Journal of Molecular Structure, 58 (1980) 323–336
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

A QUANTUM-KINETIC APPROACH TO THE THEORY OF NUCLEAR QUADRUPOLE RELAXATION

M.A. MARTSENJUK and I.G. SHAPOSHNIKOV
Department of Theoretical Physics, University of Perm, Perm (U.S.S.R.)

ABSTRACT

A generalization of the approach to the magnetic resonance and relaxation problems based on the treating of the lattice as a classical system with random parameters is presented. The main point is taking into account the mutual influence of the spin system and the lattice motions more completely than it conventionally used to be done. The method developed is applied to the problem of the nuclear quadrupole relaxation due to the random rotations of nuclei with $I=3/2$ in the case of the axially symmetric electric field gradient. The relaxation time temperature dependence is obtained in the temperature region where the Bayer theory is not valid.

INTRODUCTION

To study the magnetic resonance and relaxation phenomena, in particular, the nuclear quadrupole relaxation problems, different methods of the quantum theory of non-equilibrium processes are used. In many cases the lattice is treated as a classical system with random parameters (random trajectory method). When realizing this approach, one usually takes account of the fact that the spin system motion is modulated by the random lattice motion but neglects the backward influence of the spin system on the lattice motion. Technically, one puts down the quantum mechanical equation of motion for the spin system with Hamiltonian containing the lattice random parameters but uses the Einstein-Fokker equation for these parameters only, and then one tries to use the distribution function given by this Einstein-Fokker equation to get average characteristics of the spin system motion (see, for example, (ref.1)). In the paper presented a generalization of this procedure is proposed aimed at the taking into account the mutual influence of the spin system and lattice motions more completely.

The main points of the method here proposed are these: since the Hamiltonian H(t) of the spin system contains the lattice random parameters $x_i(t)$, the spin system state vector components $c_m(t)$ are the random functions, too (the spin system states are supposed to be pure); the states of the whole system consisting of the spin system and the lattice as sub-systems are described statistically by means of the distribution function $W(c_m, x_i, t)$; the Schrödinger equation for c_m and the classical dynamical equations for x_i with regular and random "forces" (to get these equations, one has to know the concrete kind of the lattice motion in question) are to be taken as the Langevin equations of the problem; in the way known from the theory of random processes (see (ref. 2)), these equations lead to the Einstein-Fokker equation for W; finally, the kinetic theory method similar to that used in the theory of gases with inner degrees of freeedom (ref. 3) give the equations of motion for the first order moments $\langle\varphi_\alpha\rangle(t)$ of the random functions $\varphi_\alpha(c_m, x_i)$ of t chosen so as to make it possible to obtain the macroscopic coordinates of the spin system we are interested in; such a choice, like the choice of macroscopic coordinates themselves, is always a hypothesis. This method makes no use of any perturbation theory technics, therefore it allows one to consider the relaxation problems in the wider temperature region than the conventional methods can do. The procedure outlined is described here-after more in detail and then applied to the Bayer problem (ref. 4); it gives some new results concerning the relaxation time temperature dependence which can be checked up experimentally.

RESULTS

General approach

Let us put down the classical equations of motion for x_1 in the form

$$\dot{x}_i = v_i + f_i \qquad (1)$$

where $v_i(x,t)$ and $f_i(x,t)$ with $x \equiv \{x_i\}$ are regular and random functions respectively. In many cases of interest f_i are δ-correlated with respect to t

$$\langle f_i(x,t) f_k(x',t')\rangle = c_{ik}(x,x',t)\,\delta(t-t') \qquad (2)$$

(white noise hypothesis) which certainly doesn't suppose the δ-correlation of x_i; here and hereafter $< >$ denotes the statistical averaging. The Schrödinger equation for the spin system is

$$i\hbar\dot{c}_m = \sum_n H_{mn} c_n \tag{3}$$

For $y \equiv \{x_i, \mathrm{Re}\, c_m, \mathrm{Im}\, c_m\}$ it follows from (1)-(3) that

$$\dot{y}_p = V_p + F_p \tag{4}$$

with regular $V_p\ (y,t)$ and δ-correlated random $F_p(y,t)$

$$<F_p(y,t)\ F_q(y',t')> = C_{pq}(y,y',t)\ \delta(t-t') \tag{5}$$

Considering (4) as the Langevin equations of the problem in question and using the method developed in (ref. 2), we get the Einstein-Fokker equation for the distribution function $W(y, t)$

