THE STOCHASTIC THEORY OF A MOLECULAR REORIENTA-TION PART. I. NONDIFFUSIONAL REORIENTATION AND ITS APPLICATION IN THE THEORY OF DIELECTRIC AND NUCLEAR RELAXATION

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In this paper on the basis of the Chapman-Kolmogoroff-Smoluchowski equation (C. K. S.) the theory of stochastic processes uniform on a point group and in time is developed and a comparison with the theory of Ivanov is given (*Zh. Eksper. Teor. Fiz.*, **45**, 1509 (1963)). It is also shown that the theory is very useful for the description of anisotropic molecular reorientation in liquids and molecular crystals. Application in the case of dipole dielectric relaxation gives the rule: if a molecular reorientation is uniform in time, the molecules having C_n with $n \geqslant 2$ or a higher symmetry and strong intermolecular interactions and dispersion of local electric field are neglected, then the Cole-Cole diagram must be a semi-circle. Calculations of T_1 and T_2 for nuclear dipole reorientational relaxation in the case of N like spins I are also presented. The results in the case of diffusional reorientation are equivalent to those of Huntress (*J. Chem. Phys.*, **48**, 3524 (1968)).

1. Introduction

In the last few years there have been many papers published about the anisotropic rotational motions in liquids. Most of the theoretical works (Mishima [1], Kometani, Shimizu [2], Huntress [3]) are based on different versions of the rotational diffusion equation (Favro [4], Steele [5]) with constant or time-dependent diffusion coefficients. The diffusion coefficients if they depend on time are deduced from the Langevin equation. A different method which may be used also for jump reorientation was given by Ivanov [6]. He obtained the density of the conditional probability of a molecular reorientation from the group properties of the molecular motion, making same special assumptions about the stochastic nature of the processes. Our considerations follow along the same lines because we also omit the rotational diffusion equation. However, the theory given by us is more general and concise since it is based on the Chapman-Kolmogoroff-Smoluchowski equation.

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2. Stochastic processes on the O_3^+ group

Every space orientation of a rigid molecule can be described by using the element $g \in O_3^+$ which transforms the molecular frame into the laboratory frame. Thus the density of the conditional probability that a molecule will have an orientation g at a time t if it has the orientation g_0 at the time t_0, is the function of all four arguments given above. As a result we should write this density as $P(g, t; g_0, t_0)$. The range of this function is the Cartesian product $O_3^+ \times O_3^+$ thus we are able to give it as a double series of generalized spherical harmonics $D_{mn}^l(g)$ in the meaning of Wigner's or Gelfand's definitions. The harmonics $D_{mn}^l(g)$ create a base in Hilbert space $H(O_3^+)$ on the O_3^+ group and

$$P(g, t; g_0, t_0) = \frac{1}{8\pi^2} \sum_{l,l'=0}^{\infty} \sum_{m,n=-l}^{l} \sum_{m',n'=-l'}^{l'} C_{m,n;m',n'}^{ll'}(t, t_0) \times$$

$$\times \sqrt{(2l+1)(2l'+1)}\, D_{nm}^l(g^{-1}) D_{n'm'}^{l'}(g_0). \tag{2.1}$$

The above-written series is constructed in the following way. For $t = t_0$

$$C_{m, n; m', n'}^{ll'}(t_0, t_0) = \delta_{ll'}\delta_{mm'}\delta_{nn'}$$

and (2.1) gives us the Dirac delta function $\delta(g^{-1}g_0)$. The last conditions must be fulfilled because at the time t_0 the molecule must have the orientation g_0. We assume now that the reorientation represents a certain continuous Markoff process, so the C. K. S. equation is valid in this case

$$P(g, t; g_0, t_0) = \int_{O_3^+} P(g, t; g_1, t_1) P(g_1, t_1; g_0, t_0) dg_1 \tag{2.2}$$

where $\int_{O_3^+}$ denotes the invariant integration on the O_3^+ group. This integration cannot be normed to unity but to $8\pi^2$ because probability properties demand such a normalization. Let us construct the operator $C(t, t_0)$ in the space $H(O_3^+)$ with the matrix representation $C_{m,n;m',n'}^{ll'}(t, t_0)$ where rows are numbered by l, m, n and columns by l', m', n'. Using (2.2) and (2.1) as well as the properties of the harmonics we have

$$C(t, t_0) = C(t, t_1)\, C(t_1, t_0) \tag{2.3}$$

and additional conditions

$$C(t_0, t_0) = E \qquad C(\infty, t_0) = \begin{pmatrix} 1 & 0 & \dots \\ 0 & 0 & \\ \vdots & & \ddots \\ \vdots & & \end{pmatrix}. \tag{2.4}$$

