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Rotational Brownian motion of an asymmetric top

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We describe a method which enables us to calculate both the orientational and the angular-velocity autocorrelation functions of an asymmetric top driven by white noise. The results are valid for both short and long times, and provide inertial corrections to the classical result of Perrin. They are applied to the calculation of complex polarizabilities for asymmetric-top molecules and the correlation times associated with the dipolar broadening of nuclear magnetic resonance lines. We take the angular-velocity vector to be the stationary solution of the Euler-Langevin equation, and obtain it in the form of a perturbation series. The random angular velocity drives the random orientational motion, and we use methods of stochastic differential equations to obtain an equation of motion for the aftereffect function. This cannot be solved in general by direct integration, and we use the method of averaging to obtain the aftereffect function in a form which is asymptotically correct both for large and small times.

I. INTRODUCTION

In this paper we compute inertial corrections to the classical theory of Perrin[1] of the rotational diffusion of an asymmetric top. Perrin's theory is the extension to the asymmetric top of the well-known Debye theory[2] of the rotational diffusion of a sphere. Inertial corrections to the Debye theory have been obtained by many authors for special cases.[3-10] They are usually expressed in the form of an expansion in powers of the quantity kT/IB^2, where I is the moment of inertia of the sphere and B is the frictional decay rate. Since $(3kT/I)^{1/2}$ is the mean thermal angular velocity, inertial corrections to the Debye theory will be small when the mean thermal angular velocity is small compared with the frictional decay rate. Our results for the asymmetric top are expressed in terms of a similar expansion; there are three distinct principal moments of inertia and three frictional decay rates.

Our starting point is the Euler-Langevin equations of motion for the angular velocity of a body-fixed coordinate frame, including the effects of frictional relaxation and random (white-noise) torques. In Sec. II we solve these equations for the stationary random angular velocity in the form of a perturbation series. We then use this solution to form various angular-velocity correlations needed in the later discussion. Such correlations have been derived by Hubbard[11] using a Fokker-Planck equation.

The random angular velocity drives the random orientational motion. In Sec. III we use methods of stochastic differential equations, described and applied to the sphere in Ref. 9, to obtain an equation of motion for the after effect function, again in the form of a perturbation series. For the asymmetric top this equation of motion, which is explicitly time-dependent, cannot be solved in general by direct integration. Instead, in Sec. IV we use the method of averaging to produce a solution for the after effect function in a form which is asymptotically correct both for large and small times. Finally, in Secs. V and VI we use our results to compute the complex polarizability and correlation times.

II. ANGULAR-VELOCITY CORRELATIONS

We begin with the Euler-Langevin equation of motion, which we write in the form

$$\frac{d}{dt}\vec{L}+\vec{\omega}\times\vec{L}+\mathsf{F}\vec{\omega}=\vec{N}(t)\,, \tag{2.1}$$

where $\vec{L}$ is the angular momentum and $\vec{\omega}$ is the angular velocity, related by the moment of inertia tensor I.

$$\vec{L}=\mathsf{I}\vec{\omega}\,. \tag{2.2}$$

Equation (2.1) is just the well-known Euler equations for the angular velocity of a body-fixed coordinate frame[12] supplemented by a frictional torque $\mathsf{F}\vec{\omega}$ and a random torque $\vec{N}$. The random torque is Gaussian white noise with mean zero and covariance determined by the generalized Einstein relation,[13]

$$\langle\vec{N}(t)\vec{N}(t')\rangle=2kT\,\mathsf{F}\,\delta(t-t')\,. \tag{2.3}$$

The brackets $\langle\cdots\rangle$ denote an average over the white-noise ensemble of the stochastic variables contained within them. The moment of inertia tensor I and the friction tensor F are both positive definite symmetric quadratic forms which we assume are simultaneously diagonalizable. The eigenvalues of I are the principal moments of inertia, I_x, I_y, I_z; those of F are I_xB_x, I_yB_y, and I_zB_z, where the B's are the frictional decay rates.

We seek the *stationary* stochastic process $\vec{\omega}(t)$ which is a solution of (2.1). We use a perturbation expansion in powers of the quantity

$$(kT/I)^{1/2}B^{-1}, \tag{2.4}$$

where I is a typical moment of inertia and B is a typical frictional decay rate. Because of the dissipative character of the friction term this stationary process must satisfy

$$\langle\vec{\omega}(t)\rangle = 0, \tag{2.5}$$

and so the zero-order term in the perturbation series is identically zero. It follows from this and the structure of Eq. (2.1) that

$$\vec{\omega}(t) = \vec{\omega}^{(1)}(t) + \vec{\omega}^{(2)}(t) + \vec{\omega}^{(3)}(t) + \cdots, \tag{2.6}$$

where $\omega^{(n)}(t)$ is a homogeneous functional of degree n in the random torque $\vec{N}$.

For a rigorous discussion of stochastically perturbed dynamical systems such as our Eq. (2.1), see Ref. 14. Inserting the expansion in (2.6) in Eq. (2.1) and equating separately terms involving functionals of the same degree, we get a sequence of equations determining the $\vec{\omega}^{(n)}(t)$. They can be written

$$\vec{L}^{(1)}(t) = \int_{-\infty}^{t} dt' \exp[-B(t-t')]\vec{N}(t'), \tag{2.7}$$

and

$$\vec{L}^{(n)}(t) = \int_{-\infty}^{t} dt' \exp[-B(t-t')] \times \prod_{j=1}^{n-1} \vec{L}^{(n-j)}(t') \times \vec{\omega}^{(j)}(t'), \tag{2.8}$$

where

$$\vec{L}^{(n)}(t) = I\vec{\omega}^{(n)}(t), \tag{2.9}$$

and

$$B = I^{-1}F \tag{2.10}$$

is the frictional decay rate tensor. The first-order term $\vec{\omega}^{(1)}(t)$ is a Gaussian Markov process with mean zero and covariance

$$\langle\vec{\omega}^{(1)}(t)\vec{\omega}^{(1)}(t')\rangle = kTI^{-1}\exp(-B|t-t'|). \tag{2.11}$$

It is clear from (2.8) that $\vec{\omega}^{(n)}(t)$ will be a homogeneous functional of degree n in $\vec{\omega}^{(1)}(t)$, so that using (2.11) we can form correlations of $\vec{\omega}(t)$ to any desired order.

More explicitly, with the principal directions of I as the coordinate frame, (2.8) becomes for $n=2$,

$$\begin{aligned} \omega_x^{(2)}(t) &= \lambda_x \int_{-\infty}^{t} dt'\, e^{-B_x(t-t')}\omega_y^{(1)}(t')\omega_z^{(1)}(t'), \\ \omega_y^{(2)}(t) &= \lambda_y \int_{-\infty}^{t} dt'\, e^{-B_y(t-t')}\omega_z^{(1)}(t')\omega_x^{(1)}(t'), \\ \omega_z^{(2)}(t) &= \lambda_z \int_{\infty}^{t} dt'\, e^{-B_z(t-t')}\omega_x^{(1)}(t')\omega_y^{(1)}(t'), \end{aligned} \tag{2.12}$$

where

$$\begin{aligned} &\lambda_x = (I_y - I_z)/I_x, \quad \lambda_y = (I_z - I_x)/I_y, \\ &\lambda_z = (I_x - I_y)/I_z. \end{aligned} \tag{2.13}$$

Using this in (2.8) for $n=3$, we get

$$\begin{aligned} \omega_x^{(3)}(t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt''\, e^{-B_x(t-t')}\lambda_x[\lambda_z e^{-B_z(t'-t'')}\omega_y^{(1)}(t')\omega_x^{(1)}(t'')\omega_y^{(1)}(t'') \\ + \lambda_y e^{-B_y(t'-t'')}\omega_z^{(1)}(t')\omega_x^{(1)}(t'')|\omega_z^{(1)}(t'')], \end{aligned} \tag{2.14}$$

together with two similar expressions for $\omega_y^{(3)}(t)$ and $\omega_z^{(3)}(t)$, obtained by cyclicly permuting x, y, and z. And so one can continue, finding expressions for successively higher terms in the expansion (2.6). However, in the discussion which follows we shall not need terms beyond $n=3$.

