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STOCHASTIC DIFFERENTIAL EQUATION STUDY OF NUCLEAR MAGNETIC RELAXATION BY SPIN-ROTATIONAL INTERACTIONS

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Abstract The mathematical methods based on stochastic differential equations and the rotation operator, which were developed for the study of rotational Brownian motion and its implications for dielectric dispersion and absorption, are extended so as to yield ensemble averages of certain products of orientational and angular velocity functions. As a consequence, a procedure for calculating nuclear magnetic relaxation times arising from spin-rotational interactions, when inertial effects are included, is presented for molecules of any shape.

1. INTRODUCTION

The theory of nuclear magnetic resonance relaxation caused by rotational thermal motion[1,2] was applied by Hubbard in a sequence of papers[3-7] to quadrupole interactions, intramolecular dipole-dipole interactions and spin-rotational interactions. The treatment of the last type of interactions is particularly difficult in that it involves the calculation of the ensemble average of the product of functions of orientational angle variables and angular velocity variables. In his earlier investigation Hubbard[3] regarded the angles and angular velocities as independent sets of variables, so that the ensemble average of the product was assumed to be the product of the ensemble averages of the function of the orientational variables and of the function of the angular velocity variables. However the orientational and angular velocity variables are not independent and Hubbard[4,5] later proposed a method based on a Fokker-Planck equation which enabled him to write down a general expression for the Laplace transform of the ensemble average of the product of orientational and angular velocity functions which occur in spin-rotational relaxation studies. For the case of a rotating spherical molecule Hubbard deduced expressions for the spin-rotational correlation time and for the spin-rotational contributions to the reciprocals of the longitudinal and transverse relaxation times.

A method based on Euler-Langevin stochastic differential equations, the ensemble average of the stochastic rotation operator and the Krylov-Bogoliubov solution of nonlinear differential equations has been found very powerful for the investigation of dielectric relaxation processes when inertial effects are included[8]. Indeed the method is generally applicable to processes whose investigation is based on the correlation functions of spherical harmonics. Confining our attention to nuclear magnetic resonance phenomena we have already applied the method to the calculation of spin-lattice relaxation times.[9] It may be applied without difficulty to the contributions of intramolecular dipole-dipole interactions and of quadrupole interactions to the nuclear magnetic relaxation rate of identical nuclei, but not to the contributions of spin-rotational interactions.

It is the purpose of the present paper to extend the above mathematical method so that it will provide the ensemble average of the product of the orientational and angular velocity functions encountered in the study of spin-rotational interactions. In Section 2 the formalism for these interactions will be summarized, definitions given and the extended mathematical method will be presented in a manner applicable to molecules of any shape. In Section 3 a detailed study will be made for the spherical model of the molecules, and the results will be compared with those derived by other methods. Finally in Section 4 the problem for asymmetric molecules will be considered.

2. SPIN-ROTATIONAL INTERACTIONS

2.1. Definitions and basic equations

We consider the contribution to nuclear magnetic relaxation of identical nuclei in identical molecules. The spin-rotational interaction is the sum over all molecules in a system of the sum of the interactions of the magnetic moments of the nuclei in a molecule with the magnetic field produced by the rotation of that molecule. For later comparison with the results of Hubbard we follow fairly closely the notation of ref. 5. Let us denote by $\underset{\sim}{I}_i$ the spin operator of the ith nucleus and by $\hbar \underset{\sim}{J}_i$ the angular momentum of the molecule that contains this nucleus. The spin-rotational Hamiltonian of the ith nucleus,

$$\hbar G_1^i = \hbar \underset{\sim}{I}_i \cdot \underset{\sim}{C}^i \cdot \underset{\sim}{J}_i, \tag{2.1}$$

where $\underset{\sim}{C}^i$ is a dyadic with the dimensions of a frequency. Hubbard expresses (2.1) as

$$G_1^i = \sum_{k=-1}^{1} V_i^k U_i^k ,$$

where V_i^k are the spherical components of $\underset{\sim}{I}_i$ in the laboratory system and

$$U_i^k = \sum_{\nu=1}^{3} \sum_{m=-1}^{1} b_{m\nu}^i D_{km}^1(\alpha_i, \beta_i, \gamma_i) J_{i\nu}. \tag{2.2}$$

In this equation

$$b_{0\nu}^i = C_{3\nu}^i , \quad b_{\pm 1,\nu}^i = \mp \frac{C_{1\nu}^i \mp i C_{2\nu}^i}{\sqrt{2}} , \tag{2.3}$$

where $C_{m\nu}^i$ are the constant cartesian components of the dyadic referred to axes fixed in the molecule. In (2.2) D_{km}^1 is the rotation matrix for the transformation of a spherical tensor[10] and $\alpha_i, \beta_i, \gamma_i$ are the Euler angles specifying the molecular system with respect to the laboratory coordinate system. We see from (2.3) that

$$b^{i\,*}_{m\nu} = (-)^m\, b^{i}_{-m,\nu}\,. \tag{2.4}$$

The contributions $(1/T_1)_1, (1/T_2)_1$ from the spin-rotational interactions to the reciprocals $1/T_1$, $1/T_2$ of the longitudinal and transverse relaxation times T_1, T_2, respectively, are given by

$$\left(\frac{1}{T_1}\right)_1 = 2\,J_1(\omega_0)\,, \quad \left(\frac{1}{T_2}\right)_1 = J_1(0) + J_1(\omega_0), \tag{2.5}$$

where ω_0 is the angular velocity of the Larmor precession,

$$J_1(\omega) = \frac{1}{2}\int_0^\infty \left[\, C^{00}_{ii}(t)\,e^{i\omega t} + C^{00}_{ii}(t)\,e^{-i\omega t}\right] dt \tag{2.6}$$

and $C^{\ell k}_{ii}(t)$, not to be confused with the dyadic components, is defined by

$$C^{\ell k}_{ii}(t) = \langle U^{\ell}_{i}(t)\, U^{k}_{i}(0)\rangle, \tag{2.7}$$

where the angular brackets denote ensemble average for thermal equilibrium. We see from (2.2) that

$$C^{\ell k}_{ii}(t) = \sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b^{i}_{n\mu}\, b^{i}_{m\nu} \langle D^{1}_{\ell n}(\alpha_i(t),\beta_i(t),\gamma_i(t))\, D^{1}_{km}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, J_{i\mu}(t)\, J_{i\nu}(0)\rangle. \tag{2.8}$$

We take for the molecular frame of reference the principal axes of inertia through the centre of mass and write the components of angular momentum as $I_1\omega_1, I_2\omega_2, I_3\omega_3$, where I_1, I_2, I_3 are the principal moments of inertia and $\omega_1, \omega_2, \omega_3$ the corresponding cartesian components of angular velocity. Then replacing $\hbar J_{i\mu}(t)$ by $I_\mu \omega_\mu(t)$ we express (2.8) as

$$C^{\ell k}_{ii}(t) = \hbar^{-2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b^{i}_{n\mu}\, b^{i}_{m\nu}\, I_\mu I_\nu \langle D^{1}_{\ell n}(\alpha_i(t),\beta_i(t),\gamma_i(t))\, D^{1}_{km}(\alpha_i(0),\beta_i(0),\gamma_i(0))\,\omega_\mu(t)\,\omega_\nu(0)\rangle, \tag{2.9}$$

a sum of ensemble averages over the product of a function of angle variables and a function of angular velocity variables.

At this stage we introduce the stochastic rotation operator $R(t)$. We see from (2.9) that

$$C^{00}_{ii}(t) = \hbar^{-2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b^{i}_{n\mu}\, b^{i}_{m\nu}\, I_\mu I_\nu \langle D^{1}_{0n}(\alpha_i(t),\beta_i(t),\gamma_i(t))\, D^{1}_{0m}(\alpha_i(0),\beta_i(0),\gamma_i(0))\,\omega_\mu(t)\,\omega_\nu(0)\rangle. \tag{2.10}$$

Now

$$D^{1}_{0n}(\alpha_i(t),\beta_i(t),\gamma_i(t)) = D^{1\,*}_{n0}(-\gamma_i(t),-\beta_i(t),-\alpha_i(t)) = \left(\frac{4\pi}{3}\right)^{1/2} Y_{1n}(-\beta_i(t),-\alpha_i(t)),$$

so

$$C^{00}_{ii}(t) = \frac{4\pi}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b^{i}_{n\mu}\, b^{i}_{m\nu}\, I_\mu I_\nu \langle Y_{1m}(-\beta_i(0),-\alpha_i(0))\, Y_{1n}(-\beta_i(t),-\alpha_i(t))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$

$$= \frac{4\pi}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} (-)^m\, b^{i}_{n\mu}\, b^{i}_{m\nu}\, I_\mu I_\nu \langle Y^{*}_{1,-m}(-\beta_i(0),-\alpha_i(0))\, R^{+}(t)\, Y_{1n}(-\beta_i(0),-\alpha_i(0))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$

where $R(t)$ is the rotation operator that brings the molecular frame at time zero to the molecular frame at time t and $R^{+}(t)$ is its adjoint[11]. Since $R(t)$ involves the angular velocity through the relation

$$\frac{dR(t)}{dt} = -i\,(\underset{\sim}{J}_i\cdot\underset{\sim}{\omega}(t))\,R(t), \tag{2.11}$$

it follows that

$$\langle Y^{*}_{1,-m}(-\beta_i(0),-\alpha_i(0))\, R^{+}(t)\, Y_{1n}(-\beta_i(0),-\alpha_i(0))\, \omega_\mu(t)\,\omega_\nu(0)\rangle$$
$$\neq \langle Y^{*}_{1,-m}(-\beta_i(0),-\alpha_i(0))\, R^{+}(t)\, Y_{1n}(-\beta_i(0),-\alpha_i(0))\rangle \langle \omega_\mu(t)\,\omega_\nu(0)\rangle .$$

However the angle and angular velocity variables though not independent are separable. This allows us to take the ensemble average firstly over the angular velocity variables, denoting it by $\langle\cdots\rangle_\omega$, and then over the angle variables at time zero. Thus

$$C^{00}_{ii}(t) = \frac{1}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b^i_{n\mu} b^i_{m\nu} I_\mu I_\nu \int_0^{2\pi} d[-\alpha_i(0)] \int_0^{\pi} d[-\beta_i(0)] \sin[-\beta_i(0)]$$
$$\times\, Y^{*}_{1,-m}(-\beta_i(0),-\alpha_i(0)) \langle R^{+}(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle_\omega\, Y_{1n}(-\beta_i(0),-\alpha_i(0))$$
$$= \frac{1}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b^i_{n\mu} b^i_{m\nu} I_\mu I_\nu \left(\langle R^{+}(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle_\omega\right)^{*}_{-m,n},$$

where $-m,n$ denotes the $-m,n$—element with respect to the basis $Y_{1,-1}(\beta(0),\alpha(0))$, $Y_{1,0}(\beta(0),\alpha(0))$, $Y_{1,1}(\beta(0),\alpha(0))$. We conclude that

$$C^{00}_{ii}(t) = \frac{1}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b^i_{n\mu} b^i_{m\nu} I_\mu I_\nu \left(\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle_\omega\right)_{n,-m} \tag{2.12}$$

If we succeed in calculating $\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle_\omega$, we may be able to find $(1/T_1)_1$ and $(1/T_2)_1$ from (2.5), (2.6) and (2.12).

