian University, Cracow*

Institute of Nuclear Physics, Cracow

(*Received December 11, 1969*)

Numerical results for the interference effect of different intramolecular interactions in nuclear magnetic relaxation are presented for one- and two-spin systems. The dipolar, quadrupolar and spin-rotational interaction and anisotropy of electronic screening are taken into account.

In the previous publication (paper II) the theory of interference effect in nuclear magnetic relaxation was presented for like and unlike two-spin systems. It was shown that in the presence of intramolecular dipolar interaction G^d, quadrupolar interaction G^Q and anisotropy of electronic screening G^σ one can find three possibile kinds of interference: $D\sigma$, $Q\sigma$ and QD.

Due to the interference effects a nonexponential (multi-exponential) time dependence of longitudinal component $\langle I_z\rangle(t)$ and transversal component $\langle I_+\rangle(t) = \langle I_x\rangle(t)+i\langle I_y\rangle(t)$ of the nuclear spin (magnetization) can appear

$$I_0-\langle I_z\rangle(t) = [I_0-\langle I_z\rangle(0)] \sum_k c_k e^{-\lambda_k \frac{t}{T_1}}, \tag{1}$$

$$\langle I_+\rangle(t) = \langle I_+\rangle(0)e^{i\omega_0 t} \sum_k c'_k e^{-\lambda'_k \frac{t}{T_2}}, \tag{2}$$

where

$$\sum_k c_k = \sum_k c'_k = \sum_k \lambda_k c_k = \sum_k \lambda'_k c'_k = 1, \tag{3}$$

T_1 and T_2 are the spin-lattlice and spin-spin relaxation times respectively, I_0 is the equilibrium value of $\langle I_z\rangle$ and $\omega_0 = \gamma H_0$ is the Larmor precession frequency.

In the case of a system containing two identical nuclei of spin $I = 1/2$ (such as F_2 molecule) at sufficiently high magnetic field H_0 the interference $D\sigma$ of interaction G^d and G^σ gives two-exponential decay both for $[I_0-\langle I_z\rangle(t)]$ and $\langle I_+\rangle(t)$.

* Address: Instytut Fizyki UJ, Kraków 16, Reymonta 4, Polska.

The values c_k and λ_k for $\langle I_z \rangle(t)$ were calculated in paper I as a function of the parameter $\varepsilon = \omega_0 \Delta\sigma/d$, which is proportional to the external magnetic field. In the case of $\varepsilon = 3/2$ it was shown that $c_1 = c_2 = 1/2$ and $\lambda_1 = 1.58$, $\lambda_2 = 0.42$. It was also pointed out that in the presence of a strong spin-rotation interaction G^r (if the spin-rotational and dipolar contribution to the relexation rate are comparable, *i.e.* $\beta_0 = (1/T_1)_{SR}/(1/T_1)_d = 1$) the interference effect $D\sigma$ plays a small role and in consequence the time dependence of $\langle I_z \rangle(t)$ is practically a pure exponential function.

In the present paper numerical results for $D\sigma$ interference are shown in the case of transversal magnetization (Fig. 1). The c_k and λ_k values are presented as a function of ε