These explicit expressions for $\omega^{(n)}(t)$ in terms of $\omega^{(1)}(t)$ can be used to form various correlations. A useful general principle follows from the fact that $\omega_x^{(1)}(t)$, $\omega_y^{(1)}(t)$, and $\omega_z^{(1)}(t)$ are independent Gaussian processes, namely that only correlations involving an even number of factors of each will be nonzero. As an application of this principle we can verify that the condition (2.5) holds term by term in the expansion (2.6), i.e.,

$$\langle \vec{\omega}^{(n)}(t)\rangle = 0 . \tag{2.15}$$

The proof consists in noting that when n is odd, $\omega_x^{(n)}$ contains an odd number of $\omega_x^{(1)}$ and an even number of factors of each of $\omega_y^{(1)}$ and $\omega_z^{(1)}$, while when n is even $\omega_x^{(n)}$ contains an even number of factors of $\omega_x^{(1)}$ and an odd number of factors of each of $\omega_y^{(1)}$ and $\omega_z^{(1)}$; and correspondingly for $\omega_y^{(n)}$ and $\omega_z^{(n)}$. This is obvious for $n=1,2,3$ from the explicit expressions (2.12) and (2.14), while for general n it is a simple exercise to verify it from (2.8) by induction.

III. EQUATION OF MOTION FOR THE AFTEREFFECT OPERATOR

The operator $R(t)$ describing the rotation of the body-fixed coordinate frame during time t satisfies the kinematical equation of motion

$$\dot{R} = \vec{\omega}(t)\cdot\vec{\sigma}R , \tag{3.1}$$

where

$$\vec{\omega}(t)\cdot\vec{\sigma} = \omega_x(t)\sigma_x + \omega_y(t)\sigma_y + \omega_z(t)\sigma_z \tag{3.2}$$

in which $\omega_x(t)$, $\omega_y(t)$, and $\omega_z(t)$ are the components of the angular velocity of the frame referred to axes fixed in the frame and σ_x, σ_y, and σ_z are time-independent operators satisfying

$$[\sigma_x, \sigma_y] = -\sigma_z \tag{3.3}$$

and its cyclic permutations. Since $R(t)$ depends on the stochastic process $\omega(t)$ it is a stochastic operator. The reason for the minus sign in these commutation relations is that x, y, and z refer to body-fixed axes.[15] In general for the jth irreducible representation of the rotation group, R and the σ's are $(2j+1)$-dimensional matrices. In particular for $j=1$, R may be taken to be the familiar 3×3 matrix describing rotation of a rigid body,[16] in which case

$$\sigma_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{3.4}$$

The after effect function, or rather, the after effect operator, is the mean $\langle R(t)\rangle$, subject to the condition that R is the identity at $t=0$,

$$R(0) = \langle R(0)\rangle = 1 . \tag{3.5}$$

We now insert the expansion (2.6) in (3.1), which we now write in the form

$$\dot{R} = [\epsilon K^{(1)}(t) + \epsilon^2 K^{(2)}(t) + \cdots]R \tag{3.6}$$

where $K^{(n)}(t)$ is the stochastic operator defined by

$$\epsilon^n K^{(n)}(t) = \vec{\omega}^{(n)}(t)\cdot\vec{\sigma} . \tag{3.7}$$

Here the formal parameter ϵ, which has been introduced to keep track of the orders in the expansion, may be taken to be the quantity (2.4). So-called multiplicative stochastic differential equations, of which (3.6) is an example, have been studied by a number of authors using cumulant techniques.[10,17] We shall, however, use a somewhat different approach,[18] inspired by the averaging methods of nonlinear mechanics,[19,20] and applied earlier by us to the discussion of the rotational Brownian motion of the sphere[9] and the linear rotor.[21]

For ϵ small, the solution of (3.6) will consist of a slowly varying mean $\langle R(t)\rangle$ about which there will be small-amplitude random fluctuations. We accordingly seek a solution in the form

$$R(t) = [1 + \epsilon F^{(1)}(t) + \epsilon^2 F^{(2)}(t) + \cdots]\langle R(t)\rangle , \tag{3.8}$$

where $F^{(n)}(t)$ is a stochastic operator with zero mean

$$\langle F^{(n)}(t)\rangle = 0 . \tag{3.9}$$

Then $\langle R(t)\rangle$ satisfies the nonstochastic differential equation

$$\langle \dot{R}\rangle = \{\epsilon\Omega^{(1)}(t) + \epsilon^2\Omega^{(2)}(t) + \cdots\}\langle R\rangle \tag{3.10}$$

with $\Omega^{(n)}(t)$ a nonstochastic operator

$$\langle \Omega^{(n)}(t)\rangle = \Omega^{(n)}(t) . \tag{3.11}$$

Since differentiating with respect to the time and averaging over the white-noise ensemble are operations which commute with one another, we have $\langle dR(t)/dt\rangle = d\langle R(t)\rangle/dt$; we denote their common value by $\langle \dot{R}\rangle$. Inserting (3.8) in (3.6), using (3.10), and equating the coefficients of equal powers of ϵ on either side of the equation, we get the following sequence of equations determining the Ω's and the F's,

$$\Omega^{(1)} + \dot{F}^{(1)} = K^{(1)} , \tag{3.12}$$

$$\Omega^{(2)} + \dot{F}^{(2)} = K^{(2)} + K^{(1)}F^{(1)} - F^{(1)}\Omega^{(1)} , \tag{3.13}$$

$$\Omega^{(3)} + \dot{F}^{(3)} = K^{(3)} + K^{(2)}F^{(1)} + K^{(1)}F^{(2)} - F^{(1)}\Omega^{(2)} - F^{(2)}\Omega^{(1)} , \tag{3.14}$$

$$\Omega^{(4)} + \dot{F}^{(4)} = K^{(4)} + K^{(3)}F^{(1)} + K^{(2)}F^{(2)} + K^{(1)}F^{(3)} - F^{(1)}\Omega^{(3)} - F^{(2)}\Omega^{(2)} - F^{(3)}\Omega^{(1)} , \tag{3.15}$$

and so on.

Each of these equations is of the same form, the right-hand side being expressed in terms of the solutions of the previous equations. The solution of the first equation is therefore typical. Forming the mean of both sides, using (3.9) and (3.11), we find

$$\Omega^{(1)}(t)=\langle K^{(1)}(t)\rangle\,. \tag{3.16}$$

Using this, we can integrate to express

$$F^{(1)}(t)=\int_0^t dt_1\,[K^{(1)}(t_1)-\langle K^{(1)}(t_1)\rangle]\,. \tag{3.17}$$

Here we have chosen the lower limit of integration to be zero, in accordance with (3.5). Finally, using (2.15) we see that

$$\langle K^{(n)}(t)\rangle=0\,, \tag{3.18}$$

so (3.16) becomes

$$\Omega^{(1)}(t)=0\,. \tag{3.19}$$

In this same way we can continue. Inserting (3.17) and (3.19) in the second-order Eq. (3.13) and forming the mean, we find

$$\Omega^{(2)}(t_1)=\int_0^{t_1} dt_2\,\langle K^{(1)}(t_1)K^{(1)}(t_2)\rangle\,, \tag{3.20}$$

where we have again used (3.18). Using this, we can integrate (3.13) to find

$$F^{(2)}(t)=\int_0^t dt_1 K^{(2)}(t_1)+\int_0^t dt_1\int_0^{t_1} dt_2[K^{(1)}(t_1)K^{(1)}(t_2)-\langle K^{(1)}(t_1)K^{(1)}(t_2)\rangle]\,. \tag{3.21}$$