To perform these calculations it is helpful to define the Laplace transform $c^{\ell k}_{ii}(s)$ of $C^{\ell k}_{ii}(t)$:

$$c^{\ell k}_{ii}(s) = \int_0^\infty e^{-st}\, C^{\ell k}_{ii}(t)\, dt \tag{2.13}$$

with $C^{\ell k}_{ii}(t)$ given by (2.9). Then, from (2.12),

$$c^{00}_{ii}(s) = \frac{1}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b^i_{n\mu} b^i_{m\nu} I_\mu I_\nu \left(\int_0^\infty e^{-st}\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle_\omega dt\right)_{n,-m} \tag{2.14}$$

and, from (2.6),

$$J_1(\omega) = \tfrac{1}{2}\left(c^{00}_{ii}(-i\omega) + c^{00}_{ii}(i\omega)\right). \tag{2.15}$$

As will be explained below in subsection 3.3, we may replace $J_1(\omega_0)$ by $J_1(0)$ in the extreme narrowing case. Then (2.5) and (2.15) yield

$$\left(\frac{1}{T_1}\right)_1 = \left(\frac{1}{T_2}\right)_1 = 2J_1(0) = 2c^{00}_{ii}(0). \tag{2.16}$$

We write $1/T_{sr}$ for the common value in the extreme narrowing case of $(1/T_1)_1$ and $(1/T_2)_1$, and so

$$\frac{1}{T_{sr}} = 2c^{00}_{ii}(0). \tag{2.17}$$

The spin-rotational correlation time τ_{sr} is defined as the integral from zero to infinity of the normalized autocorrelation function of $U^k_i(t)$, so that

$$\tau_{sr} = \frac{\int_0^\infty \langle U^{k}_i(0)^{*}\, U^{k}_i(t)\rangle dt}{\langle U^{k}_i(0)^{*}\, U^{k}_i(0)\rangle}. \tag{2.18}$$

From (2.2) and $\hbar J_{i\nu} = I_\nu \omega_\nu$ we deduce that

$$\langle U_i^{k*}(0)\, U_i^{k}(t)\rangle = \hbar^{-2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b_{m\nu}^{i*}\, b_{n\mu}^{i}\, I_\mu I_\nu$$
$$\times \langle D_{km}^{1*}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{kn}^{1}(\alpha_i(t),\beta_i(t),\gamma_i(t))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$
$$= \frac{(-)^k}{\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b_{-m,\nu}^{i}\, b_{n\mu}^{i}\, I_\mu I_\nu$$
$$\times \langle D_{-k,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{kn}^{1}(\alpha_i(t),\beta_i(t),\gamma_i(t))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$

where we have used (2.4) and the property of Wigner functions[12]

$$D_{km}^{j*}(\alpha,\beta,\gamma) = (-)^{k+m} D_{-k,-m}^{j}(\alpha,\beta,\gamma). \tag{2.19}$$

From a result of Hubbard[13] we find that

$$\langle D_{-k,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{kn}^{1}(\alpha_i(t),\beta_i(t),\gamma_i(t))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$
$$= (-)^k \langle D_{0,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{0n}^{1}(\alpha_i(t),\beta_i(t),\gamma_i(t))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$

Hence

$$\langle U_i^{k*}(0)\, U_i^{k}(t)\rangle = \hbar^{-2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1} b_{-m,\nu}^{i}\, b_{n\mu}^{i}\, I_\mu I_\nu$$
$$\times \langle D_{0,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{0n}^{1}(\alpha_i(t),\beta_i(t),\gamma_i(t))\,\omega_\mu(t)\,\omega_\nu(0)\rangle \tag{2.20}$$
$$= C_{ii}^{00}(t),$$

by (2.10), since m and n are summation indices. It follows from (2.13) that

$$\int_0^\infty e^{-st}\langle U_i^{k}(0)^*\, U_i^{k}(t)\rangle\, dt = c_{ii}^{00}(s), \tag{2.21}$$
$$\int_0^\infty \langle U_i^{k}(0)\, U_i^{k}(t)\rangle\, dt = c_{ii}^{00}(0). \tag{2.22}$$

To obtain the denominator in (2.18) we note that $R(0)$ is the identity operator, that the Wigner functions in (2.20) for $t=0$ are consequently independent of the angular velocity, and therefore that

$$\langle D_{0,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{0n}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$
$$= \langle D_{0,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{0n}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\rangle\langle \omega_\mu(0)\,\omega_\nu(0)\rangle. \tag{2.23}$$

For a rotator of any shape[14])

$$\langle \omega_\mu(0)\,\omega_\nu(0)\rangle = \delta_{\mu\nu}\frac{kT}{I_\mu}. \tag{2.24}$$

Then employing (2.19) and the orthogonality relation

$$\int_0^{2\pi} d\gamma \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta\, D_{p\tau}^{j*}(\alpha,\beta,\gamma)\, D_{p'\tau'}^{j'}(\alpha,\beta,\gamma) = \frac{8\pi^2\delta_{jj'}\delta_{pp'}\delta_{\tau\tau'}}{2j+1}$$

we see that

$$\langle D_{0,-m}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{0n}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0))\rangle$$
$$= \frac{(-)^m}{8\pi^2}\int_0^{2\pi} d\gamma_i(0)\int_0^{2\pi} d\alpha_i(0)\int_0^{\pi} d\beta_i(0)\sin\beta_i(0)\, D_{0m}^{1*}(\alpha_i(0),\beta_i(0),\gamma_i(0))\, D_{0n}^{1}(\alpha_i(0),\beta_i(0),\gamma_i(0)) \tag{2.25}$$
$$= \frac{(-)^m\,\delta_{mn}}{3}.$$

Hence from (2.20), (2.23) - (2.25)

$$\langle U_i^{k*}(0)\, U_i^{k}(0)\rangle = \frac{kT}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}\delta_{\mu\nu}\,\delta_{mn}(-)^m b_{-m,\nu}^{i}\, b_{n\mu}^{i}\, I_\nu$$
$$= \frac{kT}{3\hbar^2}\sum_{\mu=1}^{3}\sum_{m=-1}^{1}(-)^m b_{-m,\mu}^{i}\, b_{m\mu}^{i}\, I_\mu. \tag{2.26}$$

We conclude from (2.18), (2.22) and (2.26) that

$$\tau_{sr} = \frac{3\hbar^2}{kT}\,\frac{c_{ii}^{00}(0)}{\sum_{\mu=1}^{3}\sum_{m=-1}^{1}(-)^m b_{-m,\mu}^{i}\, b_{m\mu}^{i}\, I_\mu}, \tag{2.27}$$

the value of $c_{ii}^{00}(0)$ to be obtained from (2.14).

In the extreme narrowing case we deduce from (2.17) and (2.27) that

$$\frac{1}{T_{sr}} = \frac{2kT\tau_{sr}}{3\hbar^2}\sum_{\mu=1}^{3}\sum_{m=-1}^{1}(-)^m b^{i}_{-m,\mu}\, b^{i}_{m\mu}\, I_\mu \,. \tag{2.28}$$

Thus the spin-rotational contributions to the reciprocals of the longitudinal and transverse relaxation times are proportional to the spin-rotational correlation time.

2.2. General method of calculating $\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$

We have seen in the previous subsection that the evaluation of $(1/T_1)_1$, $(1/T_2)_1$, τ_{sr} is deduced from the value of the ensemble average over angular velocity space of $R(t)\,\omega_\mu(t)\,\omega_\nu(0)$, where $R(t)$ is the rotation operator that brings the molecular coordinate system at time zero to its orientation at time t. In studies on dielectric phenomena we were concerned only with the average over the angular velocity space of $R(t)$, and we shall now show how in principle the previous method may be adapted so as to meet the requirements of the spin-rotational problem.

The rotation operator obeys the stochastic differential equation (2.11), which we now write

$$\frac{dR(t)}{dt} = -i\left(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t)\right)R(t) \tag{2.29}$$

omitting the subscript of $\underset{\sim}{J}$ because we shall focus attention on one molecule only. In (2.29) $\underset{\sim}{J}$ has components J_1, J_2, J_3 in the rotating molecular coordinate frame that obey the commutation relations

$$[J_2, J_3] = -iJ_1 \,,\ [J_3, J_1] = -iJ_2 \,,\ [J_1, J_2] = -iJ_3 \,,$$

which we express briefly as

$$[J_\mu, J_\nu] = -i\left(\underset{\sim}{J}\cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu\right), \tag{2.30}$$

$\underset{\sim}{e}_\mu$, $\underset{\sim}{e}_\nu$ being unit vectors in the μ- and ν- directions. We suppose that the rotation of the molecule is due to thermal motion in a steady state and that the components $\omega_1(t)$, $\omega_2(t)$, $\omega_3(t)$ of $\underset{\sim}{\omega}(t)$ in (2.29) obey the Euler-Langevin equations

$$
\begin{aligned}
I_1\dot{\omega}_1 - (I_2 - I_3)\omega_2\omega_3 &= -I_1B_1\omega_1 + I_1\frac{dW_1(t)}{dt}, \\
I_2\dot{\omega}_2 - (I_3 - I_1)\omega_3\omega_1 &= -I_2B_2\omega_2 + I_2\frac{dW_2(t)}{dt}, \\
I_3\dot{\omega}_3 - (I_1 - I_2)\omega_1\omega_2 &= -I_3B_3\omega_3 + I_3\frac{dW_3(t)}{dt},
\end{aligned} \tag{2.31}
$$

where B_1, B_2, B_3 are frictional constants and W_1, W_2, W_3 are Wiener processes. Equations (2.31) are nonlinear and $\omega_1(t)$, $\omega_2(t)$, $\omega_3(t)$ will be centred but in general non-Gaussian[15]. If the molecule is spherical or linear, $\underset{\sim}{\omega}(t)$ obeys a Langevin equation and is a centred Gaussian random variable.