$$\frac{\partial W}{\partial t} + \sum_p \frac{\partial}{\partial y_p}(A_p W) - \frac{1}{2}\sum_{p,q}\frac{\partial^2}{\partial y_p \partial y_q}(B_{pq} W) = 0 \tag{6}$$

with

$$\begin{aligned} A_p(y,t) &= V_p(y,t) + \frac{1}{2}\left[\sum_q \frac{\partial}{\partial y'_q} C_{pq}(y,y',t)\right]_{y'=y} \\ B_{pq}(y,t) &= C_{pq}(y,y,t) \end{aligned} \tag{7}$$

We are in need of the equations of motion for the first order moments

$$<\varphi_\alpha> = \int dy\, W \varphi_\alpha \tag{8}$$

of the properly chosen random functions $\varphi_\alpha(y)$ of t. Let us look for the non-equilibrium solution of the equation (6) in the form

$$W = W_0\left(1 + \sum_\alpha \alpha_\alpha \varphi_\alpha\right) \tag{9}$$

where $W_0(y)$ is the equilibrium (steady-state) solution supposed to be known and the regular functions $\alpha_\alpha(t)$ are to be obtained from (6). From (8) and (9) we get

$$<\varphi_\alpha> = <\varphi_\alpha>_0 + \sum_\beta <\varphi_\alpha \varphi_\beta>_0\ \alpha_\beta \tag{10}$$

where $< >_0$ denots the equilibrium statistical averaging, that is, $< >$ with W_0. Finally, multiplication of (6) by φ_α, integration with respect to y, and taking into account (10) give the linear equations of motion for $<\varphi_\alpha>(t)$

$$<\dot{\varphi}_\alpha> = -\sum_\beta K_{\alpha\beta} <\varphi_\beta> \tag{11}$$

Bayer problem

To illustrate the possibilities of using the method outlined in the theory of the nuclear quadrupole relaxation phenomena, let us consider the Bayer problem (ref. 4), that is, the problem of the nuclear quadrupole relaxation due to the random rotations of each nucleus around a fixed axis (one well potential) in the case of the axial symmetry of the electric field gradient at moving nuclei, the direct internuclear interactions being neglected.

Let $\vec{n}$ and $\vec{e}$ be, for a nucleus considered, the unit vectors of the fixed axis mentioned and of the field gradient symmetry axis (supposed to be coinciding with the symmetry axis of the molecule containing the nucleus in question) respectively, so that the direction of $\vec{n}$ is the equilibrium direction of $\vec{e}$; and let θ be the angle between the directions of $\vec{e}$ and $\vec{n}$. In the theory developed in (ref.4) the smallness of the amplitude of random motion $\theta(t)$ is assumed which makes it possible, firstly, to consider this motion as that of a randomly influenced torsional harmonic oscillator which is treated in (ref. 4) in the quantum way, and, secondly, to apply the conventional perturbation theory calculation of the relaxation transition probabilities. It gives the temperature dependence of the measured relaxation time T_1 (T) which proved to be very complicated; in the temperature region of practical interest

$$T_D \lesssim T \ll T_m \qquad (12)$$

where T_D and T_m are the Debye temperature for the torsional phonons and the orientational melting-point respectively, the simple approximate result takes place

$$(T_1)^{-1} \sim T^2 \qquad (13)$$

In the region $T \lesssim T_m$ which is certainly of interest as well (in particular, from the point of view of the study of phase transitions) the theory (ref. 4) is not valid, these temperatures being too high for the harmonic oscillator approximation could be sufficient.

To apply our method to the problem in question, we have to assume that $T \gtrsim T_D$ as in (12); it is necessary for the classical treatment of the lattice motion would be acceptable. On the other hand, we abandon the assumption $T \ll T_m$, our theory using no perturbation theory calculation; so the temperatures $T \lesssim T_m$ are included in the consideration, too.