From the third-order Eq. (3.14), we find

$$\Omega^{(3)}(t)=0\,, \tag{3.22}$$

and

$$\begin{aligned}F^{(3)}(t)=&\int_0^t dt_1 K^{(3)}(t_1)+\int_0^t dt_1\int_0^{t_1} dt_2[K^{(2)}(t_1)K^{(1)}(t_2)+K^{(1)}(t_1)K^{(2)}(t_2)]\\&+\int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3[K^{(1)}(t_1)K^{(1)}(t_2)K^{(1)}(t_3)-K^{(1)}(t_1)\langle K^{(1)}(t_2)K^{(1)}(t_3)\rangle\\&-K^{(1)}(t_2)\langle K^{(1)}(t_1)K^{(1)}(t_3)\rangle-K^{(1)}(t_3)\langle K^{(1)}(t_1)K^{(1)}(t_2)\rangle]\,.\end{aligned} \tag{3.23}$$

Finally, from the fourth-order Eq. (3.15) we find

$$\begin{aligned}\Omega^{(4)}(t_1)=&\int_0^{t_1} dt_2\langle K^{(3)}(t_1)K^{(1)}(t_2)+K^{(2)}(t_1)K^{(2)}(t_2)+K^{(1)}(t_1)K^{(3)}(t_2)\rangle\\&+\int_0^{t_1} dt_2\int_0^{t_2} dt_3\langle K^{(2)}(t_1)K^{(1)}(t_2)K^{(1)}(t_3)+K^{(1)}(t_1)K^{(2)}(t_2)K^{(1)}(t_3)+K^{(1)}(t_1)K^{(1)}(t_2)K^{(2)}(t_3)\rangle\\&+\int_0^{t_1} dt_2\int_0^{t_2} dt_3\int_0^{t_3} dt_4[\langle K^{(1)}(t_1)K^{(1)}(t_2)K^{(1)}(t_3)K^{(1)}(t_4)\rangle-\langle K^{(1)}(t_1)K^{(1)}(t_2)\rangle\langle K^{(1)}(t_3)K^{(1)}(t_4)\rangle\\&-\langle K^{(1)}(t_1)K^{(1)}(t_3)\rangle\langle K^{(1)}(t_2)K^{(1)}(t_4)\rangle-\langle K^{(1)}(t_1)K^{(1)}(t_4)\rangle\langle K^{(1)}(t_2)K^{(1)}(t_3)\rangle]\,.\end{aligned} \tag{3.24}$$

Since our aim is to calculate the after-effect operator $\langle R(t)\rangle$, the principal result of our discussion so far is the formal expressions (3.19), (3.20), (3.22), and (3.24) for the Ω's occurring in Eq. (3.10). Clearly the $\Omega^{(n)}$ with n odd vanish in general, so the right-hand side of (3.10) is in fact an expansion in powers of the square of the quantity (2.4), just as in the case of the sphere.[9] To evaluate the expressions for $\Omega^{(n)}$, we use (3.7) and the expressions for $\omega^{(n)}(t)$ constructed in Sec. II, being careful to preserve the order of the σ operators. Thus, in (3.20) using (3.7) and

(2.11), we find

$$\epsilon^2\Omega^{(2)}(t) = \frac{kT}{I_x B_x}(1-e^{-B_x t})\sigma_x^2 + \frac{kT}{I_y B_y}(1-e^{-B_y t})\sigma_y^2 + \frac{kT}{I_z B_z}(1-e^{-B_z t})\sigma_z^2 . \quad (3.25)$$

Next, consider the expression (3.24). Using (3.7), the expressions (2.12) and (2.14), and the principle that only correlations involving an even number of factors of each of the processes $\omega_x^{(1)}(t)$, $\omega_y^{(1)}(t)$, and $\omega_z^{(1)}(t)$ are nonvanishing, we can write

$$\epsilon^4\Omega^{(4)}(t_1) = \int_0^{t_1} dt_2 \sum_{x,y,z} \langle \omega_x^{(1)}(t_1)\omega_x^{(3)}(t_2) + \omega_x^{(2)}(t_1)\omega_x^{(2)}(t_2) + \omega_x^{(3)}(t_1)\omega_x^{(1)}(t_2)\rangle \sigma_x^2$$
$$+ \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \sum_P \langle \omega_x^{(1)}(t_1)\omega_y^{(1)}(t_2)\omega_z^{(2)}(t_3) + \omega_x^{(1)}(t_1)\omega_y^{(2)}(t_2)\omega_z^{(1)}(t_3) + \omega_x^{(2)}(t_1)\omega_y^{(1)}(t_2)\omega_z^{(1)}(t_3)\rangle \sigma_x\sigma_y\sigma_z$$
$$+ \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \sum_P [\langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_4)\rangle \langle \omega_y^{(1)}(t_2)\omega_y^{(1)}(t_3)\rangle (\sigma_x\sigma_y^2\sigma_x - \sigma_x^2\sigma_y^2)$$
$$+ \langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_3)\rangle \langle \omega_y^{(1)}(t_2)\omega_y^{(1)}(t_4)\rangle (\sigma_x\sigma_y\sigma_x\sigma_y - \sigma_x^2\sigma_y^2)] . \quad (3.26)$$

Here $\sum_{x,y,z}$ means the sum of the given term and the two terms obtained by cyclically permuting x, y, and z; while $\sum_P$ means the sum of the six terms obtained by permuting x, y, and z. In the last term in (3.26) we have used the fact that $\omega_x^{(1)}(t)$, $\omega_y^{(1)}(t)$, and $\omega_z^{(1)}(t)$ are independent *Gaussian* processes, so correlations involving an even number of factors are equal to the sum of products of pair correlations, for example,

$$\langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_2)\omega_x^{(1)}(t_3)\omega_x^{(1)}(t_4)\rangle = \langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_2)\rangle\langle \omega_x^{(1)}(t_3)\omega_x^{(1)}(t_4)\rangle$$
$$+ \langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_3)\rangle\langle \omega_x^{(1)}(t_2)\omega_x^{(1)}(t_4)\rangle + \langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_4)\rangle\langle \omega_x^{(1)}(t_2)\omega_x^{(1)}(t_3)\rangle . \quad (3.27)$$

We now use (2.12) and (2.14) together with (2.11) to evaluate the various terms in (3.26). The integrals involved, being multiple integrals of simple exponentials, are elementary but tedious. In our subsequent discussion we shall only need $\Omega^{(4)}(t_1)$ in the limit of infinitely large t_1, so we will only quote the results in this limit. These are

$$\lim_{t_1\to\infty} \int_0^{t_1} dt_2 \langle \omega_x^{(1)}(t_1)\omega_x^{(3)}(t_2) + \omega_x^{(2)}(t_1)\omega_x^{(2)}(t_2) + \omega_x^{(3)}(t_1)\omega_x^{(1)}(t_2)\rangle = -\frac{(kT)^2\lambda_x^2}{I_y I_z B_x^2 (B_y+B_z)}, \quad (3.28)$$

$$\lim_{t_1\to\infty} \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \langle \omega_x^{(1)}(t_1)\omega_y^{(1)}(t_2)\omega_z^{(2)}(t_3) + \omega_x^{(1)}(t_1)\omega_y^{(2)}(t_2)\omega_z^{(1)}(t_3) + \omega_x^{(2)}(t_1)\omega_y^{(1)}(t_2)\omega_z^{(1)}(t_3)\rangle$$
$$= (kT)^2 \left[\frac{\lambda_x}{I_y I_z} \frac{1}{(B_y+B_z)B_x B_z} - \frac{\lambda_z}{I_x I_y} \frac{1}{(B_x+B_y)B_x B_z} \right], \quad (3.29)$$

$$\lim_{t_1\to\infty} \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_4)\rangle\langle \omega_y^{(1)}(t_2)\omega_y^{(1)}(t_3)\rangle = \frac{(kT)^2}{I_x I_y} \frac{1}{(B_x+B_y)B_x^2}, \quad (3.30)$$

$$\lim_{t_1\to\infty} \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle \omega_x^{(1)}(t_1)\omega_x^{(1)}(t_3)\rangle\langle \omega_y^{(1)}(t_2)\omega_y^{(1)}(t_4)\rangle = \frac{(kT)^2}{I_x I_y} \frac{1}{(B_x+B_y)B_x B_y}. \quad (3.31)$$