Ford[16] has given a general method based on earlier studies of Krylov and Bogoliubov[17] of solving a nonlinear stochastic differential equation of the type

$$\frac{dx(t)}{dt} = \varepsilon\, O(t)\, x(t), \tag{2.32}$$

where $x(t)$ is a random variable that may be an operator, ε a small parameter and $O(t)$ a stochastic operator. Since accounts of Ford's method have been published[8,18], we shall just quote results that are relevant for our purposes. Equation (2.29) is obtained from (2.32) by the substitutions

$$x \mapsto R(t) \quad , \quad \varepsilon\, O(t) \mapsto -i\,(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t)).$$

Then we write

$$R(t) = \left(\underset{\sim}{I} + \varepsilon F^{(1)}(t) + \varepsilon^2 F^{(2)}(t) + \varepsilon^3 F^{(3)}(t) + \varepsilon^4 F^{(4)}(t) + \dots\right)\langle R(t)\rangle, \tag{2.33}$$

where $\underset{\sim}{I}$ is the identity operator and $F^{(i)}(t)$ are stochastic operators with zero ensemble averages. The non-stochastic $\langle R(t)\rangle$ obeys an equation

$$\frac{d\langle R(t)\rangle}{dt} = \left(\varepsilon\Omega^{(1)}(t) + \varepsilon^2\Omega^{(2)}(t) + \varepsilon^3\Omega^{(3)}(t) + \varepsilon^4\Omega^{(4)}(t) + \dots\right)\langle R(t)\rangle. \tag{2.34}$$

In our previous investigations we were concerned only with the solution of (2.34) but now we must find $R(t)$ in order to calculate the average value of $R(t)\,\omega_\mu(t)\,\omega_\nu(0)$. Since

$$\langle \varepsilon\, O(t)\rangle \mapsto -i\,\langle(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))\rangle = 0$$

because $\langle\underset{\sim}{\omega}(t)\rangle = 0$, it is found that

$$
\begin{aligned}
\varepsilon F^{(1)}(t) &= -i\int_0^t (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))\,dt_1 \\
\varepsilon^2 F^{(2)}(t) &= -\int_0^t dt_1\int_0^{t_1} dt_2\left[(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2)) - \langle(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))\rangle\right] \\
\varepsilon^3 F^{(3)}(t) &= i\int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3\Big[(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3)) \\
&\quad - (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))\langle(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle - (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))\langle(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle \\
&\quad - (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\langle(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))\rangle - \langle(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle,
\end{aligned} \tag{2.35}
$$

and that in general

$$\varepsilon^n\dot{F}^{(n)}(t) = -\varepsilon^n\Omega^{(n)}(t) - i(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))\,\varepsilon^{n-1}F^{(n-1)}(t) - \varepsilon^n\sum_{j=1}^{n-1}F^{(j)}(t)\,\Omega^{(n-j)}(t). \tag{2.36}$$

We also have

$$\varepsilon\Omega^{(1)}(t) = 0\,, \quad \varepsilon^2\Omega^{(2)}(t) = -\int_0^t \langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))\rangle\, dt_1$$

$$\varepsilon^3\Omega^{(3)}(t) = i\int_0^t dt_1 \int_0^{t_1} dt_2 \langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))\rangle$$

$$\begin{aligned}\varepsilon^4\Omega^{(4)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{ &\langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle \\ &- \langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))\rangle\langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle \\ &- \langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))\rangle\langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle \\ &- \langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_3))\rangle\langle (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))(\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_2))\rangle\}\,.\end{aligned} \tag{2.37}$$

On substituting the values of $\Omega^{(i)}(t)$ into (2.34) we may be able to obtain $\langle R(t)\rangle$ in a form suitable for further computation. Then finding $F^{(i)}(t)$ from (2.35), or from (2.36) and (2.37), and substituting into (2.33) we have $R(t)$ and may proceed to calculate $\langle R(t)\,\omega_\mu(t)\omega_\nu(0)\rangle$ required in (2.12).

In these investigations the operators are independent of the angle variables and so we may denote ensemble averages either by $\langle\cdots\rangle_\omega$ or by $\langle\cdots\rangle$. For convenience we shall adopt the latter notation.

All the above considerations are applicable to molecules of any shape. We shall now apply the general theory of this section to a spherical molecular model.

3. SPHERICAL MOLECULES

3.1 Calculation of $\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$

When the rotating molecule is spherical in shape, eq. (2.31) reduce to

$$I\,\dot{\underset{\sim}{\omega}}(t) = -I\,B\,\underset{\sim}{\omega}(t) + I\,\frac{d\underset{\sim}{W}(t)}{dt} \tag{3.1}$$

and $\underset{\sim}{\omega}(t)$ is a Gaussian random variable with zero mean. Then, since the mean value of the product of an odd number of such ω's vanishes, $\Omega^{(3)}(t)$ given in (2.37) vanishes, as indeed do $\Omega^{(5)}(t)$, $\Omega^{(7)}(t)$, etc.. It has been shown that[9)]

$$\begin{aligned}\langle R(t)\rangle = \Big[\underset{\sim}{I} &+ \gamma J^2(1-e^{-Bt}) + \gamma^2\{J^2[\tfrac{5}{4} - (Bt+1)e^{-Bt} - \tfrac{1}{4}e^{-2Bt}] \\ &+ (J^2)^2[\tfrac{1}{2} - e^{-Bt} + \tfrac{1}{2}e^{-2Bt}]\} \\ &+ \gamma^3\{J^2[\tfrac{19}{9} - (\tfrac{1}{2}B^2t^2 + 2Bt + 1)e^{-Bt} - (\tfrac{3}{4}Bt+1)e^{-2Bt} - \tfrac{1}{9}e^{-3Bt}] \\ &+ (J^2)^2[\tfrac{5}{4} - (Bt+\tfrac{9}{4})e^{-Bt} + (Bt+\tfrac{3}{4})e^{-2Bt} + \tfrac{1}{4}e^{-3Bt}] \\ &+ (J^2)^3[\tfrac{1}{6} - \tfrac{1}{2}e^{-Bt} + \tfrac{1}{2}e^{-2Bt} - \tfrac{1}{6}e^{-3Bt}]\} + \dots\Big]\,e^{-BG_j t},\end{aligned} \tag{3.2}$$

where

$$G_j = j(j+1)\gamma\{1 + \tfrac{1}{2}\gamma + \tfrac{7}{12}\gamma^2 + [\tfrac{17}{18} - \tfrac{j(j+1)}{8}]\gamma^3 + \dots\}, \tag{3.3}$$

$j(j+1)$ being the eigenvalue of J^2 and

$$\gamma = \frac{kT}{IB^2}, \tag{3.4}$$

where k is the Boltzmann constant and T the absolute temperature. It is found in dielectric absorption experiments that the value of γ does not exceed a few per cent[19,20)]. We see from (3.2) that $\langle R(t)\rangle$ is a multiple of the identity and so commutes with J_1, J_2, J_3.

We wish to calculate $R(t)$ from (2.33), (2.35) and (3.2), and use the value so calculated to obtain $\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$. Let us suppose that n is an odd integer. The contribution to $R(t)\,\omega_\mu(t)\,\omega_\nu(0)$ corresponding to $\varepsilon^n F^{(n)}(t)$ contains only terms with an odd number of ω's and so the ensemble average of the contribution vanishes. We may therefore deduce from (2.33) that

$$\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle = \langle (\underset{\sim}{I} + \varepsilon^2 F^{(2)}(t) + \varepsilon^4 F^{(4)}(t) + \varepsilon^6 F^{(6)}(t) + \ldots)\omega_\mu(t)\omega_\nu(0)\rangle \langle R(t, \tag{3.5}$$

For a steady state solution of (3.1) we have[21]

$$\langle \omega_i(t_\ell)\omega_p(t_m)\rangle = \delta_{ip}\frac{kT}{I}e^{-B|t_\ell - t_m|}, \quad (i, p = 1, 2, 3) \tag{3.6}$$

It follows from (2.37) that[22]

$$\varepsilon^2\Omega^{(2)}(t_1) = -\frac{kT}{I}J^2\int_0^{t_1} e^{-B(t_1-t_2)}dt_2 = \frac{kT}{IB}J^2(1-e^{-Bt_1}), \tag{3.7}$$

$$\varepsilon^4\Omega^{(4)}(t_1) = -\left(\frac{kT}{I}\right)^2 J^2\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\, e^{-B(t_1+t_2-t_3-t_4)}. \tag{3.8}$$

We see from (2.36) that

$$\varepsilon^4 F^{(4)}(t) = -\int_0^t \varepsilon^4\Omega^{(4)}(t_1)dt_1 - \int_0^t \varepsilon^2 F^{(2)}(t_1)\varepsilon^2\Omega^{(2)}(t_1)dt_1 - i\int_0^t (\underset{\sim}{J}\cdot\underset{\sim}{\omega}(t_1))\varepsilon^3 F^{(3)}(t_1)dt_1. \tag{3.9}$$

Let us calculate $\langle \underset{\sim}{I}\,\omega_\mu(t)\omega_\nu(0)\rangle$, $\langle \varepsilon^2 F^{(2)}(t)\omega_\mu(t)\omega_\nu(0)\rangle$, $\langle \varepsilon^4 F^{(4)}(t)\omega_\mu(t)\omega_\nu(0)\rangle$. From (3.6)

$$\langle \underset{\sim}{I}\,\omega_\mu(t)\,\omega_\nu(0)\rangle = \delta_{\mu\nu}\underset{\sim}{I}\,\frac{kT}{I}e^{-Bt},$$

since $t \geq 0$ in (2.6) and all subsequent equations of Section 2. From

(2.35) and (3.6)

$$\varepsilon^2 F^{(2)}(t) = -\int_0^t dt_1\int_0^{t_1}dt_2\left[\sum_{r,s=1}^{3} J_r J_s\,\omega_r(t_1)\omega_s(t_2) - \frac{kT}{I}J^2\int_0^t dt_1\int_0^{t_1}dt_2\, e^{-B(t_1-t_2)}\right], \tag{3.10}$$

and therefore

$$\langle \varepsilon^2 F^{(2)}(t)\omega_\mu(t)\omega_\nu(0)\rangle = -\sum_{r,s=1}^{3} J_r J_s\int_0^t dt_1\int_0^{t_1}dt_2\langle \omega_\mu(t)\omega_r(t_1)\omega_s(t_2)\omega_\nu(0)\rangle + \gamma\frac{kT}{I}J^2\delta_{\mu\nu}(Bt - 1 + e^{-Bt}), \tag{3.11}$$

on introducing γ from (3.4). From the properties of Gaussian variables[23]

$$\begin{aligned}&\langle \omega_\mu(t)\omega_r(t_1)\omega_s(t_2)\omega_\nu(0)\rangle \\ &= \langle \omega_\mu(t)\omega_r(t_1)\rangle\langle \omega_s(t_2)\omega_\nu(0)\rangle + \langle \omega_\mu(t)\omega_s(t_2)\rangle\langle \omega_r(t_1)\omega_\nu(0)\rangle \\ &\quad + \langle \omega_\mu(t)\omega_\nu(0)\rangle\langle \omega_r(t_1)\omega_s(t_2)\rangle \\ &= \left(\frac{kT}{I}\right)^2\{\delta_{\mu r}\delta_{s\nu}e^{-B(t-t_1+t_2)} + (\delta_{\mu s}\delta_{r\nu} + \delta_{\mu\nu}\delta_{rs})e^{-B(t+t_1-t_2)}\}.\end{aligned} \tag{3.12}$$