Let the molecule considered move in a potential field $U(\vec{e})$ according to the following equation of motion for the angular velocity $\vec\omega$:

$$J\dot{\vec\omega} = -\lambda\vec\omega - \hat{\vec L}U + \vec K \qquad (14)$$

with

$$\hat{\vec L} \equiv \vec e \times \frac{\partial}{\partial \vec e} \qquad (15)$$

where J and λ are the moment of inertia of the molecule and the coefficient of friction respectively and $\vec K$ is the δ-correlated random turning moment. The characteristic time of the regular part of the change of $\vec\omega$ is of the order of magnitude of $J/\lambda \ll \nu_Q^{-1}$ where ν_Q is proportional to the quadrupole resonance frequency (see (ref. 4)). It means that for the time intervals of interest we may put $\dot{\vec\omega} = 0$; then (14) gives

$$\vec\omega = -\lambda^{-1}(\hat{\vec L}U - \vec K) \qquad (16)$$

Putting (16) into the kinematical expression $\dot{\vec e} = \vec\omega \times \vec e$, we obtain for $\vec e$ the equation of motion of the type (1)

$$\dot{\vec e} = -\lambda^{-1}[(\hat{\vec L}U)\times\vec e] + \lambda^{-1}\vec K\times\vec e \qquad (17)$$

The Hamiltonian of the quadrupole nucleus in the molecule interacting with the inhomogeneous electric field of its surroundings may be put down as follows:

$$\hat H = \hbar\nu\left[e_i e_k - (1/3)\delta_{ik}\right]\hat T_{ik} \qquad (18)$$

with

$$\hat T_{ik} \equiv (1/2)\left[\hat I_i \hat I_k + \hat I_k \hat I_i - (2/3)\hat I^2 \delta_{ik}\right] \qquad (19)$$

where $\nu \equiv \nu_Q(0)$, $\nu_Q(T)$ being proportional to the NQR frequency in function of temperature; here and hereafter the usual summation rule is used. The equation (17) and the Schrödinger equation (3) in the I_z-representation, the z-axis being chosen along the direction of $\vec n$, with $\hat H$ from (18) lead to the Einstein-Fokker equation (6) for $W(\vec e,\{c_n\},t)$ which may be written down in the following form:

$$\frac{\partial W}{\partial t} + \hat D W = 0 \qquad (20)$$

with

$$\hat{D} \equiv (i\hbar)^{-1}\sum_{m,n}\left[\frac{\partial}{\partial c_m}(H_{mn}c_n) - \frac{\partial}{\partial c_m^*}(H_{mn}^* c_n^*)\right] - \tau_B^{-1}\hat{\vec{L}}\cdot\left[\hat{\vec{L}} + (kT)^{-1}(\hat{\vec{L}}U)\right] \qquad (21)$$

(for the orientational term in the right hand side of (21) see (ref. 5)); here $\tau_B \equiv \lambda/kT$ is the characteristic time of the orientational Brownian diffusion. The equilibrium solution of (20) is

$$W_0 \sim \exp(-U/kT) \qquad (22)$$

Now, we have to choose the macroscopic coordinates of the spin system and the random functions of t whose first order moments make it possible to find the macroscopic coordinates chosen. It seems reasonable to take as the macroscopic coordinates the statistically averaged populations $\langle P_m\rangle \equiv N_m$ of the $\langle\hat{H}\rangle_0$ eigenstates and their change rates $\dot{N}_m \equiv R_m$. Let $\hat{\rho}$ be the state operator of the spin system. In the I_z - representation which we have accepted we have $\rho_{mn} = c_m c_n^*$ (the spin system states have been supposed to be pure), $P_m = c_m c_m^*$, and

$$N_m = \langle c_m c_m^* \rangle = \int d\{\vec{e},\{c_n\}\} W c_m c_m^* \qquad (23)$$

