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Rotational Brownian Motion*

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A Fokker–Planck equation for the joint probability density of the orientation and angular velocity of a body of general shape is derived by use of a rotational Langevin equation. Equations governing the seperate distributions of orientation and angular velocity are deduced from the equation for the joint probability density. For the special case of a spherical body, two expressions for the orientation distribution are calculated, one valid for small values of the frictional constant occurring in the rotational Langevin equation, and the other valid for large values of the frictional constant. The latter expression includes previously presented results of rotational-diffusion theory and Steele's modification of rotational-diffusion theory, and the calculation provides conditions of validity for these theories. Expressions are calculated for time-correlation functions of spherical tensors, such as spherical harmonics, which involve functions of the orientation of a body.

I. INTRODUCTION

The theory of translational Brownian motion is concerned with the calculation of the joint probability density for the position and velocity of a particle in a fluid. The theory is usually based on Langevin's equation, which is Newton's second law with the assumption that the force acting on the particle is the sum of a viscous retarding force proportional to the velocity of the particle and a rapidly fluctuating force whose statistical properties are such that the probability for the velocity of a particle approaches a Maxwell–Boltzmann distribution. By use of Langevin's equation, a Fokker–Planck equation for the distribution function of position and velocity can be derived, and the equation can be solved.[1–3]

The analogous problem of rotational Brownian motion is concerned with the calculation of the joint probability density for the orientation and angular velocity of a body in a fluid. The rotational problem is more complicated than the translational problem, primarily because it is not possible to specify the orientation of a rigid body by a vector whose time derivative is the angular velocity of the body. The specification of the orientation of a body requires three coordinates, such as Euler angles, whose relations to the components of angular velocity are not particularly simple. Nevertheless, if the rotational analog of Langevin's equations, based on Euler's equation, is introduced, and the orientation is specified by some appropriate coordinates, it is possible to derive a Fokker–Planck equation for the distribution function for orientation and angular velocity.[4] However, an analytic solution of such an equation for the general case has not been given.

Theories of rotational diffusion, concerned with the probability density just for orientation and not also for angular velocity, have been developed by several authors.[5–8] Ivanov has obtained a theory of rotational diffusion as a limiting case of his solution of the rotational random-walk problem.[9,10] Steele has presented a theory of rotational diffusion which includes inertial effects not contained in the results of Refs. 5–10.[11] However, all of these theories of rotational diffusion, including Steele's, have the fault that they do not reduce in the appropriate limit to the correct result for a freely rotating body.

Fixman and Rider have derived a theory of rotational Brownian motion for the special case in which the direction of a single vector fixed in a body is of interest, rather than the complete orientation of the body. They have numerically evaluated $\langle P_n(\cos\theta(t))\rangle$ for a symmetric top, where P_n is a Legendre polynomial and $\theta(t)$ is the angle made by the symmetry axis with its initial direction.[12]

Gordon has calculated dipole-correlation functions for a linear molecule by assuming that the molecule undergoes collisions in which either (i) both the magnitude and the direction of the angular velocity of the molecule are randomized (J diffusion) or (ii) the orientation of the angular velocity is randomized but its magnitude remains unchanged (M diffusion).[13] McClung has applied Gordon's model to spherical-top molecules to calculate correlation functions of orientation and also of orientation and angular velocity.[14] Fixman and Rider have also employed Gordon's model to calculate correlation functions involving the orientation of a spherical molecule.[12]

In Sec. II, a Fokker–Planck equation for the joint probability density of the orientation and angular velocity of a body of general shape is derived in terms of Euler angles specifying the orientation and in terms of the components of angular velocity in a principal body-coordinate system. In Sec. III the probability density is expanded in terms of rotation matrices, which leads to matrix equations for the probability density and its Fourier transform with respect to angular velocity, which are useful because they involve quantum-mechanical angular-momentum matrices whose properties are relatively simple. In Sec. IV, the distribution of angular velocity is obtained by integrating over orientations, the primary purpose being to establish the relation between the frictional constants and the fluctuating torques that occur in the rotational Langevin equation. In Sec. V the general equations governing the distribution of orientation are obtained. Section VI is concerned with the distribution of orientation of a spherical body. A generalization of the procedure used by Wilcox to derive the Magnus expansion[15] is employed to derive two expressions for the distribution of orientation of a spherical body, one valid for small frictional torques, and the other for large frictional torques. An important consequence in the latter case is the establishment of the conditions under which rotational-diffusion theory,[5–10] and Steele's modification of it,[11] are valid. In Sec. VII expressions are derived for time-correlation functions of spherical tensors, such as spherical harmonics, which involve functions of the orientation of a body.