Thus

$$\begin{aligned}&\int_0^t dt_1\int_0^{t_1}dt_2\,\langle \omega_\mu(t)\omega_r(t_1)\omega_s(t_2)\omega_\nu(0)\rangle \\ &= \gamma\frac{kT}{I}e^{-Bt}\{(e^{Bt} - 1 - Bt)\delta_{\mu r}\delta_{s\nu} + (e^{-Bt} - 1 + Bt)(\delta_{\mu s}\delta_{r\nu} + \delta_{\mu\nu}\delta_{rs})\}\end{aligned} \tag{3.13}$$

and on employing (2.30) we deduce that

$$\langle \varepsilon^2 F^{(2)}(t)\omega_\mu(t)\omega_\nu(0)\rangle = -\gamma\frac{kT}{I}\{(1 - 2e^{-Bt} + e^{-2Bt})J_\mu J_\nu + (-e^{-Bt} + Bte^{-Bt} + e^{-2Bt})\,i(\underset{\sim}{J}\cdot\underset{\sim}{e}_\mu\times\underset{\sim}{e}_\nu)\}. \tag{3.14}$$

Since $\Omega^{(2)}$ and $\Omega^{(4)}$ are non-stochastic, we see from (3.9) that

$$\langle \varepsilon^4 F^{(4)}(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle = -\frac{kT}{I}\delta_{\mu\nu}e^{-Bt}\int_0^t \varepsilon^4\Omega^{(4)}(t_1)\,dt_1 - \int_0^t \varepsilon^2\Omega^{(2)}(t_1)\langle \varepsilon^2 F^{(2)}(t_1)\,\omega_\mu(t)\,\omega_\nu(0)\rangle\,dt_1 \qquad (3.15)$$
$$- i\int_0^t \langle \omega_\mu(t)\,(\underline{J}\cdot\underline{\omega}(t_1))\,\varepsilon^3 F^{(3)}(t_1)\,\omega_\nu(0)\rangle\,dt_1 .$$

Now, by (3.8),

$$-\frac{kT}{I}\delta_{\mu\nu}e^{-Bt}\int_0^t \varepsilon^4\Omega^{(4)}(t_1)\,dt_1$$
$$=\left(\frac{kT}{I}\right)^3\delta_{\mu\nu}J^2e^{-Bt}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\; e^{-B(t_1+t_2-t_3-t_4)}, \qquad (3.16)$$

which is a convolution[24]. Next we have from (3.7) and (3.10)

$$-\int_0^t \varepsilon^2\Omega^{(2)}(t_1)\langle \varepsilon^2 F^{(2)}(t_1)\,\omega_\mu(t)\,\omega_\nu(0)\rangle\,dt_1$$
$$= -\frac{kT}{IB}J^2\int_0^t dt_1(1-e^{-Bt_1})\Big\langle \omega_\mu(t)\Big[\int_0^{t_1}dt_2\int_0^{t_2}dt_3\sum_{r,s=1}^{3}J_rJ_s\,\omega_r(t_2)\,\omega_s(t_3) \qquad (3.17)$$
$$-\gamma J^2(Bt_1-1+e^{-Bt_1})\Big]\omega_\nu(0)\Big\rangle .$$

Using (3.12) we deduce that

$$\int_0^{t_1}dt_2\int_0^{t_2}dt_3\sum_{r,s=1}^{3}J_rJ_s\langle\omega_\mu(t)\,\omega_r(t_2)\,\omega_s(t_3)\,\omega_\nu(0)\rangle$$
$$=\gamma\frac{kT}{I}e^{-Bt}\Big\{\delta_{\mu\nu}J^2(e^{-Bt_1}-1+Bt_1)+J_\mu J_\nu(e^{Bt_1}-2+e^{-Bt_1}) \qquad (3.18)$$
$$+(e^{-Bt_1}-1+Bt_1)\,i\,(\underline{J}\cdot\underline{e}_\mu\times\underline{e}_\nu)\Big\} .$$

Cancelling terms in (3.17) and (3.18) and integrating with respect to t_1 we obtain

$$-\int_0^t \varepsilon^2\Omega^{(2)}(t_1)\langle \varepsilon^2 F^{(2)}(t_1)\,\omega_\mu(t)\,\omega_\nu(0)\rangle\,dt_1$$
$$= -\gamma^2\frac{kT}{I}J^2\Big\{J_\mu J_\nu\left(1+\tfrac{3}{2}e^{-Bt}-3Bte^{-Bt}-3e^{-2Bt}+\tfrac{1}{2}e^{-3Bt}\right) \qquad (3.19)$$
$$+i(\underline{J}\cdot\underline{e}_\mu\times\underline{e}_\nu)\left(\tfrac{1}{2}e^{-Bt}-Bte^{-Bt}+\tfrac{1}{2}B^2t^2e^{-Bt}-e^{-2Bt}+Bte^{-2Bt}+\tfrac{1}{2}e^{-3Bt}\right)$$

The equation in (2.35) for $\varepsilon^3 F^{(3)}(t)$ gives

$$\varepsilon^3F^{(3)}(t_1)= i\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\Big\{\sum_{b=1}^{3}\sum_{c=1}^{3}\sum_{d=1}^{3}J_bJ_cJ_d\,\omega_b(t_2)\,\omega_c(t_3)\,\omega_d(t_4)$$
$$-\frac{kT}{I}J^2\Big[\sum_{b=1}^{3}J_b\,\omega_b(t_2)\,e^{-B(t_3-t_4)}+\sum_{c=1}^{3}J_c\,\omega_c(t_3)\,e^{-B(t_2-t_4)} \qquad (3.20)$$
$$+\sum_{d=1}^{3}J_d\,\omega_d(t_4)\,e^{-B(t_2-t_3)}\Big]\Big\} ,$$

so that

$$-i\int_0^t\langle\omega_\mu(t)\,(\underline{J}\cdot\underline{\omega}(t_1))\,\varepsilon^3F^{(3)}(t_1)\,\omega_\nu(0)\rangle\,dt_1$$
$$=\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\,(A-B-C-D), \qquad (3.21)$$

where

$$A=\sum_{a,b,c,d=1}^{3}J_aJ_bJ_cJ_d\langle\omega_\mu(t)\,\omega_a(t_1)\,\omega_b(t_2)\,\omega_c(t_3)\,\omega_d(t_4)\,\omega_\nu(0)\rangle$$
$$B=\frac{kT}{I}J^2\sum_{a,b=1}^{3}J_aJ_b\langle\omega_\mu(t)\,\omega_a(t_1)\,\omega_b(t_2)\,\omega_\nu(0)\rangle e^{-B(t_3-t_4)}$$
$$C=\frac{kT}{I}J^2\sum_{a,c=1}^{3}J_aJ_c\langle\omega_\mu(t)\,\omega_a(t_1)\,\omega_c(t_3)\,\omega_\nu(0)\rangle e^{-B(t_2-t_4)} \qquad (3.22)$$
$$D=\frac{kT}{I}J^2\sum_{a,d=1}^{3}J_aJ_d\langle\omega_\mu(t)\,\omega_a(t_1)\,\omega_d(t_4)\,\omega_\nu(0)\rangle e^{-B(t_2-t_3)} .$$

To evaluate A we extend (3.12) to the product of six ω's and employ (2.30) to derive the relations:

$$
\begin{aligned}
&\sum_{a=1}^{3} J_a J_\mu J_a J_\nu = \sum_{a=1}^{3} J_\mu J_a J_\nu J_a = (J^2 - \underset{\sim}{I}) J_\mu J_\nu \\
&\sum_{a=1}^{3} J_a J_\mu J_\nu J_a = (J^2 - 3\underset{\sim}{I}) J_\mu J_\nu + \delta_{\mu\nu} J^2 - i(\underset{\sim}{J} \cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu) \\
&\sum_{a,b=1}^{3} J_a J_b J_a J_b = J^2 (J^2 - \underset{\sim}{I}) \\
&\sum_{a,b,c=1}^{3} J_a J_b J_c J_a J_b J_c = J^2 (J^2 - \underset{\sim}{I})(J^2 - 2\underset{\sim}{I}) \qquad (3.23) \\
&\sum_{a,b,c=1}^{3} J_a J_b J_c J_a J_c J_b = \sum_{a,b,c=1}^{3} J_a J_b J_c J_b J_a J_c \\
&= \sum_{a,b,c=1}^{3} J_a J_b J_a J_c J_b J_c = J^2 (J^2 - \underset{\sim}{I})^2 .
\end{aligned}
$$

After a long but elementary calculation we deduce from (3.21) - (3.23) that

$$
\begin{aligned}
&-i \int_0^t \langle \omega_\mu(t) (\underset{\sim}{J} \cdot \underset{\sim}{\omega}(t_1)) \, \varepsilon^3 F^{(3)}(t_1) \, \omega_\nu(0) \rangle dt_1 \\
&= \left(\frac{kT}{I}\right)^3 \Big\{ - J_\mu J_\nu \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \, e^{-B(t - t_1 + t_2 + t_3 - t_4)} \\
&\quad + [2J^2 - \underset{\sim}{I}] J_\mu J_\nu \int_0^t dt_1 \cdots \int_0^{t_3} dt_4 \, e^{-B(t_1 + t_1 - t_2 - t_3 + t_4)} \\
&\quad + \{ [3J^2 - 4\underset{\sim}{I}] J_\mu J_\nu + 2[J^2 - \underset{\sim}{I}] \, i (\underset{\sim}{J} \cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu) \\
&\qquad + J^4 \delta_{\mu\nu} \} \int_0^t dt_1 \cdots \int_0^{t_3} dt_4 \, e^{-B(t + t_1 - t_2 + t_3 - t_4)} \qquad (3.24) \\
&\quad + \{ [4J^2 - 7\underset{\sim}{I}] J_\mu J_\nu + [4J^2 - 6\underset{\sim}{I}] \, i (\underset{\sim}{J} \cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu) \\
&\qquad + [2J^4 - 2J^2] \delta_{\mu\nu} \} \int_0^t dt_1 \cdots \int_0^{t_3} dt_4 \, e^{-B(t + t_1 + t_2 - t_3 - t_4)} \Big\},
\end{aligned}
$$

and we see that the multiple integrals are convolutions.