On obtaining (3.29) it is useful to note the identity

$$I_x\lambda_x + I_y + \lambda_y + I_z\lambda_z = 0. \quad (3.32)$$

Before using these results in (3.26), we first use the commutation rules (3.3) to demonstrate the following identities:

$$\sigma_x\sigma_y\sigma_z = \frac{1}{6}\left(\sum_P \sigma_x\sigma_y\sigma_z\right) - \tfrac{1}{2}(\sigma_x^2 - \sigma_y^2 + \sigma_z^2),$$
$$\sigma_z\sigma_y\sigma_x = \frac{1}{6}\left(\sum_P \sigma_x\sigma_y\sigma_z\right) + \tfrac{1}{2}(\sigma_x^2 - \sigma_y^2 + \sigma_z^2),$$
$$\sigma_x\sigma_y^2\sigma_x - \sigma_x^2\sigma_y^2 = \frac{1}{3}\left(\sum_P \sigma_x\sigma_y\sigma_z\right) + \sigma_y^2 - \sigma_z^2,$$
$$\sigma_y\sigma_x^2\sigma_y - \sigma_y^2\sigma_x^2 = -\frac{1}{3}\left(\sum_P \sigma_x\sigma_y\sigma_z\right) - \sigma_z^2 + \sigma_x^2, \qquad (3.33)$$
$$\sigma_x\sigma_y\sigma_x\sigma_y - \sigma_x^2\sigma_y^2 = \frac{1}{6}\left(\sum_P \sigma_x\sigma_y\sigma_z\right) + \tfrac{1}{2}(\sigma_x^2 + \sigma_y^2 - \sigma_z^2),$$
$$\sigma_y\sigma_x\sigma_y\sigma_x - \sigma_y^2\sigma_x^2 = -\frac{1}{6}\left(\sum_P \sigma_x\sigma_y\sigma_z\right) + \tfrac{1}{2}(\sigma_x^2 + \sigma_y^2 - \sigma_z^2).$$

From each of these identities, two more may be obtained by cyclically permuting x, y, and z. In these expressions

$$\sum_P \sigma_x\sigma_y\sigma_z = \sigma_x\sigma_y\sigma_z + \sigma_z\sigma_y\sigma_x + \sigma_y\sigma_z\sigma_x + \sigma_x\sigma_z\sigma_y + \sigma_z\sigma_x\sigma_y + \sigma_y\sigma_x\sigma_z. \qquad (3.34)$$

Using these identities and the results (3.28)–(3.31) in (3.26) we obtain a result which may be expressed in the form:

$$\epsilon^4\Omega^{(4)}(\infty) = \frac{(kT)^2}{I_xI_yI_z}\Bigg\{\left[I_x\frac{B_z - B_y}{B_y^2B_z^2} + I_y\frac{B_x - B_z}{B_x^2B_z^2} + I_z\frac{B_y - B_x}{B_y^2B_x^2}\right]\frac{1}{3}\left(\sum_P \sigma_x\sigma_y\sigma_z\right)$$
$$+ \sum_{x,y,z}\left[I_x\frac{2B_yB_z(B_y+B_z) - B_x(B_y^2 + B_yB_z + B_z^2)}{B_xB_y^2B_z^2(B_y+B_z)} + I_y\frac{B_y(B_y+B_z) - 2B_z^2}{B_xB_yB_z^2(B_y+B_z)}\right.$$
$$\left. + I_z\frac{B_z(B_y+B_z) - 2B_y^2}{B_xB_y^2B_z(B_y+B_z)} - \frac{(I_y - I_z)^2}{I_xB_x^2(B_y+B_z)}\right]\sigma_x^2\Bigg\}, \qquad (3.35)$$

where $\sum_{x,y,z}$ means the sum over the three terms obtained by cyclically permuting x, y, and z. This expression, together with (3.25) are all we shall need in forming the aftereffect operator in the next section.

The calculations made so far enable us to obtain correlation functions for the components of angular velocity. We see from (2.6) that

$$\langle\omega_x(t)\omega_x(s)\rangle = \langle\omega_x^{(1)}(t)\omega_x^{(1)}(s)\rangle + \langle\omega_x^{(1)}(t)\omega_x^{(3)}(s) + \omega_x^{(2)}(t)\omega_x^{(2)}(s) + \omega_x^{(3)}(t)\omega_x^{(1)}(s)\rangle + \cdots, \qquad (3.36)$$

the terms $\langle\omega_x^{(1)}(t)\omega_x^{(2)}(s)\rangle$, $\langle\omega_x^{(2)}(t)\omega_x^{(1)}(s)\rangle$ vanishing because they involve the mean of an odd number of $\omega^{(1)}$'s. Similarly $\langle\omega_x(t)\omega_y(s)\rangle$ vanishes because it is the sum of terms, each of which is the mean value of an odd number of $\omega_x^{(1)}$'s or $\omega_y^{(1)}$'s or $\omega_z^{(1)}$'s. On substituting (2.12) and (2.14) into (3.36), employing (2.11) and performing the integrations we deduce that

$$\langle\omega_x(t)\omega_x(s)\rangle = \frac{kT}{I_x}e^{-B_x|t-s|} + \frac{(I_y - I_z)^2(kT)^2e^{-B_x|t-s|}}{I_x^2I_yI_z(B_y+B_z-B_x)^2} \times[1 - (B_y+B_z-B_x)|t-s| - e^{-(B_y+B_z-B_x)|t-s|}].$$

This agrees with Eq. (6.2) of Hubbard.[11]

As a check on the results of the present section we made independent calculations of $\Omega^{(2)}(t)$ and $\Omega^{(4)}(t)$ for the symmetric rotator. These confirmed our results. The results for the symmetric rotator may, of course, always be obtained as special cases of those for the asymmetric top.

IV. SOLUTION FOR THE AFTEREFFECT OPERATOR

The aftereffect operator is the solution of Eq. (3.10) corresponding to the initial value

$$\langle R(0)\rangle = 1. \qquad (4.1)$$

As we have seen in Sec. III, all the odd-order terms vanish in the expansion of the right-hand side of (3.10), so we write this equation in the form

$$\langle\dot{R}\rangle = \{\gamma S^{(1)}(t) + \gamma^2S^{(2)}(t) + \cdots\}\langle R\rangle, \qquad (4.2)$$

where the operator $S^{(n)}(t)$ is defined by

$$\gamma^nS^{(n)}(t) = \epsilon^{2n}\Omega^{(2n)}(t), \qquad (4.3)$$

and the formal parameter γ may be taken to be the square of the quantity (2.4). Explicitly, using (3.25) we can write

$$\gamma S^{(1)}(t) = D_x^{(1)}(1 - e^{-B_xt})\sigma_x^2 + D_y^{(1)}(1 - e^{-B_yt})\sigma_y^2 + D_z^{(1)}(1 - e^{-B_zt})\sigma_z^2), \qquad (4.4)$$

where

$$D_x^{(1)} = \frac{kT}{I_x B_x}, \quad D_y^{(1)} = \frac{kT}{I_y B_y}, \quad D_z^{(1)} = \frac{kT}{I_z B_z}, \tag{4.5}$$

are the well-known rotational diffusion constants of the Perrin theory.[1,22] Using (3.35), we can write

$$\gamma^2 S^{(2)}(\infty) = D_x^{(2)}\sigma_x^2 + D_y^{(2)}\sigma_y^2 + D_z^{(2)}\sigma_z^2 + a^{(2)}\frac{1}{3}\left(\sum_P \sigma_x\sigma_y\sigma_z\right), \tag{4.6}$$

where

$$a^{(2)} = \frac{(kT)^2}{I_x I_y I_z}\left(I_x\frac{B_z - B_y}{B_y^2 B_z^2} + I_y\frac{B_x - B_z}{B_x^2 B_z^2} + I_z\frac{B_y - B_x}{B_x^2 B_y^2}\right), \tag{4.7}$$

and

$$D_x^{(2)} = \frac{(kT)^2}{I_x I_y I_z}\left[I_x\frac{2B_y B_z(B_y + B_z) - B_x(B_y^2 + B_y B_z + B_z^2)}{B_x B_y^2 B_z^2(B_y + B_z)} + I_y\frac{B_y(B_y + B_z) - 2B_z^2}{B_x B_y B_z^2(B_y + B_z)} + I_z\frac{B_z(B_y + B_z) - 2B_y^2}{B_x B_y^2 B_z(B_y + B_z)} - \frac{(I_y - I_z)^2}{I_x B_x^2(B_y + B_z)}\right], \tag{4.8}$$

with similar formulas for $D_y^{(2)}$ and $D_z^{(2)}$ obtained by cyclically permuting x, y, and z.