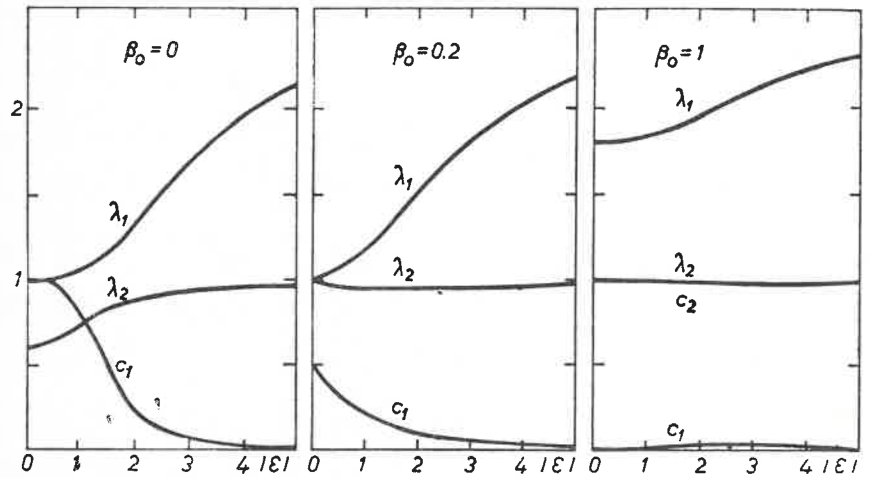

Fig. 1. Calculated values c_k and λ_k as a function of ε and $\beta_0 = 0, 0.2, 1$ for transversal magnetization in the presence of $D\sigma$ interference for a system of two identical spins $I = 1/2$

for $\beta_0 = 0$, 0.2, 1 respectively. Moreover, the $Q\sigma$ and QD interference effect is calculated both for longitudinal and transversal relaxation.

The $Q\sigma$ interference is considered for a nuclear spin $S = 1$ (such as ^{6}Li). The longitudinal magnetization $\langle S_z \rangle$ can be described as a function of time by Eq. (68) and (74) of paper II. The transversal magnetization $\langle S_+ \rangle$ in the presence of $Q\sigma$ interference is governed by the differential equations presented below following from Redfield's density matrix (Redfield 1957)

$$\frac{dy_i}{dt} + i\omega_0 y_i = \sum_k a_{ik} y_k, \qquad (i, k = 1, 2) \tag{4}$$

where

$$y_1 = \langle S_+ \rangle, \quad y_2 = \langle S_+ S_z + S_z S_+ \rangle \tag{5}$$

$$a_{ik} T_{1Q} = \frac{1}{135} \begin{pmatrix} 135 + 56\varepsilon_1^2 + 135\beta_1 & -36\varepsilon_1 \\ -36\varepsilon_1 & 81 + 152\varepsilon_1^2 + 405\beta_1 \end{pmatrix} \tag{6}$$

$$\frac{1}{T_{1Q}} = \frac{3}{8}\,b^2\tau_c = \frac{3}{8}\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c \tag{7}$$

$$\varepsilon_1 = \omega_0\Delta\sigma/b, \qquad \beta_1 = \left(\frac{1}{T_1}\right)_{SR}\Big/\frac{1}{T_{1Q}}. \tag{8}$$

We consider the QD interference effect for a two-spin containing nuclei of spin $I = 1/2$ and $S = 1$ (such as HD). The longitudinal magnetization for these spins can be calculated from Eq. (80) of paper II, whereas transversal magnetization $\langle I_+\rangle(t)$ and $\langle S_+\rangle(t)$ is given by Eq. (4) with indexes (I) and (S) respectively:

$$y_1^{(I)} = \langle I_+\rangle, \quad y_2^{(I)} = \frac{1}{\sqrt{2}}\langle P_2 I_+\rangle = \frac{1}{\sqrt{2}}\langle (3S_z^2 - S(S+1))I_+\rangle \tag{9}$$

$$a_{ik}^{(I)}T_{1Q} = \frac{1}{45}\begin{pmatrix} 320\varepsilon_2^2 + 45\beta_1^{(I)} & 4\sqrt{2}\,\varepsilon_2^2 \\ 4\sqrt{2}\,\varepsilon_2^2 & 27 + 208\varepsilon_2^2 + 45\beta_1^{(I)} + 135\beta_1^{(S)} \end{pmatrix} \tag{10}$$

$$y_1^{(S)} = \langle S_+\rangle, \quad y_2^{(S)} = \frac{2\sqrt{2}}{3}\langle [P_2, S_+]I_z\rangle \tag{11}$$

$$a_{ik}^{(S)}T_{1Q} = \frac{1}{15}\begin{pmatrix} 15 + 24\varepsilon_2^2 + 15\beta_1^{(S)} & -18\varepsilon_2 - 10\varepsilon_2^2 \\ -18\varepsilon_2 - 10\varepsilon_2^2 & 9 + 64\varepsilon_2^2 + 15\beta_1^{(I)} + 45\beta_1^{(S)} \end{pmatrix} \tag{12}$$