The last of these follows from $P(\infty, g; t_0, g_0) = \frac{1}{8\pi^2}$. Now we may see that any Markoff process which describes the reorientation of a rigid molecule, can be performed by a two-parameter operator $C(t, t_0)$. This operator maintains (2.3) and (2.4) and must

guarantee the reality and non-negativity of (2.1). In practice neither the necessity nor the possibility of using this description exists. However, now we are able to see how much simpler the situation is when the reorientational process occurs uniform in time and on the group. It means that

$$P(g, t; g_0, t_0) = P(g^{-1}g_0; t-t_0) \tag{2.5}$$

and now

$$P(g^{-1}g_0, t-t_0) \in H(O_3^+)$$

so (2.1) is replaced by

$$P(g^{-1}g_0, t-t_0) = \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \sum_{m,n=-l}^{l} (2l+1)C_{mn}^l(t-t_0)D_{nm}^l(g^{-1}g_0). \tag{2.6}$$

Eventually if we construct a $(2l+1)$-dimensional matrix $C^l(t-t_0)$ using C_{mn}^l for every single l number (2.6) can be written in the form

$$P(g^{-1}g_0, t-t_0) = \frac{1}{8\pi^2} \sum_{l=0}^{\infty} (2l+1)\,\mathrm{Tr}\,[C^l(t-t_0)D^l(g^{-1}g_0)] \tag{2.7}$$

where $D^l(g)$ is the irreducible representation with the weight l of the O_3^+ group. Short calculations of (2.6) and (2.2) lead at once to the conclusion

$$C^l(t-t_0) = C^l(t-t_1)C^l(t_1-t_0). \tag{2.8}$$

The initial conditions and the condition at $t-t_0 = \infty$ give

$$C^l(0) = E, \quad C^l(\infty) = E\delta_{l,0}. \tag{2.9}$$

If, in addition we assume continuity with t, the $C^l(t)$ matrices are $(2l+1)$-dimensional representations of a one-parameter Abelian group with $-\infty < t < \infty$. Obviously we are interested only in $t \geqslant 0$. The representations discussed have the form

$$C^l(t) = e^{B^l \cdot t} \tag{2.10}$$

where B^l for $l > 0$ are nonsingular matrices which have eigenvalues with a negative real part, as a consequence of (2.9). The real parts of these eigenvalues taken with opposite signs are simply equal to correlation times $\tau^{(l,m)}$. Thus for every representation $C^l(t)$ there exist no more than $2l+1$ different correlation times.

One of the conditions which can cause a reduction of the number of different correlation times for some l is the reality of $P(g^{-1}g_0, t-t_0)$. It may easily be seen if we take into account $D_{mn}^l(g)$ given by the definition of Gelfand [7]. In this case the part of $D_{mn}^l(g)$ depending on ϑ (second Euler angle) $P_{mn}^l(\vartheta)$ fulfills the relation

$$\overline{P_{mn}^l(\vartheta)} = (-1)^{m+n}P_{-m,-n}^l(\vartheta).$$

This relation together with (2.6) gives us

$$\overline{C_{mn}^l(t)} = (-1)^{m+n}C_{-m,-n}^l(t).\tag{2.11}$$

Introducing the matrix R by the following definition

$$(R_l)_{mn'} \equiv \delta_{m,-n'}(-1)^m$$

we may have (2.11) in the form

$$\overline{C_l(t)} = RC_l(t)R^{-1}.\tag{2.12}$$

The second cause which may reduce the number of different correlation times is the molecular symmetry. For greater molecules it should not be the total symmetry but rather an "external" symmetry connected with the most external atoms. This is because external atoms determine the short range interaction with the environment and produce the "free volume".