The integration of Eq. (4.2) is not entirely straightforward since the operators $S^{(n)}(t)$ do not commute at different times. The solution can be expressed formally as a time-ordered exponential, but in practice this amounts to an expansion in powers of γ which, because of the appearance of secular terms, is only useful for short times. Instead we shall apply the method of averaging[19,20] to obtain a form of the solution which, for small γ, will be valid for all times. The idea is that there are two time-scales entering in (4.2). The first is what we may call the frictional decay time $\tau_f \approx B^{-1}$ and is the scale of the explicit time dependence of $\gamma S^{(n)}$. The second is what we may call the Debye time $\tau_D \approx (kT/IB)^{-1}$ and is the scale of the magnitude of $\gamma S^{(1)}$. The ratio of these scales is the quantity $\gamma \approx \tau_f/\tau_D$. For γ small, therefore, the solution of (4.2) will have a slowly varying (on the scale of τ_D) average behavior, about which there will be small-amplitude (on the scale of τ_f) oscillations. We accordingly seek a solution in the form

$$\langle R\rangle = (1 + \gamma A^{(1)}(t) + \gamma^2 A^{(2)}(t) + \cdots)\mathfrak{R}, \tag{4.9}$$

where the $A^{(n)}(t)$ are operators whose time-dependence is on the scale τ_f. The operator $\mathfrak{R}$ is to exhibit only slowly varying behavior on the scale τ_D and must therefore satisfy an equation of the form

$$\dot{\mathfrak{R}} = \{\gamma G^{(1)} + \gamma^2 G^{(2)} + \cdots\}\mathfrak{R}, \tag{4.10}$$

where $G^{(n)}$ is a time-independent operator. Inserting (4.9) in (4.2), using (4.10), and then equating the coefficients of equal powers of γ on either side of the equations, we get a sequence of equations for determining the $G^{(n)}$ and the $A^{(n)}(t)$. The first two of these equations are

$$G^{(1)} + \dot{A}^{(1)} = S^{(1)}, \tag{4.11}$$

$$G^{(2)} + \dot{A}^{(2)} = S^{(2)} + S^{(1)}A^{(1)} - A^{(1)}G^{(1)}. \tag{4.12}$$

These equations are of the same form, the right-hand side of each being expressed in terms of the solutions of the previous equations. Consider the first-order Eq. (4.11). Since for a long time we require $A^{(1)}(t)$ to be bounded, the operator $G^{(1)}$ must be chosen to cancel the long-time behavior of $S^{(1)}(t)$;

$$G^{(1)} = S^{(1)}(\infty). \tag{4.13}$$

Then

$$A^{(1)}(t) = \int_0^t dt'\,[S^{(1)}(t') - S^{(1)}(\infty)]. \tag{4.14}$$

Here the lower limit of integration has been chosen so that

$$A^{(n)}(0) = 0. \tag{4.15}$$

With these results the second-order Eq. (4.12) becomes

$$G^{(2)} + \dot{A}^{(2)}(t) = S^{(2)}(t) + S^{(1)}(t)\int_0^t dt'\,[S^{(1)}(t') - S^{(1)}(\infty)] - \int_0^t dt'\,[S^{(1)}(t') - S^{(1)}(\infty)]S^{(1)}(\infty). \tag{4.16}$$

Since $G^{(2)}$ must cancel the long-time limit of the right-hand side, we have

$$G^{(2)} = S^{(2)}(\infty) + \int_0^\infty dt\,[S^{(1)}(\infty), S^{(1)}(t)]. \tag{4.17}$$

This gives a first-order correction to $\gamma G^{(1)}$ in (4.10). Since $A^{(1)}(t)$ gives a first-order correction to 1 in (4.9), we do not need to calculate $A^{(2)}(t)$ or $G^{(3)}(t)$ if we confine our investigations to first-order corrections as we shall.

Using (4.4), we find from (4.14) the explicit expressions

$$\gamma A^{(1)}(t) = -\frac{D_x^{(1)}}{B_x}(1-e^{-B_x t})\sigma_x^2 - \frac{D_y^{(1)}}{B_y}(1-e^{-B_y t})\sigma_y^2 - \frac{D_z^{(1)}}{B_z}(1-e^{-B_z t})\sigma_z^2, \qquad (4.18)$$

and using (4.4) and (4.6) we find from (4.13)

$$\gamma G^{(1)} = D_x^{(1)}\sigma_x^2 + D_y^{(1)}\sigma_y^2 + D_z^{(1)}\sigma_z^2, \qquad (4.19)$$

and from (4.17)

$$\gamma^2 G^{(2)} = D_x^{(2)}\sigma_x^2 + D_y^{(2)}\sigma_y^2 + D_z^{(2)}\sigma_z^2 - a^{(2)}\frac{1}{3}\Big(\sum_P \sigma_x\sigma_y\sigma_z\Big). \qquad (4.20)$$

Note that this last expression differs from (4.6) in the signs of the last term. This difference arises from the nonvanishing commutator in the integrand in (4.17). Finally, the integration of (4.10) is now straightforward, since the right-hand side is time independent. Using (4.1) we can express the after-effect operator in the form

$$\langle R(t)\rangle = [1 + \gamma A^{(1)}(t) + \cdots]\, e^{Gt}, \qquad (4.21)$$

where

$$G = \gamma G^{(1)} + \gamma^2 G^{(2)} + \cdots. \qquad (4.22)$$

The expression (4.21), with (4.18), (4.19), and (4.20), is our solution for the aftereffect operator, including the lowest-order inertial effects. It should be clear that with our methods one can, in principle, continue to any desired order, but that the calculations will be very laborious.

V. COMPLEX POLARIZABILITY

The complex polarizability of a polar molecule is given by the expression[22]:

$$\alpha(\omega) = \frac{1}{3kT}\Big(\vec{M}^2 - i\omega\int_0^\infty dt\, e^{-i\omega t}\langle \vec{M}(0)\cdot\vec{M}(t)\rangle\Big), \qquad (5.1)$$

where $\vec{M}(t)$ is the permanent electric dipole moment vector at time t. The correlation entering in this expression can be expressed in terms of the after-effect operator in the three-dimensional $(j=1)$ representation where the σ operators are given by the matrices (3.4). The expression (5.1) can then be written in matrix notation

$$\alpha(\omega) = \frac{1}{3kT}M^+\Big[1 - i\omega\int_0^\infty dt\, e^{-i\omega t}\langle R(t)\rangle_{j=1}\Big]M, \qquad (5.2)$$

where M is the column matrix whose rows are M_x, M_y, and M_z, the components of $\vec{M}$ along the principal body-fixed axes. For this three-dimensional representation it is easy to verify directly using (3.4) that the operator $\sum_P \sigma_x\sigma_y\sigma_z$ given by (3.34) vanishes identically and that the squares of the σ operators are diagonal and therefore commute. Hence, we can write, using (4.21) and (4.18)–(4.20),

$$1 - i\omega\int_0^\infty dt\, e^{-i\omega t}\langle R(t)\rangle_{j=1} = -G(-G+i\omega)^{-1} + i\omega\sum_{x,y,z} D_x^{(1)}\sigma_x^2(-G+i\omega)^{-1} \times(-G+B_x+i\omega)^{-1} + \cdots, \qquad (5.3)$$

where, again, $\sum_{x,y,z}$ means the sum over the three terms obtained by cyclically permuting x, y, and z. In this expression

$$G = \sum_{x,y,z} D_x\sigma_x^2, \qquad (5.4)$$

where

$$D_x = D_x^{(1)} + D_x^{(2)} + \cdots \qquad (5.5)$$

with $D_x^{(1)}$ given by (4.5) and $D_x^{(2)}$ given by (4.8). We can put this expression in a more perspicuous form by noting that to the same order of approximation, i.e., neglecting terms of order $\gamma^2 \approx (kT/IB^2)^2$, we can replace $D_x^{(1)}$ by D_x in the second term in (5.3). Then putting the sum (5.4) for the first factor in the first term of (5.3) and then rearranging, we can write

$$1 - i\omega\int_0^\infty dt\, e^{-i\omega t}\langle R(t)\rangle_{j=1} \approx -\sum_{x,y,z} D_x\sigma_x^2(-G+B_x) \times(-G+i\omega)^{-1}(-G+B_x+i\omega)^{-1}, \qquad (5.6)$$

where the approximation consists in neglecting second-order terms.