where $\varepsilon_2 = d/b$ is the ratio of the dipolar to the quadrupolar constants, $\beta_1^{(I)}$, $\beta_1^{(S)}$ are relative spin-rotational contributions, defined by Eq. (8), for spin I and spin S respectively and $\beta_1^{(I)}/\beta_1^{(S)} \cong (\gamma_I/\gamma_S)^2$. As a special case (such as HD) we take $\beta_1^{(S)} \ll \beta_1^{(I)} \equiv \beta_1$.

The numerical results for the $Q\sigma$ and QD interference effect are presented in Figs. 2–7. It is shown that multi-exponential time dependence can appear both for longitudinal and

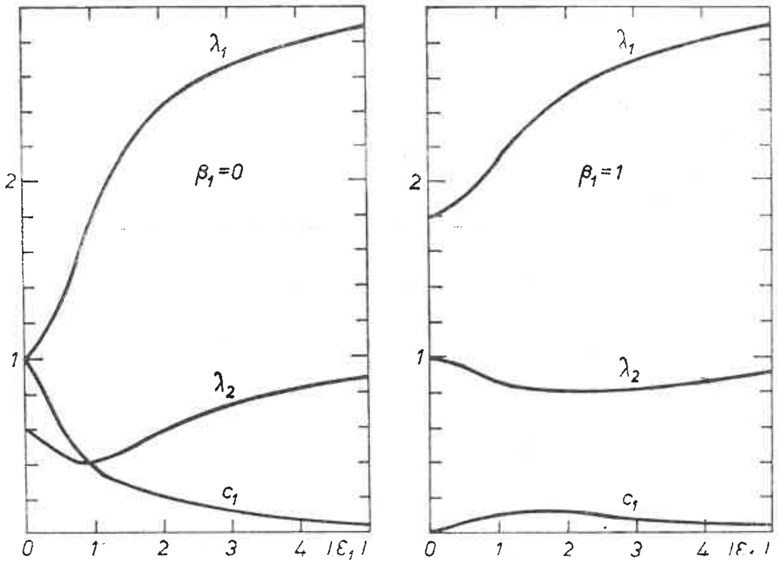

Fig. 2. Calculated values of c_k and λ_k as a function of ε_1 and $\beta_1 = 0, 1$, for longitudinal magnetization in the presence of $Q\sigma$ interference for spin $S = 1$

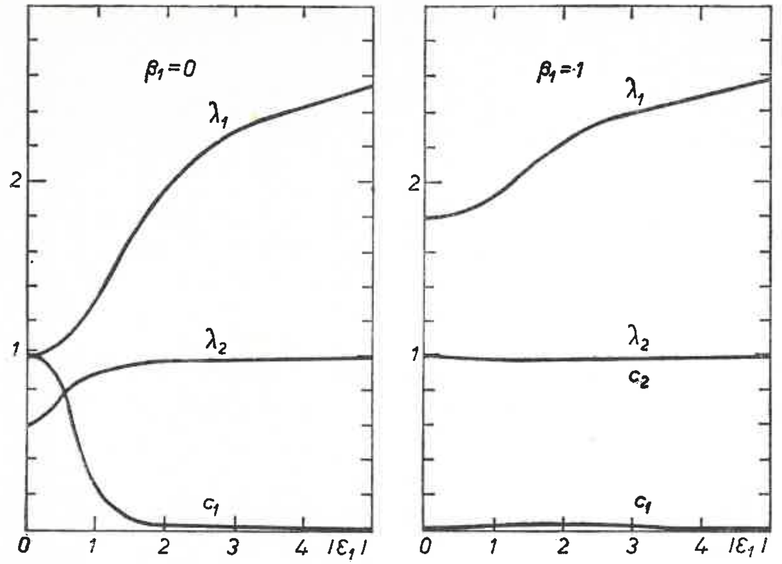

Fig. 3. **Calculated** values c_k and λ_k as a function of ε_1 and $\beta_1 = 0, 1$, for transversal magnetization in the presence of $Q\sigma$ interference for a spin $S = 1$