Let us suppose that $s \in G_s$ where G_s is a molecular symmetry group. The symmetry leads to the following relation for the conditional probability of density

$$P(t, g^{-1}g_0) = P(t, s^{-1}g^{-1}ss^{-1}g_0s)\tag{2.13}$$

and together with (2.7) we obtain

$$D^l(s)C^l(t)D^l(s^{-1}) = C^l(t).\tag{2.14}$$

However, $D^l(s)$ as the G_s group representation in many cases can be reduced. So after a transformation to the canonical base (the base in which the matrix $D^l(s)$ has an irreducible quasidiagonal form):

$$QD^l(s)Q^{-1} = \bigoplus_k E_{(k)} \otimes \Gamma_k(s)$$

where $E_{(k)}$ describes the unity matrix. The dimension of this unity matrix is equal to the multiplicity of the appearance of the irreducible representation $\Gamma_k(s)$ in the $D^l(s)$ representation. The equality shown above may be written in the following way:

$$C_Q^l(t) = QC^l(t)Q^{-1} = \bigoplus_k \lambda^{(l,k)}(t) \otimes E^{(k)}.\tag{2.15}$$

Here

$$\text{Dim } \lambda^{(l'k)} = \text{Dim } E_{(k)}, \quad \text{Dim } E^{(k)} = \text{Dim } \Gamma_k$$

and $E^{(k)}$ is another unity matrix. Bringing together (2.11) and (2.15) and writing $T = \overline{Q}RQ^{-1}$ we obtain the equation

$$T\left\{\bigoplus_k \lambda^{(l,k)}(t) \otimes E^{(k)}\right\}T^{-1} = \bigoplus_k \overline{\lambda^{(l'k)}(t)} \otimes E^{(k)}\tag{2.16}$$

which can reduce the number of the linear independent $\lambda^{(l,k)}$ matrix elements or, which means the same, the number of different correlation times for a given l. Let the correlation times for different l be independent as long as additional physical conditions do not exist.

A simple illustration can be found for spherical molecules. In this case $\lambda^{(l,k)}$ is one-dimensional and one can write $\lambda^{(l,k)} = \lambda_l$, so

$$C_Q^l(t) = C^l(t) = \lambda_l E^l.$$

Moreover, from (2.16) $\lambda_l = \bar{\lambda}_l$ which results in

$$C^l(t) = e^{-\frac{t}{\tau^l}} E^l$$

where τ^l is the correlation time. Inserting the last equation into (2.7) we obtain

$$P(g^{-1}g_0, t-t_0) = \frac{1}{8\pi^2} \sum_{l=0}^{\infty} (2l+1) e^{-\frac{t}{\tau^l}} \chi^l(g^{-1}g_0) \tag{2.17}$$

where

$$\chi^l(g) = Tr D^l(g).$$

Such a result is valid for an isotropic reorientation. If we want, however, to have not only the isotropic reorientation but also diffusional reorientation, (2.17) should fulfill the rotational diffusion equation [8]. This gives us an example of the above-discussed additional condition because (2.12) represents the solution of the isotropic rotational diffusion equation only if $(\tau^l)^{-1} = l(l+1) D_r$, where D_r is the rotational diffusion coefficient. As a result ties are established between all correlation times τ^l.

3. Comparison with the method of Ivanov and the role of molecular symmetry in this method

Ivanov has proposed a different method for investigating the reorientational process uniform in time and on the O_3^+ group. Following him, we assume that the molecular rotational motion is a jumping one. By analogy to the previous paragraph one can introduce the function $P(g, N; g_0, N_0)$ with gives us the density of the conditional probability for an orientation g after N jumps if after N_0 jumps g_0 orientation was observed. The uniformity in time and jump space leads to the following relation

$$P(g, N; g_0, N_0) = P(g^{-1}g_0, N-N_0). \tag{3.1}$$

Now replacing in (2.2) and (2.6) $t-t_0$ by $N-N_0$ and $C^l(t-t_0)$ by $A^l(N-N_0)$ after applying to (3.1) a procedure similar to that in (2.5) we find

$$A^l(N-N_0) = A^l(N-N_1) A^l(N_1-N_0). \tag{3.2}$$

Taking into account the initial condition $P(g^{-1}g_0\ 0) = \delta(g^{-1}g_0)$ one may easily prove that the discussed processes are determined by the function

$$P(g^{-1}g_0) = P(g^{-1}g_0, 1) = \frac{1}{8\pi^2} \sum_{l=0}^{\infty} (2l+1)\ \text{Tr}\ [A^l(1)D^l(g^{-1}g_0)] \tag{3.3}$$