The matrices appearing in the expression (5.6) are all diagonal, so it is a simple matter to evaluate the matrix products explicitly, using (3.4). Putting the result in (5.2) we obtain the explicit expression

$$\alpha(\omega) \approx \frac{1}{3kT}\sum_{x,y,z}\frac{M_x^2}{(D_y+D_z+i\omega)}\left[\frac{D_y(D_y+D_z+B_y)}{(D_y+D_z+B_y+i\omega)} + \frac{D_z(D_y+D_z+B_z)}{(D_y+D_z+B_z+i\omega)}\right] \qquad (5.7)$$

where, again, the approximation consists in neglecting terms of second order in the quantity $\gamma \approx (kT/IB^2)$.

Let us apply (5.7) to the case of a spherical molecule. Then from (4.5) and (4.8),

$$D = (kT/IB)(1 + \tfrac{1}{2}\gamma + \cdots), \tag{5.8}$$

where $\gamma = kT/(IB^2)$, and

$$\alpha(\omega) \approx \frac{M^2}{3kT} \frac{2D(2D+B)}{(2D+i\omega)(2D+B+i\omega)},$$

where

$$M^2 = \sum M_x^2,$$

so that

$$\alpha(\omega) \approx \frac{M^2}{3kT} \frac{1 + i(\omega/B)\frac{1}{2}\gamma}{[1+i(\omega IB/2kT)(1-\frac{1}{2}\gamma)][1+i(\omega/B)(1-2\gamma)]}. \tag{5.9}$$

If we neglect the corrections of order γ, we have

$$\alpha(\omega) \approx \frac{M^2}{3kT} \frac{1}{[1+i(\omega IB/2kT)][1+i(\omega/B)]}.$$

Putting $\alpha(\omega) = \alpha'(\omega) - i\alpha''(\omega)$, where α', α'' are real, we deduce that

$$\alpha'(\omega) \approx \frac{M^2}{3kT} \frac{1-(I\omega^2/2kT)}{[1+(\omega^2/B^2)][1+(\omega IB/2kT)^2]}.$$

This agrees with Eq. (8) of Rocard,[23] if in it we put $8\pi\eta a^3 = IB$, replace the Avogadro number by unity and correct the erroneous sign in the numerator. Equation (5.9) is therefore a first-order correction to Rocard's result.

VI. CORRELATION TIME

As we show in the Appendix, the correlations occurring in physical applications can be expressed in terms of matrix elements in the body-fixed frame of the mean rotation operator $\langle R(t)\rangle$. In interpreting nuclear-magnetic-resonance measurements in terms of dipolar interaction, one needs to know these matrix elements (or rather their one-sided Fourier transform) in the $j=2$ representation.[24] We will first form this quantity in the general representation and then exhibit explicit results for the $j=2$ representation. We consider, therefore,

$$J(\omega) = \int_0^\infty dt\, e^{-i\omega t}\langle R(t)\rangle. \tag{6.1}$$

Using (4.21) and (4.18), this becomes

$$J(\omega) \approx (-G+i\omega)^{-1} - \sum_{x,y,z} D_x^{(1)}\sigma_x^2(-G+B_x+i\omega)^{-1} \times (-G+i\omega)^{-1}, \tag{6.2}$$

where the approximation symbol means that we have neglected terms of relative order of the fourth power of the quantity (2.4).

In further rearranging (6.2), we will assume that ω is of the order of kT/IB; again, I is a typical moment of inertia and B a typical frictional decay rate. Since G and $D^{(1)}$ are of this same order, this is clearly the region of ω where $J(\omega)$ shows interesting structure. Moreover, most experimental interpretations involve only the correlation time, which is proportional to the matrix elements of J at $\omega = 0$. Keeping these orders in mind, we see that the first term in (6.2) is of order $(kT/IB)^{-1}$, the second term is of order B^{-1}, and we have neglected terms of order kT/IB^3. Within this same approximation we can, in the second term of (6.2), put

$$(-G+B_x+i\omega)^{-1} \approx B_x^{-1}. \tag{6.3}$$

Next we note from (4.22), (4.19), and (4.20) that we can write

$$G \approx G_0 - \frac{a^{(2)}}{3} \sum_P \sigma_x\sigma_y\sigma_z, \tag{6.4}$$

where

$$G_0 = \sum_{x,y,z} D_x\sigma_x^2 \tag{6.5}$$

with

$$D_x \approx D_x^{(1)} + D_x^{(2)}. \tag{6.6}$$

Since the second term in (6.4) is of order kT/IB^2 relative to the first, we can expand

$$(-G+i\omega)^{-1} \approx (-G_0+i\omega)^{-1} - (-G_0+i\omega)^{-1}\frac{a^{(2)}}{3} \times \left(\sum_P \sigma_x\sigma_y\sigma_z\right)(-G_0+i\omega)^{-1}. \tag{6.7}$$

Putting this in the first term of (6.2), and in the second term using (6.3) and the first term of (6.7), we find

$$J(\omega)\approx(-G_0+i\omega)^{-1}-\sum_{x,y,z}\frac{D_x^{(1)}}{B_x}\sigma_x^2(-G_0+i\omega)^{-1}$$
$$-(-G_0+i\omega)^{-1}\frac{a^{(2)}}{3}\left(\sum_P\sigma_x\sigma_y\sigma_z\right)(-G_0+i\omega)^{-1}. \tag{6.8}$$

Next, from (4.5), (4.7), and the commutation relations (3.3), we can demonstrate the identity

$$\frac{a^{(2)}}{3}\left(\sum_P\sigma_x\sigma_y\sigma_z\right)=\frac{1}{2}\left[\sum_{x,y,z}D_x^{(1)}\sigma_x^2,\ \sum_{x,y,z}\frac{D_x^{(1)}}{B_x}\sigma_x^2\right]. \tag{6.9}$$

We use this in (6.8) and then note that, within our approximation, we can replace $D_x^{(1)}$ by D_x in the second and third terms of the resulting expression. Since with this replacement the first term in the commutator (6.9) is just G_0, we obtain the final result

$$J(\omega)\approx(-G_0+i\omega)^{-1}-\frac{1}{2}\left(\sum_{x,y,z}\frac{D_x}{B_x}\sigma_x^2\right)(-G_0+i\omega)^{-1}$$
$$-\frac{1}{2}(-G_0+i\omega)^{-1}\left(\sum_{x,y,z}\frac{D_x}{B_x}\sigma_x^2\right). \tag{6.10}$$

This is our final form for the operator $J(\omega)$, valid for frequencies ω less than or of the order of kT/IB, and neglecting quantities of the order of kT/IB^3.