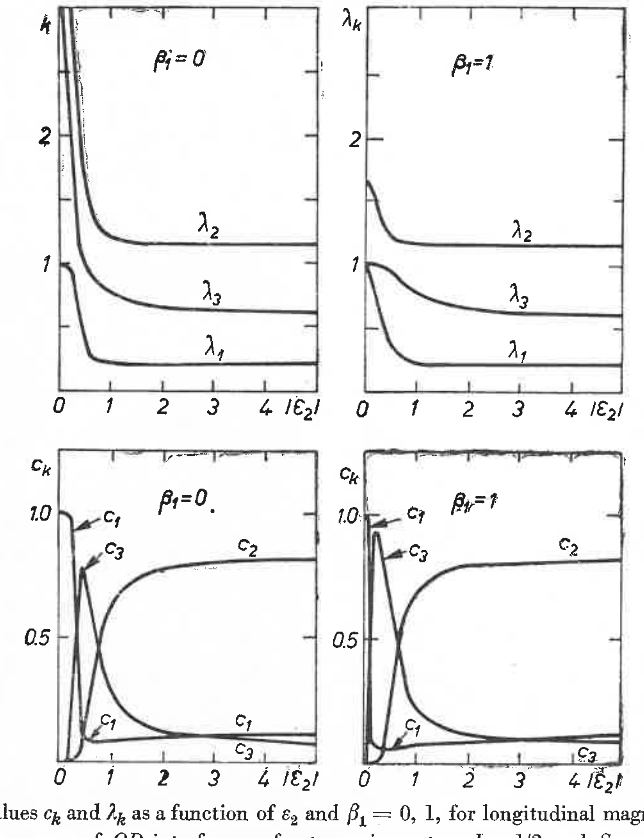

Fig. 4. Calculated values c_k and λ_k as a function of ε_2 and $\beta_1 = 0, 1$, for longitudinal magnetization $\langle I_z \rangle$ in the presence of QD interference for two-spin system $I = 1/2$ and $S = 1$

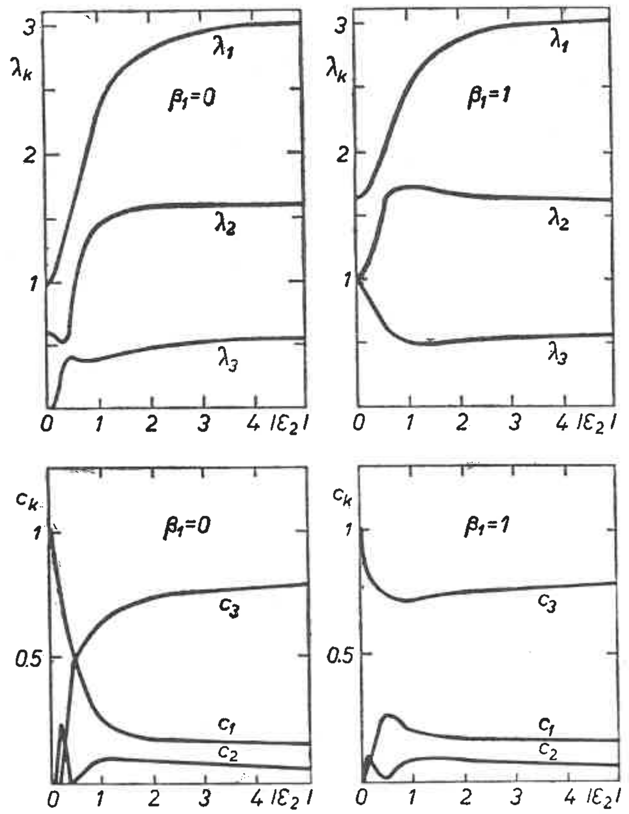

Fig. 5. Calculated values c_k and λ_k as a function of ε_2 and $\beta_1 = 0, 1$, for longitudinal magnetization $\langle S_z \rangle$ in the presence of *QD* interference for two-spin system $I = 1/2$ and $S = 1$