II. BASIC EQUATIONS

Let S' be a principal coordinate system fixed in a rigid body. The orientation of the body is specified by the Euler angles $g\equiv(\alpha,\ \beta,\ \gamma)$ of S' with respect to a laboratory coordinate system S.[16] The components with respect to S' of the angular velocity of the body are denoted by ω_1, ω_2, and ω_3. When $\vec{\omega}$ occurs as the argument of a function, it represents ω_1, ω_2, and ω_3.

Let $P(\vec{\omega},g,t;\vec{\omega}_0,g_0)$ represent the conditional probability density that at time $t\geq 0$ the body has angular velocity $\vec{\omega}$ in $d^3\omega$ and orientation g in $dg\equiv\sin\beta\, d\alpha\, d\beta\, d\gamma$, if it had angular velocity $\vec{\omega}_0$ and orientation g_0 at $t=0$. An equation for $P(\vec{\omega},g,t;\vec{\omega}_0,g_0)$ can be derived by a procedure similar to the derivation of the Fokker–Planck equation for translational Brownian motion.[2,3]

It is assumed that the rotational motion is a Markov process, so that

$$P(\vec{\omega},g,t+\Delta t;\vec{\omega}_0,g_0)$$
$$=\int d^3(\Delta\omega)\int d(\Delta g)\, P(\vec{\omega},g,\Delta t;\vec{\omega}-\Delta\vec{\omega},g-\Delta g)$$
$$\times P(\vec{\omega}-\Delta\vec{\omega},g-\Delta g,t;\vec{\omega}_0,g_0)\ . \quad (2.1)$$

Δg is defined by the fact that the orientation g is obtained from the orientation $g-\Delta g$ by a rotation Δg.

The last P in Eq. (2.1) can be expressed as

$$P(\vec{\omega}-\Delta\vec{\omega},g-\Delta g,t;\vec{\omega}_0,g_0)$$
$$=e^{-i\vec{\theta}\cdot\vec{J}}e^{-\Delta\vec{\omega}\cdot\nabla_\omega}P(\vec{\omega},g,t;\vec{\omega}_0,g_0)\ , \quad (2.2)$$

where $\vec{J}$ is the quantum-mechanical angular-momentum operator for the body, in units of $\hbar$, and Δg is a rotation through angle θ about the direction of $\vec{\theta}$.[17,18]

It is assumed that, for small values of Δt, $P(\vec{\omega},g,\ \Delta t;\vec{\omega}-\Delta\vec{\omega},g-\Delta g)$ is zero unless $\vec{\theta}=\vec{\omega}\Delta t$, so that Eqs. (2.1) and (2.2) give

$$P(\vec{\omega},g;\ t+\Delta t;\ \vec{\omega}_0,g_0)=\int d^3(\Delta\omega)p(\vec{\omega},\ \Delta t;\ \vec{\omega}-\Delta\vec{\omega})$$
$$\times e^{-i\vec{\omega}\cdot\vec{J}\Delta t}e^{-\Delta\vec{\omega}\cdot\nabla_\omega}P(\vec{\omega},g,t;\ \vec{\omega}_0,g_0)$$
$$=\int d^3(\Delta\omega)e^{-i\vec{\omega}\cdot\vec{J}\Delta t}e^{-\Delta\vec{\omega}\cdot\nabla_\omega}p(\vec{\omega}+\Delta\vec{\omega},\ \Delta t;\ \vec{\omega})$$
$$\times P(\vec{\omega},g,t;\ \vec{\omega}_0,g_0)\ , \quad (2.3)$$

where $p(\vec{\omega}+\Delta\vec{\omega},\ \Delta t;\ \vec{\omega})$ is the probability density of a change in angular velocity from $\vec{\omega}$ to $\vec{\omega}+\Delta\vec{\omega}$ in time Δt; p is assumed to be independent of the orientation of the body, since $\vec{\omega}$ represents components of the angular velocity in the body coordinate system S'.