(one has to take into account that $\sum_i e_i^2 = 1$ and $\sum_k |c_k|^2 = 1$ when calculating the integral in (23)). Using the operators $\hat{E}_m$ defined by $(\hat{E}_m)_{pq} = \delta_{pm}\delta_{qm}$ and having the properties $[\hat{E}_m, \hat{E}_n] = 0$, $Sp\,\hat{E}_m\hat{E}_n = \delta_{mn}$, we obtain from (23)

$$N_m = \langle Sp\,\hat{\rho}\hat{E}_m \rangle \qquad (24)$$

which gives

$$R_m = (i\hbar)^{-1}\langle Sp[\hat{H},\hat{\rho}]\hat{E}_m \rangle \qquad (25)$$

here and herafter $[\,,\,]$ denotes a commutator. Expressions (24) and (25) show that the random functions of t above mentioned are $Sp\hat{\rho}\hat{E}_m$ and $(i\hbar)^{-1}Sp[\hat{H},\hat{\rho}]\hat{E}_m$. According to our procedure, we put down the non-equilibrium solution of (20) as follows:

$$W = W_0\left(1 + \sum_m \alpha_m Sp\hat{\rho}\hat{E}_m + \sum_m \beta_m (i\hbar)^{-1} Sp[\hat{H},\hat{\rho}]\hat{E}_m\right. \qquad (26)$$

The relations of the type (10) between the moments of the random functions and the parameters $\alpha_m(t)$, $\beta_m(t)$ are

$$N_m - N_m^{(0)} = [2(I+1)(2I+1)]^{-1}\alpha_m \tag{27}$$

$$R_m = [2\hbar^2(I+1)(2I+1)]^{-1}\sum_n M_{mn}\beta_n \tag{28}$$

here the real symmetric matrix

$$M_{mn} \equiv -< Sp[\hat{E}_m,\hat{H}][\hat{E}_n,\hat{H}]>_0 \tag{29}$$

is used, and $N_m^{(0)} = < Sp\hat{\rho}\hat{E}_m>_0$ are the equilibrium values of N_m. To get these relations, the formulae

$$< c_m c_n^* >_0 = (2I+1)^{-1}\delta_{mn} \tag{30}$$

$$< c_m c_n^* c_p c_q^* >_0 = [2(I+1)(2I+1)]^{-1}(\delta_{mn}\delta_{pq} + \delta_{mq}\delta_{np}) \tag{31}$$

have been obtained and the equality of the normalisation condition for W and for W_0 used which gives $\sum_m \alpha_m = 0$.

Finally, our scheme gives the equations of motion for the macroscopic coordinates N_m, R_m

$$\dot{N}_m' = R_m \tag{32}$$

$$\dot{R}_m = -[2\hbar^2(I+1)(2I+1)]^{-1}\sum_n(\tau^{-1}F_{mn} + \hbar^{-1}G_{mn})\beta_n - \hbar^{-2}\sum_n M_{mn}N_n' \tag{33}$$

where $N_m' \equiv N_m - N_m^{(0)}$ and the real symmetric matrix F_{mn} and real antisymmetric one G_{mn} are defined in the following manner:

$$F_{mn} \equiv -< Sp(\hat{L}_i[\hat{E}_m,\hat{H}])(\hat{L}_i[\hat{E}_n,\hat{H}])>_0 \tag{34}$$

where $\hat{L}_i$ are the i-components of the vector operator $\vec{L}$, and

$$G_{mn} \equiv -i < Sp\left[[\hat{E}_m, \hat{H}], \hat{H}\right][\hat{E}_n, \hat{H}] >_0 \qquad (35)$$

In the right hand side of (33) the term with τ_B^{-1} is the principal one, the reason being that $M_{mn} \sim F_{mn} \sim (\hbar\nu)^2$, $G_{mn} \sim (\hbar\nu)^3$ and that $\tau_B \ll \nu^{-1}$ which one easily verifies using the corresponding data from (ref. 4). So the characteristic time of change of R_m is τ_B which leads to the conclusion that we may put $\dot{R}_m=0$ for the time intervals we are interested in considering of. After doing that and neglecting $\hbar^{-1}G_{mn}$ in comparision to $\tau_B^{-1}F_{mn}$, we obtain the equations of motion for N_m' in the following final form:

$$\dot{N}_m' = \left[2\hbar^2(I+1)(2I+1)\right]^{-1} \sum_n M_{mn}\beta_n \qquad (36)$$

where β_m are to be expressed in terms of N_m' by means of solving the system of the algebraic equations

$$\sum_n F_{mn}\beta_n = -2\tau_B(I+1)(2I+1)\sum_n M_{mn}N_n' \qquad (37)$$

To continue our consideration in a somewhat more concrete manner, let us assume the following expression of the potential $U(\vec{e})$:

$$(kT)^{-1}U = -\xi\vec{n}\cdot\vec{e} \qquad (38)$$

(one well potential) with $\xi \equiv U_0/kT \sim T_m/T$ where U_0 is the depth of the well and T_m the orientational melting-point.