We turn now to the explicit construction of (6.10). We shall do this in the usual spherical basis where the rows and columns are labeled by the eigenvalues of $-i\sigma_z$. The matrix elements of the σ's in the $2j+1$-dimensional irreducible representation may be obtained from the formulas given on p. 17 of Ref. 16, with the identification $J=-i\hbar\sigma$.

$$\langle jm'|\sigma_x|jm\rangle=\tfrac{1}{2}i[(j-m)(j+m+1)]^{1/2}\delta_{m',m+1}+\tfrac{1}{2}i[(j+m)(j-m+1)]^{1/2}\delta_{m',m-1},$$
$$\langle jm'|\sigma_y|jm\rangle=\tfrac{1}{2}[(j-m)(j+m+1)]^{1/2}\delta_{m',m+1}-\tfrac{1}{2}[(j+m)(j-m+1)]^{1/2}\delta_{m',m-1}, \tag{6.11}$$
$$\langle jm'|\sigma_z|jm\rangle=im\delta_{m',m}.$$

Using these formulas for the five-dimensional $j=2$ representation, we find the operator $(-G_0+i\omega)$ has the matrix form $\langle m'|(-G_0+i\omega)|m\rangle$,

m' \ m	-2	-1	0	1	2
-2	a	0	d	0	0
-1	0	b	0	e	0
0	d	0	c	0	d
1	0	e	0	b	0
2	0	0	d	0	a

(6.12)

where

$$a=D_x+D_y+4D_z+i\omega,\quad b=\tfrac{5}{2}(D_x+D_y)+D_z+i\omega,$$
$$c=3(D_x+D_y)+i\omega,\quad d=(\tfrac{3}{2})^{1/2}e=(\tfrac{3}{2})^{1/2}(D_x-D_y). \tag{6.13}$$

The inverse of this matrix has the form $\langle m'|(-G_0+i\omega)^{-1}|m\rangle$,

m' \ m	-2	-1	0	1	2
-2	$\frac{ac-d^2}{a(ac-2d^2)}$	0	$\frac{-d}{ac-2d^2}$	0	$\frac{d^2}{a(ac-2d^2)}$
-1	0	$\frac{b}{b^2-e^2}$	0	$\frac{-e}{b^2-e^2}$	0
0	$\frac{-d}{ac-2d^2}$	0	$\frac{a}{ac-2d^2}$	0	$\frac{-d}{ac-2d^2}$
1	0	$\frac{-e}{b^2-e^2}$	0	$\frac{b}{b^2-e^2}$	0
2	$\frac{d^2}{a(ac-2d^2)}$	0	$\frac{-d}{ac-2d^2}$	0	$\frac{ac-d^2}{a(ac-2d^2)}$

(6.14)

Finally, the operator $\sum(D_x/B_x)\sigma_x^2$ has the matrix form: $\langle m'|\sum(D_x/B_x)\sigma_x^2|m\rangle$,

m' \ m	-2	-1	0	1	2
-2	$\tilde{a}$	0	$\tilde{d}$	0	0
-1	0	$\tilde{b}$	0	$\tilde{e}$	0
0	$\tilde{d}$	0	$\tilde{c}$	0	$\tilde{d}$
1	0	$\tilde{e}$	0	$\tilde{b}$	0
2	0	0	$\tilde{d}$	0	$\tilde{a}$

(6.15)

where

$$\tilde{a}=\frac{D_x}{B_x}+\frac{D_y}{B_y}+4\frac{D_z}{B_z},\quad \tilde{b}=\tfrac{5}{2}\left(\frac{D_x}{B_x}+\frac{D_y}{B_y}\right)+\frac{D_z}{B_z}, \tag{6.16}$$
$$\tilde{c}=3\left(\frac{D_x}{B_x}+\frac{D_y}{B_y}\right),\quad \tilde{d}=(\tfrac{2}{3})^{1/2}\tilde{e}=(\tfrac{3}{2})^{1/2}\left(\frac{D_x}{B_x}-\frac{D_y}{B_y}\right).$$

With the matrices (6.14) and (6.15) the matrix of the operator (6.10) in the irreducible representation has the form $\langle m'|J(\omega)|m\rangle$,

m' \ m	-2	-1	0	1	2
-2	A	0	D	0	F
-1	0	B	0	E	0
0	D	0	C	0	D
1	0	E	0	B	0
2	F	0	D	0	A

(6.17)

where

$$
\begin{aligned}
A &= \frac{(ac-d^2)(1+\tilde{a})-ad\tilde{d}}{a(ac-2d^2)},\\
B &= \frac{b+b\tilde{b}-e\tilde{e}}{b^2-e^2},\\
C &= \frac{a+a\tilde{c}-2d\tilde{d}}{ac-2d^2},\\
D &= \frac{-2d+(a+c)\tilde{d}-d(\tilde{a}+\tilde{c})}{2(ac-2d^2)},\\
E &= \frac{-e+b\tilde{e}-e\tilde{b}}{b^2-e^2},\\
F &= \frac{d^2+d(d\tilde{a}-a\tilde{d})}{a(ac-2d^2)}.
\end{aligned}
\qquad (6.18)
$$

In applications one is interested in the quantity:

$$
\tau_j(\vec{r},\vec{s};\omega)=\frac{4\pi}{(2s+1)r^j s^j}\times\sum_{m=-j}^{j}\sum_{m'=-j}^{j}\mathcal{Y}_{jm'}(\vec{r})^*\langle m'|J(\omega)|m\rangle\mathcal{Y}_{jm}(\vec{s}),\qquad(6.19)
$$

in which $\vec{r}$ and $\vec{s}$ are vectors fixed in the body and $\mathcal{Y}_{jm}$ is the solid spherical harmonic.[16] For $j=2$,

$$
\begin{aligned}
\mathcal{Y}_{2,0}(\vec{r}) &= \left(\frac{5}{16\pi}\right)^{1/2}(2r_z^2-r_x^2-r_y^2),\\
\mathcal{Y}_{2,\pm1}(\vec{r}) &= \mp\left(\frac{15}{8\pi}\right)^{1/2} r_z(r_x\pm ir_y),\qquad(6.20)\\
\mathcal{Y}_{2,\pm2}(\vec{r}) &= \left(\frac{15}{32\pi}\right)^{1/2}(r_x\pm ir_y)^2.
\end{aligned}
$$

Using these formulas and the form (6.15) in (6.17) we find for $j=2$,

$$
\begin{aligned}
\tau_2(\vec{r},\vec{s};\omega)=\frac{1}{r^2s^2}\{&[\tfrac{3}{4}A+\tfrac{3}{4}F+\tfrac{1}{4}C-(\tfrac{3}{2})^{1/2}D]r_x^2s_x^2+[\tfrac{3}{4}A+\tfrac{3}{4}F+\tfrac{1}{4}C+(\tfrac{3}{2})^{1/2}D]r_y^2s_y^2+Cr_z^2s_z^2\\
&-(\tfrac{3}{4}A+\tfrac{3}{4}F-\tfrac{1}{4}C)(r_x^2s_y^2+r_y^2s_x^2)+\tfrac{3}{4}(A-F)r_xr_ys_xs_y-[\tfrac{1}{2}C-(\tfrac{3}{2})^{1/2}D](r_x^2s_z^2+r_z^2s_x^2)\\
&+3(B-E)r_xr_zs_xs_z-[\tfrac{1}{2}C+(\tfrac{3}{2})^{1/2}D](r_y^2s_z^2+r_z^2s_y^2)+3(B+E)r_yr_zs_ys_z.
\end{aligned}
\qquad(6.21)
$$

Using now (6.13) and (6.16) in (6.18), we can write this in the final form

$$
\tau_2(\vec{r},\vec{s};\omega)=\frac{1}{r^2s^2}\sum_{x,y,z}[P_{xyz}r_x^2s_x^2-Q_{xyz}(r_y^2s_z^2+r_z^2s_y^2)+R_{xyz}r_yr_zs_ys_z],\qquad(6.22)
$$

in which the sum is over the three cyclic permutations of x,y,z and

$$
\begin{aligned}
P_{xyz} &= \frac{4D_x+D_y+D_z+i\omega+3\left[4\frac{D_xD_y}{B_y}+4\frac{D_xD_z}{B_z}+2D_yD_z\left(\frac{1}{B_y}+\frac{1}{B_z}\right)+i\omega\left(\frac{D_y}{B_y}+\frac{D_z}{B_z}\right)\right]}{12(D_xD_y+D_xD_z+D_yD_z)+4i\omega(D_x+D_y+D_z)-\omega^2},\\
Q_{xyz} &= \frac{2(D_y+D_z)-D_x+\frac{1}{2}i\omega+3\left[D_xD_y\left(\frac{3}{B_x}-\frac{1}{B_y}\right)+D_xD_z\left(\frac{3}{B_x}-\frac{1}{B_z}\right)+D_yD_z\left(\frac{1}{B_y}+\frac{1}{B_z}\right)+i\omega\frac{D_x}{B_x}\right]}{12(D_xD_y+D_xD_z+D_yD_z)+4i\omega(D_x+D_y+D_z)-\omega^2}\qquad(6.23)\\
R_{xyz} &= \frac{3\left(1+4\frac{D_x}{B_x}+\frac{D_y}{B_y}+\frac{D_z}{B_z}\right)}{4D_x+D_y+D_z}.
\end{aligned}
$$