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because

$$P(g^{-1}g_0, N-N_0) = \frac{1}{8\pi^2} \sum_{l=0}^{\infty} (2l+1) \operatorname{Tr} \{[A^l]^{N-N_0} D^l(g^{-1}g_0)\} \qquad (3.4)$$

where

$$A^l = A^l(1) = \int P(g)D^l(g)dg \qquad (3.5)$$

represents the average the $D^l(g)$ over one jump. At this place Ivanov introduces the probability $w_N(t)$ of making N jumps by a molecule in the time interval $(0, t)$ and as a result

$$P(g^{-1}g_0, t-t_0) = \sum_{N=0}^{\infty} w_{N-N_0}(t-t_0)P(g^{-1}g_0, N-N_0). \qquad (3.6)$$

Without any difficulties using (3.6), (3.4) and (2.7) we are able to establish the following relation between $C^l(t)$ and A^l

$$C^l(t) = \sum_{N=0}^{\infty} w_N(t) [A^l]^N \qquad (3.7)$$

and because simultaneously (2.10) holds true, we can write

$$B^l = f(A^l). \qquad (3.8)$$

Expanding $e^{f(A^l)t}$ as a function of A^l into a Taylor series the simple relation between the function $f(x)$ and the probability $w_N(t)$ may be obtained

$$w_N(t) = \frac{1}{N!} \left[\frac{d^N}{dx^N} e^{f(x)t} \right]. \qquad (3.9)$$

Now, for example, the function $f(x) = (-1+x)\,\tau^{-1}$ is chosen, where the constant τ is found to be the correlation time. In this situation we have for $w_N(t)$ a Poisson decay and $B^l = (-E^l+A^l)\,\tau^{-1}$ which corresponds to the case of Ivanov. From the above statements most important is the fact that different possible functions $f(x)$ determine different kinds of rotational motion. Let us study the symmetry problem. Here the symmetry is included in the A^l matrix and from (3.3) one can easily find for A^l relations like (2.12), (2.14) and (2.16). Much more symmetry may appear if the additional condition $P(g) = P(g^{-1})$ exists. Now, as was pointed out by Ivanov A^l is a Hermitian matrix (see (3.5)) and $C^l(t)$ is also a Hermitian matrix (see 3.7)).

Finally let us look at diffusional rotation, which becomes possible after taking into account Ivanov's definition of diffusional rotation. This definition demands $P(g)$ different from zero only near the unity of the O_3^+ group. Owing to this, after expanding $D^l(g)$ as a function of Lie parameters α_1, α_2, α_3 in a Taylor series and terminating this series, we have

$$A^l = E^{(l)} + I_\beta^l \int_{O_3^+} P(g)\alpha_\beta(g)dg + I_\beta^l I_\gamma^l \int_{O_3^+} P(g)\alpha_\beta(g)\alpha_\gamma(g)dg \qquad (3.10)$$

where I_β^l are infinitesimal operators for the $D^l(g)$ representation. So the tensors which describe diffusional motion are given by

$$a_\beta = \int_{O^+_3} P(g)\alpha_\beta(g)dg \tag{3.11}$$

$$b_{\beta\gamma} = \int_{O^+_3} P(g)\alpha_\beta(g)\alpha_\gamma(g)dg. \tag{3.12}$$

In the case when $P(g) = P(g^{-1})$ the first of them disappears because $P(g)\,\alpha_\beta(g)$ from (3.11) is odd as a Lie parameter function. Due to the relation (see Gelfand [7])

$$D^l(g)I_\alpha^{(l)}D^l(g^{-1}) = V_{\alpha\beta}(g^{-1})I_\beta^{(l)}$$

where $V(g)$ is the O_3^+ group irreducible representation acting in the three-dimensional real vector space, the molecular symmetry and (2.14), (3.7), (3.8) lead to the formulae

$$a_\beta = V_{\beta\beta'}(s)a_{\beta'} \tag{3.13}$$

$$b_{\beta\gamma} = V_{\beta\beta'}(s)V_{\gamma\gamma'}(s)b_{\beta'\gamma'} \tag{3.14}$$

where s belongs to the molecular symmetry group G_s. For a general decay $w_N(t)$ the tensors a_β and $b_{\beta\gamma}$ cannot be identified with diffusion tensors from the rotational diffusion equation as B^l should depend linearly on the latter. However, if $w_N(t)$ is a Poisson decay B^l depends linearly on A^l and eventually on a_β and $b_{\beta\gamma}$, too. So a_β and $b_{\beta\gamma}$ are the diffusion tensors.