The value of $\langle \varepsilon^4 F^{(4)}(t) \, \omega_\mu(t) \, \omega_\nu(0) \rangle$ is now obtained from (3.15), (3.16), (3.19) and (3.24). If we wished to find $\langle \varepsilon^6 F^{(6)}(t) \, \omega_\mu(t) \, \omega_\nu(0) \rangle$, the calculation would be extremely long; for example, corresponding to A in (3.22) we would have a summation which involves the ensemble average of the continued product of 8 ω's and this consists of 105 terms. We shall not therefore take the calculations further. For our purposes we do not require an explicit expression for the rotation operator $R(t)$ but such an expression may be written down from (2.33), (2.35), (3.6) - (3.10), (3.20), (3.2) and (3.3). The value of $\langle R(t) \, \omega_\mu(t) \, \omega_\nu(0) \rangle$ is obtainable from (3.2), (3.3), (3.5) and our calculated values of $\langle \underset{\sim}{I} \, \omega_\mu(t) \, \omega_\nu(0) \rangle$, $\langle \varepsilon^2 F^{(2)}(t) \, \omega_\mu(t) \, \omega_\nu(0) \rangle$, $\langle \varepsilon^4 F^{(4)}(t) \, \omega_\mu(t) \, \omega_\nu(0) \rangle$. Explicit values of the integrals occurring, which in fact are not required for the investigation of spin-rotational interactions, may be derived by inverting the Laplace transforms of the convolutions[25].

3.2 The Laplace transform of $\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$

In the case of a spherical molecule eq. (2.14) becomes

$$C_{ii}^{oc}(s) = \frac{I^2}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m\, b^{\,i}_{n\mu}\, b^{\,i}_{m\nu}\left(\int_0^\infty e^{-st}\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle dt\right)_{n,-m} \qquad (3.25)$$

the integral being the Laplace transform of the operator $\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$. As an illustration of the method of calculation and approximation we take the first term

$$-\left(\frac{kT}{I}\right)^3 J_\mu J_\nu \int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3\int_0^{t_3} dt_4\, e^{-B(t-t_1+t_2+t_3-t_4)} \qquad (3.26)$$

on the right hand side of (3.24) and we approximate $\langle R(t)\rangle$ in (3.2) by $e^{-BG_j t}\,\boldsymbol{I}$. We shall calculate the Laplace transform of the expression (3.26) multiplied by $e^{-BG_j t}$, noting that

$$-\left(\frac{kT}{I}\right)^3 e^{-BG_j t} J_\mu J_\nu \int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3\int_0^{t_3} dt_4\, e^{-B(t-t_1+t_2+t_3-t_4)}$$

$$= -\left(\frac{kT}{I}\right)^3 J_\mu J_\nu \int_0^t dt_1\cdots\int_0^{t_3} dt_4\, e^{-(B+BG_j)(t-t_1)}\, e^{-BG_j(t_1-t_2)}\, e^{-(B+BG_j)(t_2-t_3)}$$
$$\times\, e^{-(2B+BG_j)(t_3-t_4)}\, e^{-(B+BG_j)t_4}$$

$$= -\left(\frac{kT}{I}\right)^3 J_\mu J_\nu\, e^{-(B+BG_j)t} * e^{-BG_j t} * e^{-(B+BG_j)t} * e^{-(2B+BG_j)t} * e^{-(B+BG_j)t}$$

The Laplace transform of this is

$$-\left(\frac{kT}{I}\right)^3 \frac{J_\mu J_\nu}{(s+BG_j)(s+B+BG_j)^3(s+2B+BG_j)}\,. \qquad (3.27)$$

By inverting this we may find the value of (3.26) multiplied by $e^{-BG_j t}$.

Let us write (3.27) as

$$-\gamma^2\frac{kT}{IB}\,\frac{J_\mu J_\nu}{\left(\frac{s}{B}+G_j\right)\left(1+\frac{s}{B}+G_j\right)^3\left(2+\frac{s}{B}+G_j\right)}\,. \qquad (3.28)$$

For the small values of j with which we shall be concerned, G_j defined by (3.3) is of order γ. The factors $1+(s/B)+G_j$, $2+(s/B)+G_j$ are at least of order unity. However for values of s/B of order G_j or less, and so for the extreme narrowing case when s will be taken equal to zero, $(s/B)+G_j$ is of order γ. This will raise the order of (3.28) to $J_\mu J_\nu\,\gamma\, kT/(IB)$. Then in order to obtain an approximation of order $J_\mu J_\nu\,\gamma^2 kT/(IB)$ it will be necessary to include the term $\gamma\, J^2$ in (3.2) when approximating $\langle R(t)\rangle$. Similarly, if the denominator of the Laplace transform had contained a factor $(s+BG_j)^2$, we would have had to include terms proportional to γ^2 in the approximation of $\langle R(t)\rangle$.

On performing the calculations we obtain

$$\int_0^\infty e^{-st}\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle dt$$
$$= \delta_{\mu\nu}\boldsymbol{I}\,\frac{kT}{I}\left\{\frac{\boldsymbol{I}}{s+B+BG_j}+\frac{\gamma B J^2}{(s+B+BG_j)(s+2B+BG_j)}\right.$$
$$+\gamma^2\left[\frac{\frac{1}{2}J^4+\frac{5}{4}J^2}{s+B+BG_j}-\frac{J^4+J^2}{s+2B+BG_j}-\frac{BJ^2}{(s+2B+BG_j)^2}\right.$$
$$\left.\left.+\frac{\frac{1}{2}J^4-\frac{1}{4}J^2}{s+3B+BG_j}+\frac{B^4J^2}{(s+B+BG_j)^3(s+2B+BG_j)^2}\right]\right\}$$
$$+i(\boldsymbol{J}\cdot\boldsymbol{e}_\mu\times\boldsymbol{e}_\nu)\gamma\frac{kT}{I}\left\{\frac{\boldsymbol{I}}{s+B+BG_j}-\frac{B\boldsymbol{I}}{(s+B+BG_j)^2}-\frac{\boldsymbol{I}}{s+2B+BG_j}\right.$$
$$+\gamma\left[J^2\left(\frac{\frac{1}{2}}{s+B+BG_j}-\frac{B^2}{(s+B+BG_j)^3}-\frac{1}{s+2B+BG_j}+\frac{\frac{1}{2}}{s+3B+BG_j}\right)\right.$$
$$\left.\left.+\frac{2B^4(J^2-\boldsymbol{I})}{(s+B+BG_j)^3(s+2B+BG_j)^2}+\frac{B^4(4J^2-6\boldsymbol{I})}{(s+B+BG_j)^2(s+2B+BG_j)^2(s+3B+BG_j)}\right]\right\} \qquad (3.29)$$

$$+J_\mu J_\nu \gamma \frac{kT}{I}\Big\{-\frac{\underset{\sim}{I}+2\gamma J^2+\gamma^2[\frac{3}{2}J^4+\frac{5}{4}J^2]}{s+BG_j}+\frac{2\underset{\sim}{I}+\frac{3}{2}\gamma J^2}{s+B+BG_j}$$
$$+\frac{3\gamma BJ^2}{(s+B+BG_j)^2}-\frac{1}{s+2B+BG_j}+\frac{\frac{1}{2}\gamma J^2}{s+3B+BG_j}$$
$$+\gamma B^4\Big[\frac{2J^2-2\underset{\sim}{I}+2\gamma(J^4-J^2)}{(s+BG_j)(s+B+BG_j)^3(s+2B+BG_j)}+\frac{2J^2-3\underset{\sim}{I}}{(s+B+BG_j)^3(s+2B+BG_j)^2}$$
$$+\frac{2J^2-5\underset{\sim}{I}}{(s+B+BG_j)^2(s+2B+BG_j)^2(s+3B+BG_j)}\Big]\Big\}$$

$$+\ \cdots\ .$$

We note that the quantities inside the brackets are multiples of the identity.

3.3 Spin-rotational relaxation times

We return to eq. (3.25) for $C^{00}_{ii}(s)$. Let us suppose that all the nuclei are in equivalent positions, and let us take the third axis of the molecular frame through the nucleus in which we are interested. We assume that the third axis is an n-fold axis of symmetry[27] with $n \geq 3$, and that this allows us to write[28]

$$C^i_{33} = C_{\parallel}\ ,\quad C^i_{11} = C^i_{22} = C_{\perp}$$
$$C^i_{pq} = 0. \qquad (p \neq q) \tag{3.30}$$

We then see from (2.3) that

$$b^i_{\pm 1,1} = \mp\frac{C_\perp}{\sqrt{2}}\ ,\quad b^i_{\pm 1,2} = \frac{iC_\perp}{\sqrt{2}}\ ,\quad b^i_{\pm 1,3} = 0$$
$$b^i_{01} = b^i_{02} = 0\ ,\quad b^i_{03} = C_{\parallel}. \tag{3.31}$$

The b's are independent of i and we shall henceforth omit their superscript. We shall also write $C^{00}_{ii}(s)$ simply as $C(s)$ because it is independent of i and because the zero superscripts may be discarded, since this is the only $C^{\ell k}_{ii}(s)$ function that we shall meet in this subsection. Thus we express (3.25) as

$$C(s) = \frac{I^2}{3\hbar^2}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b_{n\mu} b_{m\nu}\Big(\int_0^\infty e^{-st}\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle dt\Big)_{n,-m} \tag{3.32}$$

where $n,-m$ denotes the $n,-m$ —matrix element in the representation with basis elements $Y_{1,-1}(\beta(0),\alpha(0)),\ Y_{1,0}(\beta(0),\alpha(0)),\ Y_{1,1}(\beta(0),\alpha(0))$.