To begin with, consider briefly the case where the angle θ between $\vec{e}$ and $\vec{n}$ is small (ref. 4). As in (ref. 4), let the motion of $\vec{e}$ take place in the plane $(\vec{n}, \vec{j})$, where $\vec{j}$ is the unit vector perpendicular to $\vec{n}$. We have approximately

$$\vec{e} = \theta\vec{j} + (1-\theta^2/2)\vec{n} \qquad (39)$$

and

$$\hat{H} = \hat{H}_0 + \theta\hat{H}_1 + \theta^2\hat{H}_2$$

where $\hat{H}_0$ commutes with E_m. It gives

$$M_{mn}=-\langle\theta^2\rangle_0\,Sp[\hat{E}_m,\hat{H}_1][\hat{E}_n,\hat{H}_1]-\langle\theta^4\rangle_0\,Sp[\hat{E}_m,\hat{H}_2][\hat{E}_n,\hat{H}_2]$$

$$F_{mn}=-Sp[\hat{E}_m,\hat{H}_1][\hat{E}_n,\hat{H}_1]-\langle\theta^2\rangle_0\,Sp[\hat{E}_m,\hat{H}_2][\hat{E}_n,\hat{H}_2] \qquad (41)$$

To calculate $\langle\theta^2\rangle_0$ and $\langle\theta^4\rangle_0$, one has to accept that approximately U is proportional to θ^2 which makes (22) become the harmonic oscilator coordinate distribution. Putting (41) into (36) and (37), we find that for some transitions the temperature dependence of the invers relaxation time is $\sim$ T, and for other ones $\sim T^2$, which is just the case in Bayer theory (ref. 4).

Now let us turn to the potential (38) without assuming θ to be small but confine ourself to the practically interesting simple case I=3/2. We are in need of the formulae obtained in (ref. 6)

$$\langle\vec{e}\rangle_0 \equiv L_1\vec{n}$$

$$\langle e_i e_k\rangle_0 = L_2 n_i n_k + L_1\xi^{-1}\delta_{ik}$$

$$\begin{aligned}\langle e_i e_k e_l e_m\rangle_0 = {} & L_4 n_i n_k n_l n_m + L_3\xi^{-1}(n_i n_k\delta_{lm}+n_i n_l\delta_{km}+ \\ & + n_i n_m\delta_{il}+n_k n_l\delta_{im}+n_k n_m\delta_{il}+n_l n_m\delta_{ik})+ \\ & + L_2\xi^{-2}(\delta_{ik}\delta_{lm}+\delta_{il}\delta_{km}+\delta_{im}\delta_{kl})\end{aligned} \qquad (42)$$

here functions $L_n(\xi)$ are connected with one another by the recurrent formulae

$$L_{n-1}-L_{n+1}=(2n+1)\xi^{-1}L_n \qquad (43)$$

with

$$L_0=1\,,\quad L_1=\mathrm{cth}\,\xi-\xi^{-1} \qquad (44)$$

where L_1 is the Langevin function. Using (42), we get for arbitrary I

$$M_{mn}=-2(2L_3\xi^{-1}n_in_k+L_2\xi^{-2}\delta_{ik})\ \mathrm{Sp}[\hat{E}_m,\hat{T}_{il}][\hat{E}_n,\hat{T}_{kl}],$$

$$F_{mn}=-[(L_2-4L_3\xi^{-1})n_in_k+(L_1\xi^{-1}-2L_2\xi^{-2})\delta_{ik}]\mathrm{Sp}[\hat{E}_m,\hat{T}_{il}][\hat{E}_n,\hat{T}_{kl}] \qquad (45)$$

where for I=3/2:

$$n_in_k\,\mathrm{Sp}[\hat{E}_m,\hat{T}_{il}][\hat{E}_n,T_{kl}]=3\begin{bmatrix}-1&1&&\\1&-1&&\\&&-1&1\\&&1&-1\end{bmatrix}$$

$$\mathrm{Sp}[\hat{E}_m,\hat{T}_{ik}][\hat{E}_n,\hat{T}_{ik}]=6\begin{bmatrix}-2&1&1&\\1&-2&&1\\1&&-2&1\\&1&1&-2\end{bmatrix} \qquad (46)$$

in (46) the indices m and n increas from right to left and from up to down, the left up corner indices being -3/2, -3/2.