As an application of this result we form the correlation time associated with the dipolar broadening of the nuclear-magnetic-resonance line for two equivalent nuclei.[24] Since an asymmetric top molecule can have no symmetry other than a center of inversion or a symmetry plane coinciding with a principal plane, the line joining the two nuclei must be parallel to a principal axis. Taking this axis to be the z axis, the correlation time is the quantity (6.22) in which $\vec{r}=\vec{s}=\hat{z}$, and $\omega=0$:

$$\tau_2 = \frac{D_x + D_y + 4D_z + 3[4D_x D_z/B_x + 4D_y D_z/B_y + 2D_x D_y(1/B_x + 1/B_y)]}{12(D_x D_y + D_y D_z + D_z D_x)} \tag{6.24}$$

As a check on this result we apply it to the case of the sphere. Then, by (5.8), $D/B = \gamma(1+\frac{1}{2}\gamma+\cdots)$. Hence

$$\tau_2 = \frac{6D+36D^2/B}{36D^2} = \frac{1+6\gamma(1+\frac{1}{2}\gamma+\cdots)}{6(kT/IB)(1+\frac{1}{2}\gamma+\cdots)}$$
$$= \frac{IB}{6kT}(1+6\gamma+\cdots)(1-\frac{1}{2}\gamma+\cdots)$$
$$= \frac{IB}{6kT}(1+\tfrac{11}{2}\gamma+\cdots),$$

which agrees with the result of a direct calculation for the sphere.[25]

It is of interest to exhibit the form of the quantity (6.22) for the case of the symmetric top. Taking the symmetry axis to be the body-fixed z axis, (6.22) becomes

$$\tau_2(\vec{r},\vec{s};\omega) = \frac{1}{r^2 s^2}\left\{\frac{1+6\frac{D_x}{B_x}}{4(6D_x+i\omega)}(3r_z^2-r^2)(3s_z^2-s^2) + \frac{3}{4}\frac{1+2\frac{D_x}{B_x}+4\frac{D_z}{B_z}}{2D_x+4D_z+i\omega}[(r_x^2-r_y^2)(s_x^2-s_y^2)+r_x r_y s_x s_y] + 3\frac{1+5\frac{D_x}{B_x}+\frac{D_z}{B_z}}{5D_x+D_z+i\omega} r_z s_z(r_x s_x + r_y s_y)\right\}. \tag{6.25}$$

VII. CONCLUSIONS

We have obtained an expression (5.7) for the complex polarizability which generalizes to the case of the asymmetric top molecule the well-known Rocard[23] form of the complex polarizability for a spherical molecule, correct to terms of order (kT/IB^2). We have obtained also an expression (6.10) for the operator $J(\omega)$ which occurs in the calculation of correlation times associated with the dipolar broadening of nuclear-magnetic-resonance lines, and tabulated its matrix elements in the $j=2$ representation. As an application, we obtain the correlation time associated with the dipolar broadening for two equivalent nuclei (6.24) correct to terms of order (kT/IB^2). The methods presented can be used to compute higher-order corrections if required. A preliminary account of this work has been given in Refs. 26 and 27.

APPENDIX: EVALUATION OF CORRELATIONS OF SPHERICAL HARMONICS

Consider the correlation

$$\langle Y_{lq}[\hat{a}(t_0)]^* Y_{lq'}[\hat{b}(t_1)]\rangle, \tag{A1}$$

where Y_{lq} are spherical harmonics defined with respect to a space-fixed coordinate frame and $\hat{a}$ and $\hat{b}$ are vectors fixed in the rotating body. Here the average is over initial orientations together with the averaging used in the body of the paper. We introduce Y'_{lm} and Y''_{lm}, spherical harmonics defined, respectively, with respect to body-fixed coordinate frames at time t_0 and t_1. The point here is that

$$Y'_{lm}[\hat{a}(t_0)] = Y'_{lm}(\hat{a}), \quad Y''_{lm}[\hat{b}(t_1)] = Y'_{lm}(\hat{b}), \tag{A2}$$

are independent of t_0 and t_1, respectively. Let now R_0 be the rotation which takes the space-fixed frome to the body-fixed frame at time t_0 and $R(t)$ be the rotation which takes the body-fixed frame at t_0 to the body-fixed frame at $t_1 = t_0 + t$. Then the spherical harmonics in the various frames are related by

$$Y_{lm} = \sum_n Y'_{ln}(Y'_{ln}, R_0^{-1} Y'_{lm}), \tag{A3}$$

$$Y_{lm} = \sum_n Y''_{ln}(Y''_{ln}, [R(t)R_0]^{-1} Y''_{lm}), \tag{A4}$$

$$Y''_{lm} = \sum_n Y'_{ln}(Y'_{ln}, R(t) Y'_{lm}). \tag{A5}$$

Using (A5) and the fact that $R(t)$ is unitary, so

$$R^{-1}(t) = R(t)^{\dagger}, \tag{A6}$$

we can show that

$$(Y_{ln}'', [R(t)R_0]^{-1} Y_{lm}'') = \sum_k [Y_{ln}', R(t)^{-1} Y_{lk}'](Y_{lk}', R_0^{-1} Y_{lm}'). \tag{A7}$$

We note next that

$$(Y_{lm}', R_0^{-1} Y_{lm'}') = \mathfrak{D}_{mm'}^l (R_0^{-1}) \tag{A8}$$

is the familiar representation matrix for finite rotations.[16] Using (A8) in (A3) and in (A7), and then putting (A7) in (A4), we get the relations

$$Y_{lq} = \sum_n Y_{ln}' \mathfrak{D}_{nq}^l (R_0^{-1}) \tag{A9}$$

and

$$Y_{lq'} = \sum_{n',n''} Y_{ln'}'' [Y_{ln'}', R(t)^{-1} Y_{ln''}'] \mathfrak{D}_{n'',q'}^l (R_0^{-1}). \tag{A10}$$

Forming now (A1), using (A9) in the first factor and (A10) in the second, we get

$$\langle Y_{lq}[\hat{\hat{a}}(t_0)]^* Y_{lq'}[\hat{\hat{b}}(t_1)]\rangle = \sum_{n,n',n''} Y_{ln}[\hat{\hat{a}}(t_0)]^* [Y_{ln'}', \langle R(t)^{-1}\rangle Y_{ln''}'] \times Y_{ln'}''[\hat{b}(t_1)] \int \frac{dR_0^{-1}}{8\pi^2} \mathfrak{D}_{nq}^l (R_0^{-1})^* \mathfrak{D}_{n''q'}^l (R_0^{-1}). \tag{A11}$$

Using the orthogonality of the $\mathfrak{D}$ functions,

$$\int \frac{dR}{8\pi^2} \mathfrak{D}_{nq}^l (R)^* \mathfrak{D}_{n'q'}^l (R) = \frac{1}{2l+1} \delta_{nn'} \delta_{qq'}, \tag{A12}$$

this becomes

$$\langle Y_{lq}[\hat{\hat{a}}(t_0)]^* Y_{lq'}[\hat{\hat{b}}(t_1)]\rangle = \delta_{qq'} \frac{1}{2l+1} \sum_{m,m'} Y_{lm}'(\hat{b}) [Y_{lm}', \langle R(t)^{-1}\rangle Y_{lm'}'] Y_{lm'}'(\hat{\hat{a}})^*. \tag{A13}$$

Here we have used (A2). This result is contained in Sec. VII of Ref. 6.

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