The matrix element may be written down from (3.29) by putting $J^2 = 2\underset{\sim}{I}$ and $G_j = G_1$, where from (3.3)

$$G_1 = 2\gamma + \gamma^2 + \frac{7}{6}\gamma^3 + \cdots\ . \tag{3.33}$$

In the present representation

$$J_1 = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \quad J_2 = \frac{i}{\sqrt{2}}\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad J_3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{3.34}$$

the rows and columns being numbered in the sequence -1, 0, 1. The matrices of (3.34) may be obtained from those of Rose[29] by making the substitutions

$$M_x \mapsto -\hbar J_1, \quad M_y \mapsto -\hbar J_2, \quad M_z \mapsto -\hbar J_3$$

in order to take account of the minus sign in the commutation relation (2.30). We see from (3.33) that

$$B G_1 = 2\gamma B\left(1 + \tfrac{1}{2}\gamma + \tfrac{7}{12}\gamma^2 + \cdots\right) = O\left(\frac{kT}{IB}\right)$$

In the extreme narrowing case of $\omega_0 \ll kT/(IB)$[30] we may replace s by zero in (3.29) when calculating $J_1(\omega_0)$ from $C(s)$ as given by (2.15). Then (2.17) yields

$$\frac{1}{T_{sr}} = 2\, C(0). \tag{3.35}$$

In order to deduce $C(0)$ from (3.32) we must perform the summations over m, n, μ, ν involving the b's and the operators outside the curly brackets of (3.29). A brief calculation gives

$$\sum_{\mu,\nu=1}^{3} \sum_{m,n=-1}^{1} (-)^m b_{n\mu} b_{m\nu}\, \delta_{\mu\nu} (\mathbf{I})_{n,-m} = C_{\parallel}^2 + 2\, C_{\perp}^2, \tag{3.36}$$

where we have employed (3.31). Then we deduce from (3.34) that

$$\sum_{\mu,\nu=1}^{3} \sum_{m,n=-1}^{1} (-)^m b_{n\mu} b_{m\nu} \left[i (\mathbf{J} \cdot \mathbf{e}_\mu \times \mathbf{e}_\nu) \right]_{n,-m} = -2 C_{\perp}^2 - 4\, C_{\perp} C_{\parallel}. \tag{3.37}$$

On evaluating $J_\mu J_\nu$ from (3.34) and substituting we likewise find that

$$\sum_{\mu,\nu=1}^{3} \sum_{m,n=-1}^{1} (-)^m b_{n\mu} b_{m\nu} \left(J_\mu J_\nu\right)_{n,-m} = 0. \tag{3.38}$$

Equations (3.36) - (3.38) were already given by Hubbard[31]. In (3.29) the terms that require special attention for $s=0$ are all proportional to $J_\mu J_\nu$. On account of (3.38) they give zero contribution to $C(0)$, and for the purpose of calculating $1/T_{sr}$ from (3.35) they may be disregarded. However for the sake of completing a record of this calculation we shall retain them.

On putting $j=1$ in (3.29), employing (3.33) and expressing the results as power series in γ we find that

$$\begin{aligned} \lim_{s\to 0} \int_0^\infty & e^{-st} \langle R(t)\, \omega_\mu(t)\, \omega_\nu(0) \rangle_{j=1}\, dt \\ = \frac{kT}{IB} \Big\{ & \delta_{\mu\nu} \mathbf{I} + \gamma\left[-\delta_{\mu\nu}\mathbf{I} - \tfrac{i}{2}(\mathbf{J}\cdot \mathbf{e}_\mu \times \mathbf{e}_\nu)\right] \\ & + \gamma^2\left[\tfrac{13}{6}\delta_{\mu\nu}\mathbf{I} + \tfrac{13}{12} i (\mathbf{J}\cdot\mathbf{e}_\mu\times\mathbf{e}_\nu)\right] \\ & - \tfrac{1}{2} J_\mu J_\nu + \tfrac{1}{4}\gamma J_\mu J_\nu + \tfrac{1}{6}\gamma^2 J_\mu J_\nu + \cdots \Big\}. \end{aligned} \tag{3.39}$$

For the reason given in the previous subsection it is to be expected that, if we were to continue our calculations so as to include the $\varepsilon^6 F^{(6)}(t)$ — term on the right hand side of (3.5), the coefficient $\frac{1}{6}$ of $\gamma^2 J_\mu J_\nu$ would be altered. The other terms on the right hand side of (3.39) are in agreement with the result of Hubbard[32]. Equation (3.32) combined with (3.36) - (3.39) yield

$$\begin{aligned} C(0) &= \frac{kTI}{3\hbar^2 B}\left\{ \left(C_\parallel^2 + 2C_\perp^2\right)\left(1 - \gamma + \tfrac{13}{6}\gamma^2 + \cdots\right) + \left(2C_\perp^2 + 4C_\perp C_\parallel\right)\left(\tfrac{1}{2}\gamma - \tfrac{13}{12}\gamma^2 + \cdots\right)\right\} \\ &= \frac{kTI}{3\hbar^2 B}\left\{ \left(C_\parallel^2 + 2C_\perp^2\right) - \gamma\left(C_\perp - C_\parallel\right)^2 + \tfrac{13}{6}\gamma^2\left(C_\perp - C_\parallel\right)^2 + \cdots\right\}, \end{aligned}$$

and so, from (3.35),

$$\frac{1}{T_{sr}} = \frac{2IkT}{3\hbar^2 B}\left\{(C_{\parallel}^2 + 2C_{\perp}^2) - \gamma(C_{\perp} - C_{\parallel})^2 + \frac{13}{6}\gamma^2(C_{\perp} - C_{\parallel})^2 + \cdots\right\}. \quad (3.40)$$

To obtain τ_{sr} we note that for the sphere (2.28) becomes

$$\frac{1}{T_{sr}} = \frac{2IkT\tau_{sr}}{3\hbar^2}\sum_{\mu=1}^{3}\sum_{m=-1}^{1}(-)^m b_{-m\mu} b_{m\mu}. \quad (3.41)$$

Now

$$\sum_{\mu=1}^{3}\sum_{m=-1}^{1}(-)^m b_{-m\mu} b_{m\mu} = \sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b_{-n\mu} b_{m\nu}\delta_{mn}\delta_{\mu\nu}$$

$$= \sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^m b_{n\mu} b_{m\nu}\delta_{n,-m}\delta_{\mu\nu} = C_{\parallel}^2 + 2C_{\perp}^2,$$

by (3.36), and we may express (3.41) as

$$\frac{1}{T_{sr}} = \frac{2IkT}{3\hbar^2}\left(C_{\parallel}^2 + 2C_{\perp}^2\right)\tau_{sr}. \quad (3.42)$$

If we write $\xi = C_{\perp}/C_{\parallel}$, (3.41) and (3.42) yield

$$\tau_{sr} = \frac{1}{B}\left\{1 - \gamma\frac{(\xi-1)^2}{2\xi^2+1} + \frac{13}{6}\gamma^2\frac{(\xi-1)^2}{2\xi^2+1} + \cdots\right\} \quad (3.43)$$

in agreement with Hubbard[33]. When $C_{\perp} = C_{\parallel}$, (3.43) reduces to

$$\tau_{sr} = \tau_F,$$

where we have written B^{-1} as τ_F, the friction time that occurs in the discussion of the Debye and Langevin equations. Then τ_{sr} is independent of the orientation, as it should be according to an earlier result of Hubbard for the spherical molecule[34].

McClung[35] carried out an investigation of spin-rotational interactions for spherical molecules by employing the eigenfunction expansion procedure of Fixman and Rider[36] to obtain a series expansion for the orientational-angular velocity conditional probability density from the Fokker-Planck equation. Applying numerical methods he calculated a correlation time which characterizes the anisotropic spin-rotational interactions. If we denote this correlation time by τ'_{sr}, then in our notation[37]

$$\frac{1}{T_{sr}} = \frac{2IkT C_{\parallel}^2}{\hbar^2 B}\left\{\left(\frac{2\xi+1}{3}\right)^2 + 2\left(\frac{\xi-1}{3}\right)^2 B\tau'_{sr}\right\}.$$

On comparing this equation with (3.42) we find that

$$3(2\xi^2+1)\tau_{sr} = (2\xi+1)^2 B^{-1} + 2(\xi-1)^2\tau'_{sr}. \quad (3.44)$$

When we substitute for τ_{sr} from (3.43) into (3.44), we obtain

$$\tau'_{sr} = 1 - \frac{3}{2}\gamma + \frac{13}{4}\gamma^2 + \cdots,$$

which agrees with the result of McClung and his collaborators[38].

4. ASYMMETRIC MOLECULES

4.1. General equations

We now consider the case of a molecule with no special symmetry properties, whose rotational Brownian motion is governed by the Euler-Langevin equations (2.31). With an obvious generalization of $\gamma^{1/2}$ satisfying (3.14) we choose ε in (2.32) as given by

$$\varepsilon = \frac{(kT)^{1/2}}{(I_1 I_2 I_3 B_1^2 B_2^2 B_3^2)^{1/6}} \tag{4.1}$$

and expand the components of the steady state angular velocity:

$$\omega_i(t) = \varepsilon\,\omega_i^{(1)}(t) + \varepsilon^2 \omega_i^{(2)}(t) + \varepsilon^3 \omega_i^{(3)}(t) + \cdots . \tag{4.2}$$

Then $\omega_i^{(1)}(t)$ is a centred Gaussian random variable obeying

$$\varepsilon^2 \langle \omega_\ell^{(1)}(t)\, \omega_m^{(1)}(s) \rangle = \delta_{\ell m} \frac{kT}{I_\ell} e^{-B_\ell |t-s|} . \tag{4.3}$$

On the other hand

$$\langle \omega_\mu(t)\, \omega_\nu(s) \rangle = \delta_{\mu\nu} \Big\{ \frac{kT}{I_\mu} e^{-B_\mu |t-s|} + \left(\frac{I_\rho - I_\sigma}{I_\mu}\right)^2 \frac{(kT)^2}{I_\rho I_\sigma} \frac{e^{-B_\mu |t-s|}\left[1 - (B_\rho + B_\sigma - B_\mu)|t-s| - e^{-(B_\rho + B_\sigma - B_\mu)|t-s|}\right]}{(B_\rho + B_\sigma - B_\mu)^2} + \cdots \Big\}, \tag{4.4}$$

where μ, ρ, σ is a cyclic permutation of 1, 2, 3[39].

We immediately make some simplifications. In order to calculate relaxation times we shall work in the three-dimensional representation given by (3.34). From these we deduce that

$$J_1^2 = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}, \quad J_2^2 = \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}, \quad J_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{4.5}$$

and we see that J_1^2, J_2^2, J_3^2 commute with each other. As a consequence of this

$$\langle R(t) \rangle = \Big\{ \underset{\sim}{I} + \sum_{i=1}^{3} \frac{kT}{I_i B_i^2} (1 - e^{-B_i t}) J_i^2 + \cdots \Big\} e^{Gt}, \tag{4.6}$$

where

$$G = -\sum_{\ell=1}^{3} \left(D_\ell^{(1)} + D_\ell^{(2)}\right) J_\ell^2 \tag{4.7}$$

$$D_1^{(1)} = \frac{kT}{I_1 B_1}, \quad D_2^{(1)} = \frac{kT}{I_2 B_2}, \quad D_3^{(1)} = \frac{kT}{I_3 B_3} \tag{4.8}$$

$$D_1^{(2)} = \frac{(kT)^2}{I_1 I_2 I_3} \Big[I_1 \frac{2B_2 B_3 (B_2 + B_3) - B_1 (B_2^2 + B_2 B_3 + B_3^2)}{B_1 B_2^2 B_3^2 (B_2 + B_3)} + I_2 \frac{B_2 (B_2 + B_3) - 2B_3^2}{B_1 B_2 B_3^2 (B_2 + B_3)} + I_3 \frac{B_3 (B_2 + B_3) - 2B_2^2}{B_1 B_2^2 B_3 (B_2 + B_3)} - \frac{(I_2 - I_3)^2}{I_1 B_1^2 (B_2 + B_3)} \Big], \text{ etc.}^{40)} \tag{4.9}$$

Thus $D_l^{(2)}$ is a correction to $D_l^{(1)}$ of order γ. The same is true of the summation terms in (4.6) with respect to $\underset{\sim}{I}$. We must therefore restrict our calculations for the asymmetric rotator model of the molecule to corrections of just one order in γ to the Debye-Perrin limit[41].