Our results become much simpler to discuss if we replace N_m' by the linear combinations n_m

$$n_1\equiv(N'_{3/2}-N'_{1/2})+(N'_{-3/2}-N'_{-1/2})$$

$$n_2\equiv(N'_{3/2}-N'_{1/2})-(N'_{-3/2}-N'_{-1/2})$$

$$n_3\equiv(N'_{3/2}-N'_{-3/2})+(N'_{1/2}-N'_{-1/2}) \qquad (47)$$

$$n_4\equiv N'_{3/2}+N'_{1/2}+N'_{-1/2}+N'_{-3/2}$$

and the same for β_m ; then (36) give

$$\dot{n}_m=-(\tau_m)^{-1}n_m \qquad (48)$$

for m=1, 2, 3 and $\dot{n}_4=0$ in accordance with the normalization condition. The relaxation times entering (48) are

$$\tau_1\equiv(96\tau_B\nu^2)^{-1}(16+\xi^2)L_2\Big/(\xi L_1-3L_2)^2 \qquad (49)$$

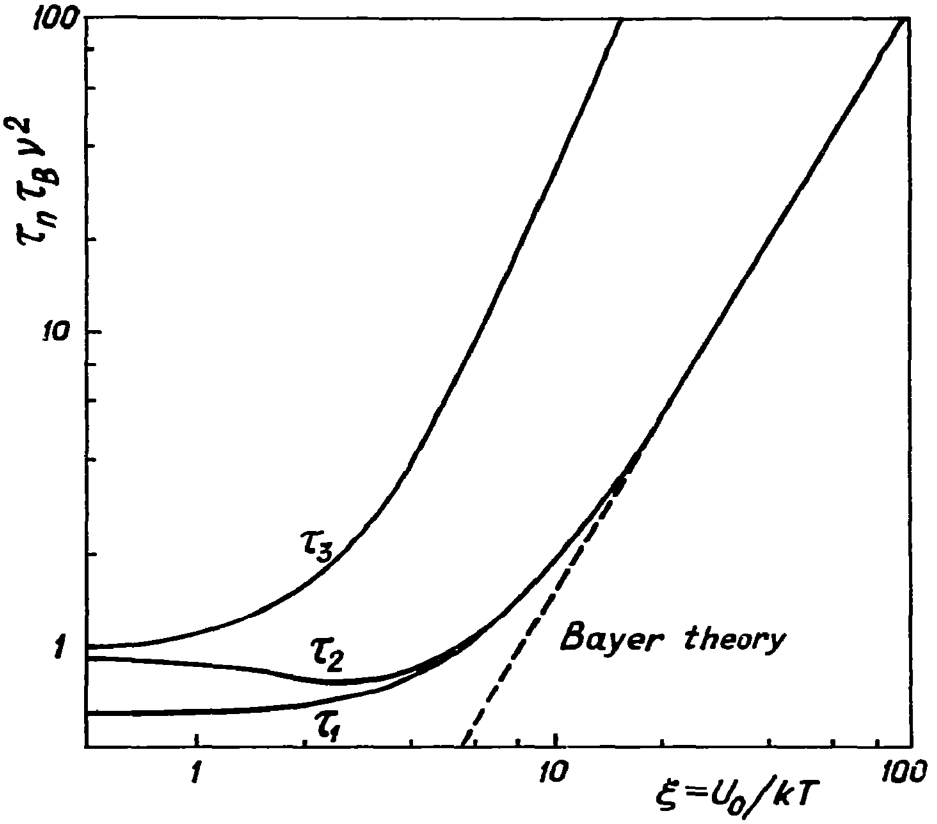

Fig. 1. The temperature dependence of the relaxation times.