4. Molecular reorientation on a point group

In solids, especially in molecular crystals, a great jump molecular reorientation very often exists. In the set of all possible reorientations creates a point group G and the process is uniform in time as well as on the group G, then by analogy to (2.6) we can write

$$P(g_l^{-1}g_k, t) = \frac{\text{Dim}\,\Gamma}{N} \sum_\Gamma \sum_{m,n=1}^{\text{Dim}\,\Gamma} C_{mn}^\Gamma(t)\Gamma_{nm}(g_l^{-1}g_k) \tag{4.1}$$

where $g_k, g_l \in G$ and $\Gamma_{mn}(g_k)$ describe the matrix elements of irreducible, nonequivalent and unitary representations of this group. Discussing once again the initial condition $P(g_l^{-1}g_k, 0) = \delta_{lk}$ and the condition $P(g_l^{-1}g_k, \infty) = P_l$, where P_l is the probability of a g_l orientation, and using the C. K. S. equation we obtain expressions like (2.8), (2.9) and (2.10) if $C^l(t)$ and $C_{mn}^l(t)$ are replaced by $C^\Gamma(t)$ and $C_{mn}^\Gamma(t)$ respectively. Moreover, as a consequence of time and group uniformity of $P(g_l^{-1}g_k, t)$ we get

$$P_l = \frac{1}{N} C^{\Gamma_1}(\infty) \tag{4.2}$$

where Γ_1 denotes a trivial representation and P_l is automatically constant over the group G.

5. *Application in the dielectric relaxation theory*

As it was shown by Glarum [9] and Cole [10], if correlations between dipole moments of the different molecules are neglected[1], the correlation function $\Phi(t)$ is given by

$$\Phi(t) = \frac{\langle \mu(t) \cdot \mu(0) \rangle}{\langle \mu(0) \cdot \mu(0) \rangle}.$$

At present it is very useful to replace in the scalar product $\mu(t) \cdot \mu(0)$ the traditional real coordinates which transform under the representation $V(g)$ (see preceding page) by coordinates proper for the $D^1(g)$ representation. Hence

$$\Phi(t) = \frac{1}{\mu^2} \langle \mu_m(t)\overline{\mu_m(0)} \rangle =$$

$$= \frac{1}{\mu^2} \int_{O^+_3} \int_{O^+_3} D^1_{mm'}(g)D^1_{nn'}(g_0)\frac{1}{8\pi^2} P(g^{-1}g_0, t)dgdg_0 \cdot \mu_{m'}\overline{\mu_{n'}}. \tag{5.1}$$

Here $\mu_{m'}$ are given in the proper molecular frame for the representation $D^1(g)$. Putting (2.6) into (5.1) we find

$$\Phi(t) = \frac{1}{\mu^2} C^1_{mn}(t)\mu_m\overline{\mu_n}. \tag{5.2}$$

Generally if the process is uniform in time (2.11) leads to $\Phi(t) = \overline{\Phi(t)}$. Moreover, in the case of C_n with $n \geqslant 2$ or a higher molecular symmetry, a local (molecular) frame can be established so that the z-axis lies along the molecular dipole moment μ. Thus

$$\Phi(t) = C^1_{00}(t) \tag{5.3}$$

and, because the $D^1(g)$ matrices, as the representation of C_n with $n \geqslant 2$ or a higher point group, have precisely in their centres the trivial representation Γ_1, (2.14) gives us

$$\Phi(t) = C^1_{00}(t) = e^{-\lambda t} \tag{5.4}$$

where λ is a real, positive number. The same result may be obtained for a reorientation over a point group. Consequently in both discussed cases the dielectric relaxation has a Debye character. Summing up, if the molecular reorientation is time and group uniform, intermolecular correlations are negligible in the meaning given earlier and molecular symmetry is C_n with $n \geqslant 2$ or higher, then the Cole-Cole diagram must be a semi-circle.