4.2. Calculation of $\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$

We return to (2.33) with ξ given by (4.1) and deduce that

$$\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle = \{\langle\omega_\mu(t)\omega_\nu(0)\rangle\underset{\sim}{I} + \langle\varepsilon F^{(1)}(t)\omega_\mu(t)\omega_\nu(0)\rangle + \langle\varepsilon^2 F^{(2)}(t)\omega_\mu(t)\omega_\nu(0)\rangle + \dots\}\langle R(t)\rangle. \qquad (4.10)$$

On account of the restricted order of approximation available for $\langle R(t)\rangle$ in the case of an asymmetric molecule we shall not proceed beyond the terms written explicitly in (4.10). In the spherical model $\langle\varepsilon F^{(1)}(t)\omega_\mu(t)\omega_\nu(0)\rangle$, which is proportional to the ensemble average of a sum of products of three angular velocity components, vanished because they were centred Gaussian variables. In the present case $\omega_i(t)$ is given by (4.2) and[42]

$$\omega_i^{(2)}(\tau) = \lambda_i \int_{-\infty}^{\tau} e^{-B_i(\tau-t_2)}\,\omega_j^{(1)}(t_2)\,\omega_k^{(1)}(t_2)\,dt_2, \qquad (4.11)$$

where i, j, k is a cyclic permutation of 1, 2, 3 and

$$\lambda_i = \frac{I_j - I_k}{I_i}. \qquad (4.12)$$

Then from (2.35)

$$\langle\varepsilon F^{(1)}(t)\omega_\mu(t)\omega_\nu(0)\rangle = -i\sum_{r=1}^{3} J_r \int_0^t \langle\omega_\mu(t)\,\omega_r(t_1)\,\omega_\nu(0)\rangle\,dt_1. \qquad (4.13)$$

On substitution from (4.2)

$$\langle\omega_\mu(t)\omega_r(t_1)\omega_\nu(0)\rangle = \varepsilon^4\langle\omega_\mu^{(2)}(t)\omega_r^{(1)}(t_1)\omega_\nu^{(1)}(0)\rangle + \varepsilon^4\langle\omega_\mu^{(1)}(t)\omega_r^{(2)}(t_1)\omega_\nu^{(1)}(0)\rangle + \varepsilon^4\langle\omega_\mu^{(1)}(t)\omega_r^{(1)}(t_1)\omega_\nu^{(2)}(0)\rangle + \dots, \qquad (4.14)$$

and we see from (4.3) and (4.11) that each term on the right hand side vanishes unless μ, ν, τ are 1, 2, 3 in some order. Moreover

$$J_\tau = (\underset{\sim}{J} \cdot \underset{\sim}{e}_\tau) = \begin{cases} (\underset{\sim}{J} \cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu) & \text{for } \mu=2, \nu=3 \text{ or } \mu=3, \nu=1 \text{ or } \mu=1, \nu=2 \\ -(\underset{\sim}{J} \cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu) & \text{for } \mu=3, \nu=2 \text{ or } \mu=1, \nu=3 \text{ or } \mu=2, \nu=1. \end{cases} \tag{4.15}$$

In evaluating $\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$ from (4.10) we already know $\langle \omega_\mu(t)\omega_\nu(0)\rangle$ from (4.4) and we now calculate $\langle \varepsilon F^{(1)}(t)\omega_\mu(t)\omega_\nu(0)\rangle$ from (4.13) and (4.14). Employing (4.3) and (4.11), and remembering that μ, ν, τ are all different we have

$$\varepsilon^4 \langle \omega_\mu^{(2)}(t)\,\omega_\tau^{(1)}(t_1)\,\omega_\nu^{(1)}(0)\rangle$$

$$= \lambda_\mu \int_{-\infty}^{t} e^{-B_\mu(t-t_2)} \langle \omega_\tau^{(1)}(t_2)\omega_\nu^{(1)}(t_2)\omega_\tau^{(1)}(t_1)\omega_\nu^{(1)}(0)\rangle \, dt_2$$

$$= \frac{\lambda_\mu (kT)^2}{I_\nu I_\tau} e^{-B_\mu t} \int_{-\infty}^{t} e^{B_\mu t_2} e^{-B_\tau |t_1 - t_2|} e^{-B_\nu |t_2|} \, dt_2$$

$$= \frac{\lambda_\mu (kT)^2}{I_\nu I_\tau} e^{-B_\mu t} \Big\{ \int_{-\infty}^{0} e^{-B_\tau t_1} e^{(B_\mu + B_\nu + B_\tau)t_2} dt_2 + \int_0^{t_1} e^{-B_\tau t_1} e^{(B_\mu - B_\nu + B_\tau)t_2} dt_2 + \int_{t_1}^{t} e^{B_\tau t_1} e^{(B_\mu - B_\nu - B_\tau)t_2} dt_2 \Big\}$$

$$= \frac{\lambda_\mu (kT)^2}{I_\nu I_\tau} e^{-B_\mu t} \Big\{ \frac{e^{-B_\tau t_1}}{B_\mu + B_\nu + B_\tau} + \frac{e^{(B_\mu - B_\nu)t_1} - e^{-B_\tau t_1}}{B_\mu - B_\nu + B_\tau} + \frac{e^{B_\tau t_1} e^{(B_\mu - B_\nu - B_\tau)t} - e^{(B_\mu - B_\nu)t_1}}{B_\mu - B_\nu - B_\tau} \Big\}.$$

Similarly we deduce that

$$\varepsilon^4 \langle \omega_\mu^{(1)}(t)\,\omega_\tau^{(2)}(t_1)\,\omega_\nu^{(1)}(0)\rangle$$

$$= \frac{\lambda_\tau (kT)^2}{I_\mu I_\nu} e^{-B_\mu t} \Big\{ \frac{e^{-B_\tau t_1}}{B_\mu + B_\nu + B_\tau} + \frac{e^{(B_\mu - B_\nu)t_1} - e^{-B_\tau t_1}}{B_\mu - B_\nu + B_\tau} \Big\},$$

$$\varepsilon^4 \langle \omega_\mu^{(1)}(t)\,\omega_\tau^{(1)}(t_1)\,\omega_\nu^{(2)}(0)\rangle$$

$$= \frac{\lambda_\nu (kT)^2}{I_\mu I_\tau} \, \frac{e^{-B_\mu t} e^{-B_\tau t_1}}{B_\mu + B_\nu + B_\tau}.$$

On using the relation

$$\frac{\lambda_\mu}{I_\nu I_\tau} + \frac{\lambda_\nu}{I_\tau I_\mu} + \frac{\lambda_\tau}{I_\mu I_\nu} = 0,$$

which is a consequence of (4.12), and (4.15), we conclude that

$$\langle \varepsilon F^{(1)}(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$$

$$= -\frac{(kT)^2}{I_1 I_2 I_3} i(\underset{\sim}{J} \cdot \underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu) \Big[(I_\mu - I_\tau) \Big\{ \frac{e^{-B_\nu t}}{(B_\mu - B_\nu)(B_\mu - B_\nu + B_\tau)} + \frac{e^{-(B_\mu + B_\tau)t}}{B_\tau (B_\mu - B_\nu + B_\tau)} - \frac{e^{-B_\mu t}}{B_\tau (B_\mu - B_\nu)} \Big\}$$
$$+ (I_\nu - I_\tau) \Big\{ \frac{e^{-B_\nu t}}{B_\tau (B_\mu - B_\nu)} + \frac{e^{-B_\mu t}}{(B_\mu - B_\nu)(B_\mu - B_\nu - B_\tau)} - \frac{e^{-(B_\nu + B_\tau)t}}{B_\tau (B_\mu - B_\nu - B_\tau)} \Big\} \Big]. \tag{4.16}$$

Lastly we require the value of $\langle \varepsilon^2 F^{(2)}(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle$ for (4.10).

From (2.35)

$$\langle \varepsilon^2 F^{(2)}(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle = -\sum_{\tau,s=1}^{3} J_\tau J_s \int_0^t dt_1 \int_0^{t_1} dt_2 \Big\{ \langle \omega_\mu(t)\omega_\tau(t_1)\omega_s(t_2)\omega_\nu(0)\rangle - \langle \omega_\tau(t_1)\omega_s(t_2)\rangle \langle \omega_\mu(t)\omega_\nu(0)\rangle \Big\}. \tag{4.17}$$

Since it was pointed out at the end of the previous subsection that we must restrict our calculations to corrections of order γ, we replace each ω_i in (4.17) by $\varepsilon\omega_i^{(1)}$. Then proceeding as in subsection 3.1 for the sphere we now obtain

$$\langle \varepsilon^2 F^{(2)}(t)\omega_\mu(t)\omega_\nu(0)\rangle$$
$$= \frac{(kT)^2}{I_\mu I_\nu}\Big\{ -\frac{(1-e^{-B_\mu t})(1-e^{-B_\nu t})}{B_\mu B_\nu} J_\mu J_\nu \tag{4.18}$$
$$-\Big[\frac{e^{-B_\nu t}}{B_\mu(B_\mu-B_\nu)} - \frac{e^{-B_\mu t}}{B_\nu(B_\mu-B_\nu)} + \frac{e^{-(B_\mu+B_\nu)t}}{B_\mu B_\nu}\Big] i(\underset{\sim}{J}\cdot\underset{\sim}{e}_\mu\times\underset{\sim}{e}_\nu)\Big\}.$$

4.2. The Laplace transform of $\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$

In calculating $\int_0^\infty e^{-st}\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$ from (4.10) and (4.6) it must be remembered that G defined by (4.7) is not a multiple of the identity, and so care must be taken in performing integrations. It may be shown that[43]

$$\lim_{t\to\infty} e^{Gt} = 0. \tag{4.19}$$

The integrals that appear in our calculations are of the types

$$\int_0^\infty e^{-at}e^{Gt}dt\ ,\ \int_0^\infty t\,e^{-bt}e^{Gt}dt. \qquad (a>0,\ b>0)$$

We write the first integral as $\int_0^\infty exp[(G-a\underset{\sim}{I})t]dt$. Since

$$\frac{d}{dt}\{(G-a\underset{\sim}{I})^{-1}exp[(G-a\underset{\sim}{I})t]\} = \frac{d}{dt}\{(G-a\underset{\sim}{I})^{-1}+t\underset{\sim}{I}+\frac{t^2}{2}(G-a\underset{\sim}{I})+\cdots\}$$
$$= exp[(G-a\underset{\sim}{I})t],$$
$$\int_0^\infty exp[(G-a\underset{\sim}{I})t]dt = (G-a\underset{\sim}{I})^{-1}\lim_{t\to\infty} exp[(G-a\underset{\sim}{I})t] - (G-a\underset{\sim}{I})^{-1},$$