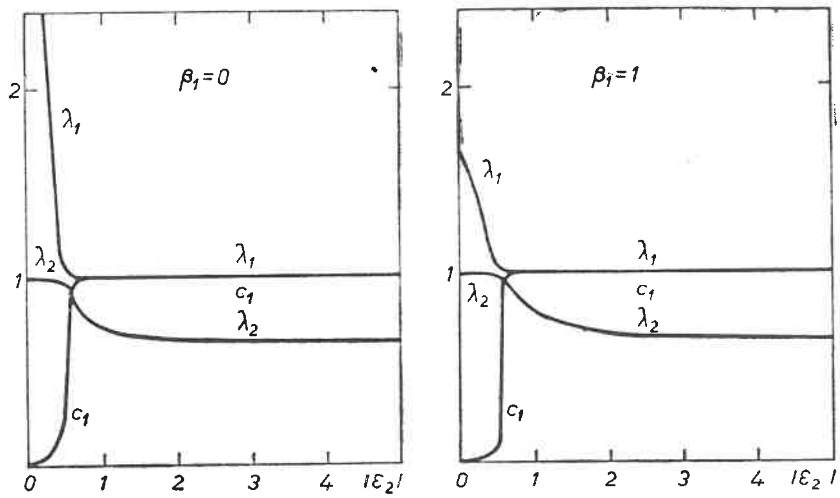

Fig. 6. Calculated values c_k and λ_k as a function of ε_2 and $\beta_1 = 0, 1$, for transversal magnetization $\langle I_+ \rangle$ in the presence of *QD* interference for two-spin system $I = 1/2$ and $S = 1$.

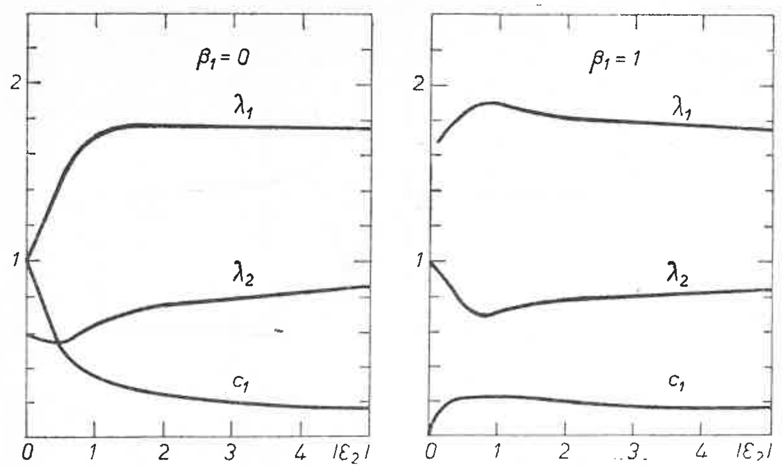

Fig. 7. Calculated values c_k and λ_k as a function of ε_2 and $\beta_1 = 0, 1$, for transversal magnetization $\langle S_+ \rangle$ in the presence of QD interference for two-spin system $I = 1/2$ and $S = 1$

transversal nuclear magnetization, according to Eq. (1) and (2). One can call it the multi-exponential relaxation process. In the case of $Q\sigma$ interference (Figs 2 and 3) the two-exponential relaxation process takes place, whereas for QD interference in the two-spin system $I = 1/2$, $S = 1$ (Figs 4–7) one can expect three-exponential and two-exponential processes for longitudinal and tranversal relaxation respectively.

REFERENCES

Blicharski, J. S., *Phys. Letters*, **24A**, 608 (1967), (paper I).
Blicharski, J. S., *Acta Phys. Polon.*, **36**, 211 (1969), (paper II).
Redfield, A. G., *IBM J. Res. Develop.*, **1**, 19 (1957).