Good examples for this rule are C_6H_5X type liquids with $X = NO_2$, F, Cl, Br, I [11]. It is worth noting that for $C_6H_5NO_2$ very strong dipol-dipol interactions [12], [13], [14] are observed, however they do not disturb the discussed rule. Also many solids hold this rule, here a good example is *t*-butyl chloride [15]. On the other hand, some liquids con-

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[1] They are negligible not only if they do not affect $\Phi(t)$ but also if they change $\Phi(t)$ by some constant rate.

taining very symmetric molecules like CCl_3Br or CCl_2Br_2 [16] break this rule. This suggests that either the intermolecular correlations are not negligible or molecular reorientation is not time uniform. The influence on Cole-Cole diagrams of a time nonuniform diffusional motion with a stochastically time-dependent diffusion coefficient was investigated by Ullman [17]. His results are potentially adequate for the interpretation of the experimental Cole-Cole diagrams in both CCl_3Br and CCl_2Br_2 cases.

6. Application to dipole nuclear relaxation in liquids

We are now going to calculate the nuclear relaxation times T_1 and T_2 for molecules containing N magnetically equivalent like I spins caused by dipole interaction and non-diffusional molecular rotation. After some modifications, the calculation scheme given by Huntress [3] may be used and for a resonance frequency ω

$$\frac{1}{T_2} = \frac{6(I+1)I}{5N} \sum_{i>j} \frac{\hbar^2\gamma^4}{r_{ij}^6} \overline{\eta_{2,p}^{(ij)}\eta_{2,q}^{(ij)}} \left(\frac{3}{2}F_0^c + \frac{5}{2}F_\omega^c + F_{2\omega}^c\right) \overline{[C_{p,q}^2(\tau)]} \tag{6.1}$$

$$\frac{1}{T_1} = \frac{6(I+1)I}{5N} \sum_{i>j} \frac{\hbar^2\gamma^4}{r_{ij}^6} \overline{\eta_{2,p}^{(ij)}\eta_{2,q}^{(ij)}}(F_\omega^c + 4F_{2\omega}^c) \overline{[C_{p,q}^2(\tau)]}. \tag{6.2}$$

Here r_{ij} is the distance between i-th and j-th spins, F_x^c describes a cosine Fourier transform at point x, the sums over p and q cover the set of numbers $0, \pm 1, \pm 2$ and

$$\eta_{2,p}^{(ij)} = \sum_{\substack{m+n=p \\ m,n=0,\pm 1}} C(112|m,n)\eta_m^{(ij)}\eta_n^{(ij)}. \tag{6.3}$$

In the last expression $C(112|m,n)$ are Clebsch-Gordan coefficients and $\eta_m^{(ij)}$ depends on the Cartesian coordinates $X_1^{(ij)}, X_2^{(ij)}, X_3^{(ij)}$ of the vector r_{ij} in some molecular frame, hence we have

$$\eta_{+1}^{(ij)} = \frac{-i}{\sqrt{2}}(X_1^{(ij)} \pm X_2^{(ij)})\frac{1}{r_{ij}}$$

$$\eta_0^{(ij)} = \frac{X_3^{(ij)}}{r_{ij}}. \tag{6.4}$$

Speaking more precisely (6.3) is a second rank spherical tensor seperated from the tensor product of (6.4) with itself. The relaxation times T_1 and T_2 given by (6.1) and (6.2) in the case of diffusional reorientation and extremal narrowing are completely equivalent to those of Huntress [3]. Also from (6.1) and (6.2) we have seen how the relaxation times depend on correlation functions $C_{p,q}^2(\tau)$ and on the spin system geometrical structure. However, these dependencies are very complicated and contrary to the dielectric relaxation problem we have not reached any general conclusions.

7. Conclusions

In this paper we have shown that the best starting point for theoretical investigations of different Markoff types of molecular reorientation is the C. K. S. equation. Using it, after some calculations, the whole problem was reduced to the discussion of the non-unitary representation of the real number group (§§ 2, 3). Also the influence of molecular symmetry on this reorientation was explained. Up to now this has only been done for diffusional reorientation, where the diffusion tensor symmetry was taken under consideration. The theory presented here is more general than that of Ivanov and the latter may be obtained as a special case. This same remark is valid for all applications where Ivanov's theory may be used. Rather special and important, as we suppose, for the interpretation of Cole-Cole diagrams, appears the symmetry rule given in § 5. In the case of diffusional reorientation in liquids this is a rather evident consequence of the results of Steele [5] or Favro [4]. In spite of this up to now we have not found any formulation of the discussed rule. Contrary to the symmetry rule, the applications of expressions (6.1) and (6.2) for nuclear relaxation are limited in practice doing to their complicated structure.

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