Now

$$\lim_{t\to\infty} exp[(G-a\underset{\sim}{I})t] = \lim_{t\to\infty}[e^{Gt}e^{-at}] = 0,$$

by (4.19), and so

$$\int_0^\infty e^{-at}e^{Gt}dt = (-G+a\underset{\sim}{I})^{-1}. \tag{4.20}$$

It may likewise be shown that

$$\int_0^\infty t\,e^{-bt}e^{Gt}dt = (-G+b\underset{\sim}{I})^{-2}. \tag{4.21}$$

Equation (4.4) yields

$$\langle \omega_\mu(t)\,\omega_\nu(0)\rangle = \delta_{\mu\nu}\left\{ \frac{kT}{I_\mu} e^{-B_\mu t} + \left(\frac{I_\rho - I_\sigma}{I_\mu}\right)^2 \frac{(kT)^2}{I_\rho I_\sigma} \frac{e^{-B_\mu t}\left[1-(B_\rho+B_\sigma-B_\mu)t - e^{-(B_\rho+B_\sigma-B_\mu)t}\right]}{(B_\rho + B_\sigma - B_\mu)^2} + \right.$$

Using this equation, (4.16) and (4.18), and employing (4.20) and (4.21) we deduce that

$$\int_0^\infty e^{-st}\langle R(t)\,\omega_\mu(t)\,\omega_\nu(0)\rangle dt$$

$$= \delta_{\mu\nu}\underset{\sim}{I}\frac{kT}{I_\mu}\left[\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1} + \sum_{i=1}^{3}\frac{kT}{I_i B_i^2}J_i^2\left\{\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1} - \left(-G+[B_\mu+B_i+s]\underset{\sim}{I}\right)^{-1}\right\}\right]$$

$$+\delta_{\mu\nu}\underset{\sim}{I}\left(\frac{I_\rho-I_\sigma}{I_\mu}\right)^2\frac{(kT)^2}{I_\rho I_\sigma(B_\rho+B_\sigma-B_\mu)^2}\left[\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1} - \left(-G+[B_\rho+B_\sigma+s]\underset{\sim}{I}\right)^{-1} - (B_\rho+B_\sigma-B_\mu)\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-2}\right]$$

$$-\frac{(kT)^2}{I_1 I_2 I_3}\,i\left(\underset{\sim}{J}\cdot \underset{\sim}{e}_\mu\times\underset{\sim}{e}_\nu\right)\left[(I_\mu-I_r)\left\{\frac{\left(-G+[B_\nu+s]\underset{\sim}{I}\right)^{-1}}{(B_\mu-B_\nu)(B_\mu-B_\nu+B_r)} + \frac{\left(-G+[B_\mu+B_r+s]\underset{\sim}{I}\right)^{-1}}{B_r(B_\mu-B_\nu+B_r)} - \frac{\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1}}{B_r(B_\mu-B_\nu)}\right\}\right.$$

$$\left. +(I_\nu-I_r)\left\{\frac{\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1}}{(B_\mu-B_\nu)(B_\mu-B_\nu-B_r)} - \frac{\left(-G+[B_\nu+B_r+s]\underset{\sim}{I}\right)^{-1}}{B_r(B_\mu-B_\nu-B_r)} + \frac{\left(-G+[B_\nu+s]\underset{\sim}{I}\right)^{-1}}{B_r(B_\mu-B_\nu)}\right\}\right] \tag{4.22}$$

$$-\frac{(kT)^2}{I_\mu I_\nu}\,i\left(\underset{\sim}{J}\cdot\underset{\sim}{e}_\mu\times\underset{\sim}{e}_\nu\right)\left[\frac{\left(-G+[B_\nu+s]\underset{\sim}{I}\right)^{-1}}{B_\mu(B_\mu-B_\nu)} - \frac{\left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1}}{B_\nu(B_\mu-B_\nu)} + \frac{\left(-G+[B_\mu+B_\nu+s]\underset{\sim}{I}\right)^{-1}}{B_\mu B_\nu}\right]$$

$$-\frac{(kT)^2}{I_\mu I_\nu}\frac{J_\mu J_\nu}{B_\mu B_\nu}\left[\left(-G+s\underset{\sim}{I}\right)^{-1} - \left(-G+[B_\mu+s]\underset{\sim}{I}\right)^{-1} - \left(-G+[B_\nu+s]\underset{\sim}{I}\right)^{-1} + \left(-G+[B_\mu+B_\nu+s]\underset{\sim}{I}\right)^{-1}\right]+\cdots.$$

In the above, ρ and σ are the numbers such that ρ, σ, μ is a cyclic permutation of 1, 2, 3 and r is the number which with distinct values of μ and ν constitutes the set 1, 2, 3.

In order to write down the matrix representatives of the operators occurring in (4.22) in the representation defined by (3.34) we put

$$D_\ell^{(1)} + D_\ell^{(2)} = D_\ell . \tag{4.23}$$

Then from (4.5) and (4.7)

$$-G + a\underset{\sim}{I} = \begin{bmatrix} \frac{1}{2}D_1 + \frac{1}{2}D_2 + D_3 + a & 0 & \frac{1}{2}D_1 - \frac{1}{2}D_2 \\ 0 & D_1 + D_2 + a & 0 \\ \frac{1}{2}D_1 - \frac{1}{2}D_2 & 0 & \frac{1}{2}D_1 + \frac{1}{2}D_2 + D_3 + a \end{bmatrix},$$

and therefore

$$\left(-G+a\underset{\sim}{I}\right)^{-1} = \begin{bmatrix} \dfrac{\frac{1}{2}D_1+\frac{1}{2}D_2+D_3+a}{(D_2+D_3+a)(D_3+D_1+a)} & 0 & -\dfrac{\frac{1}{2}(D_1-D_2)}{(D_2+D_3+a)(D_3+D_1+a)} \\ 0 & \dfrac{1}{D_1+D_2+a} & 0 \\ -\dfrac{\frac{1}{2}(D_1-D_2)}{(D_2+D_3+a)(D_3+D_1+a)} & 0 & \dfrac{\frac{1}{2}D_1+\frac{1}{2}D_2+D_3+a}{(D_2+D_3+a)(D_3+D_1+a)} \end{bmatrix}.$$

Omitting subscripts for the moment we may say that when $s=0$ in (4.22), $a = B$ or $2B$ except for $-G+s\underset{\sim}{I}$ where $a=0$. Since $D=\gamma B$ approximately by (4.8), (4.9) and (4.23), and since G defined by (4.7) is of order D, the non-vanishing elements of $\left(-G+a\underset{\sim}{I}\right)^{-1}$ are in general of order B^{-1}, the first term on the right hand side of (4.22) is of order $kT/(IB)$ and the others are of order $\gamma kT/(IB)$. However $(-G)^{-1}$ is of order $IB/(kT)$ and so produces a contribution of order $kT/(IB)$, as it did in eq. (3.29) for the sphere.

4.3. Calculation of spin-rotational relaxation times

A prerequisite for the calculation of the different spin-rotational relaxation times is the value of $\left(\int_0^\infty e^{-st}\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle dt\right)$ required for substitution into (2.14). It is seen from (4.22) that in the integral there occur operators which are more complicated than the $\underset{\sim}{I}$, $i(\underset{\sim}{J}.\underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu)$, $J_\mu J_\nu$ met in the study of the spherical rotator. A great calculational difficulty arises from the presence in $\int_0^\infty \langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle\, dt$ of terms like $(-G)^{-1} J_\mu J_\nu$. This difficulty disappeared in the spherical model where the $J_\mu J_\nu$-terms did not contribute to $C_{ii}^{\circ\circ}(0)$. In order to derive a satisfactory expression in the $J_\mu J_\nu$-terms it would be essential to extend the value of $\langle R(t)\rangle$ in (4.6) to at least one higher order in γ. This would be laborious but the means of doing it is available[39].

It is not difficult to see that, when the results of the present section are applied to a spherical molecule, we obtain agreement with those of Section 3. Indeed (4.24) reduces to

$$(-G + a\underset{\sim}{I})^{-1} = (2D + a)^{-1}\underset{\sim}{I}.$$

Then the last term in (4.22) is a multiple of $J_\mu J_\nu$ and so, as in subsection 3.3, gives no contribution to $C(0)$. To order $\gamma kT/(IB)$ the other terms in (4.22) give to $\int_0^\infty \langle R(t)\,\omega_\mu(t)\omega_\nu(0)\rangle dt$ the contribution

$$\delta_{\mu\nu}\underset{\sim}{I}\ \frac{kT}{I}\left[\frac{1}{B+2D} + 2\gamma\left(\frac{1}{B} - \frac{1}{2B}\right)\right] - \left(\frac{kT}{I}\right)^2 i(\underset{\sim}{J}.\underset{\sim}{e}_\mu \wedge \underset{\sim}{e}_\nu)\frac{(2B)^{-1}}{B^2}.$$

D may be approximated by γB and thus the last expression becomes

$$\frac{kT}{IB}\left\{(1-\gamma)\delta_{\mu\nu}\underset{\sim}{I} - \tfrac{1}{2}\gamma\, i(\underset{\sim}{J}\cdot\underset{\sim}{e}_\mu \times \underset{\sim}{e}_\nu)\right\},$$

which agrees with (3.39) in the approximation of the present section.

At the present state of our knowledge the most that one can do for a totally asymmetric molecule is to explain how the various relaxational times associated with spin-rotational interactions are related to $C_{ii}^{\circ\circ}(s)$ through the equations (2.5), (2.6), (2.13), (2.17), (2.27), to show that $C_{ii}^{\circ\circ}(s)$ is related by (2.14) to the Laplace transform of $\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$ and to express this by (4.22). The investigation is entirely theoretical. Since, as has been pointed out in a recent study of the dielectric relaxation of asymmetric polar molecules[44], there is no obvious way of determining B_1, B_2, B_3, a comparison with experiment is not yet possible.

Special cases of the asymmetric molecule, other than the spherical model, are being currently investigated.

6. CONCLUSION

It has been found possible to apply the averaging procedure used previously for functions of orientational variables to products of functions of orientational and angular velocity variables encountered in the study of nuclear magnetic spin-rotational relaxation phenomena. An analytical method has been developed and this yields results which are in agreement with those obtained, by very different methods, by Hubbard and by McClung and his collaborators for a rotating spherical molecule. It has been shown how the method could be employed for a molecule of arbitrary shape, and attention has been drawn to some of the calculational difficulties that would be encountered. It may be concluded that the mathematical approach based on the stochastic rotation operator is adequate for the investigation of the nuclear magnetic relaxation processes arising from spin-lattice, intramolecular dipole-dipole, quadrupole and spin-rotational interactions.

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