$$\tau_2 \equiv (96\,\tau_B \nu^2)^{-1}(\xi^2 L_2 - 2\xi L_1 + 16 L_2)/(\xi L_1 - 4L_2)^2 \tag{50}$$

$$\tau_3 \equiv (48\,\tau_B \nu^2)^{-1}(\xi L_1 - L_2)/L_2^2 \tag{51}$$

The temperature dependence of relaxation times τ_m is shown in Fig. 1. Using the asymptotic expressions

$$\begin{aligned} L_1 &\approx 1 - \xi^{-1} + 2\exp(-2\xi) \\ L_2 &\approx 1 - 3(\xi^{-1} - \xi^{-2}) - 6\,\xi^{-1}\exp(-2\xi) \end{aligned} \tag{52}$$

for $\xi \gtrsim 1$ and

$$L_n \to \left[(2n+1)!!\right]^{-1} \xi^n \tag{53}$$

for, $\xi \to 0$, one easily finds that inside the temperature region $T_D \lesssim T \lesssim T_m$ for the low temperatures (big ξ) we have $\tau_1 \sim \tau_2 \sim (96\tau_B \nu^2)^{-1} U_0^2 (kT)^{-2}$, $\tau_3 \sim (48\tau_B \nu^2)^{-1} U_0^3 (kT)^{-3}$, and for the high temperatures (small ξ) $\tau_1 \approx (3/2)\tau_2 \sim$ $\sim \tau_3 \sim (15/16)(\tau_B \nu^2)^{-1}$. This behaviour of τ_m is in qualitative accodance with the behaviour of the orientational relaxation times of a molecule in the potential well (38) which has been investigated in detail in (ref. 7).

The time evolution of N'_m studied in experiments is characterized by different combinations of τ_m in different experimental situations. In the case where $(N'_{3/2} - N'_{1/2}) =$ $= (N'_{-3/2} - N'_{-1/2})$ which corresponds to the absence of the circularly polarized r.f.field, it is the time evolution of $n_1 = (1/2)(N'_{3/2} - N'_{1/2})$ which is experimentaly investigated, that is, in this case our τ_1 is T_1 measured (see (ref.1)). Fig. 1 shows that for the temperatures low enough our theory gives the same temperature dependence of T_1, as the Bayer theory (ref. 4) does, but at $T \sim T_m/5$ essential discrepancy begins; as to $T \lesssim T_m$, the Bayer theory is not valid for these temperatures. It would be interesting to check up experimentally the prediction given by our theory concerning the $T_1(T)$ curve in temperature region $T_m/5 \lesssim T \lesssim T_m$.

Conclusions

In the simple (one potential well) case here considered, our theory proved to give results which couldn't be obtained by means of conventional methods; to show it, was our aim when considering the Bayer problem. But there are cases where one well model is not sufficient, the orientational motion of a molecule going on not around one equilibrium position but between several equilibrium positions as well. In a case like that the reorientational relaxation mechanism may become essential and even predominant. Our theory is capable of treating such cases; one has to choose properly the form of U instead of (38) and the set of the macroscopic coordinates. The study of a problem of this kind is in progress.

To finish up with, a few words about the temperature dependence of NQR frequency in the case of one potential well. These frequencies are defined by the eigenvalues of $\langle\hat{H}\rangle_0$. Using (18) and (47), one gets easily

$$\langle\hat{H}\rangle_0 = \hbar\nu L_2 \left[n_i n_k - (1/3)\delta_{ik}\right] \hat{T}_{ik} \qquad (54)$$

It follows from (54) that $\nu_Q(T)$ is given by $L_2(\xi)$. As it is the case for $T_1(T)$, the deflection of our $\nu_Q(T)$ from Bayer's one begins at $T \sim T_m/5$.

ACKNOWLEDGMENT

The authors would like to thank Dr. I.A. Kjunzel for valuable discussions.

REFERENCES

1 A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.
2 V.I. Kljazkin, V.I. Tatarskij, Usp. Fiz. Nauk, 110 (1973) 499.
3 S. Hess, L. Waldmann. Z. Naturforsch., 23a (1968) 1893.
4 H. Bayer, Zs. f. Phys., 130 (1951) 227.
5 L.D. Favro, Phys. Rev., 119 (1960) 53.
6 M.A. Martsenjuk, Zh. Eksp. Teor. Fiz., 66 (1974) 2279.
7 M.A. Martsenjuk, J.L.Rajcher, M.I. Schliomis, Zh. Eksp. Teor. Fis. 65 (1973) 834.