Application of the operator $e^{i\vec{\omega}\cdot\vec{J}\Delta}$ to Eq. (2.3), followed by expansion of the left-hand side of the resulting equation as a power series in Δt, and use of the expansion

$$e^{-\Delta\vec{\omega}\cdot\nabla_\omega}=\sum_{n=0}^{\infty}\frac{1}{n!}(-\Delta\vec{\omega}\cdot\nabla_\omega)^n$$

in the right-hand side, along with the fact that

$$\int d^3(\Delta\omega)p(\vec{\omega}+\Delta\vec{\omega},\ \Delta t;\ \vec{\omega})=1\ ,$$

gives the equation

$$\left(\frac{\partial}{\partial t}+i\vec{\omega}\cdot\vec{J}\right)P(\vec{\omega},g,t;\ \vec{\omega}_0,g_0)\Delta t+O(\Delta t^2)$$
$$=\sum_{n=1}^{\infty}\frac{1}{n!}\int d^3(\Delta\omega)(-\Delta\vec{\omega}\cdot\nabla_\omega)^n p(\vec{\omega}+\Delta\vec{\omega},\ \Delta t;\ \vec{\omega})$$
$$\times P(\vec{\omega},g,t;\ \vec{\omega}_0,g_0)$$
$$=-\sum_{i=1}^{3}\frac{\partial}{\partial\omega_i}[\langle\Delta\omega_i\rangle P]$$
$$+\frac{1}{2}\sum_{i,j=1}^{3}\frac{\partial}{\partial\omega_i}\frac{\partial}{\partial\omega_j}[\langle\Delta\omega_i\Delta\omega_j\rangle P]$$
$$+O(\langle\Delta\omega^3\rangle),\quad (2.4)$$

where

$$\langle\Delta\omega_1{}^\mu\Delta\omega_2{}^\nu\Delta\omega_3{}^\kappa\rangle$$
$$\equiv\int\Delta\omega_1{}^\mu\Delta\omega_2{}^\nu\Delta\omega_3{}^\kappa p(\vec{\omega}+\Delta\vec{\omega},\ \Delta t;\ \vec{\omega})\,d^3(\Delta\omega)\ ,\quad (2.5)$$

and the symbol $O(\langle\Delta\omega^3\rangle)$ in Eq. (2.4) represents terms that contain the quantity (2.5) with $\mu+\nu+\kappa>2$.

In order to evaluate the quantity (2.5), a rotational Langevin equation will be used, analogous to the Langevin equation employed in the theory of translational Brownian motion.[2,3]

The rotational motion of a rigid body is governed by Euler's equations, which can be written

$$\dot{\omega}_i = r_i \omega_j \omega_k + N_i / I_i , \tag{2.6}$$

where i, j, and k are a cyclic permutation of 1, 2, and 3; $\dot{\omega}_i$ is the derivative with respect to time of the component ω_i of the angular velocity along the ith principal axis of the body; I_i is the principal moment of inertia and N_i is the external torque about the ith principal axis; and

$$r_i \equiv (I_j - I_k)/I_i . \tag{2.7}$$

In analogy to the theory of translational Brownian motion, we assume that the external torque N_i due to the interaction of the body with its surroundings is the sum of a viscous retarding torque proportional to ω_i plus a torque $I_i A_i(t)$ that fluctuates randomly at a rate rapid compared to the rate at which ω_i changes appreciably:

$$N_i / I_i = -B_i \omega_i + A_i(t) , \tag{2.8}$$

where B_i is independent of t, $\vec{\omega}$, and the orientation of the body. Again in analogy with the theory of translational Brownian motion,[3] we assume that ensemble averages of the fluctuating quantities $A_i(t)$ satisfy the following equations:

$$\langle A_i(t) \rangle = 0 ; \tag{2.9}$$

$$\langle A_i(t_1) A_j(t_2) \rangle = 2a_i \delta_{ij} \delta(t_1 - t_2) , \tag{2.10}$$

where a_i is a constant;

$$\langle A_i(t_1) A_j(t_2) \cdots A_k(t_{2n+1}) \rangle = 0 ; \tag{2.11}$$

and

$$\langle A_i(t_1) A_j(t_2) \cdots A_k(t_{2n}) \rangle = \sum{}' \langle A_i(t_p) A_j(t_q) \rangle \langle A_k(t_r) A_l(t_s) \rangle \ldots , \tag{2.12}$$

where $\sum'$ represents a sum over the $(2n)!/n!2^n$ ways in which the $2n$ A's can be taken in pairs.

Use of expression (2.8) in the Euler equations (2.6) gives the following rotational Langevin equations:

$$\dot{\omega}_i = r_i \omega_j \omega_k - B_i \omega_i + A_i(t) . \tag{2.13}$$

The rotational Langevin equations and the properties (2.9)–(2.12) can be used to calculate the averages (2.5) that occur in Eq. (2.4). Integrating Eq. (2.13) over a short time Δt, one obtains

$$\Delta\omega_i = (r_i \omega_j \omega_k - B_i \omega_i)\Delta t + \int_t^{t+\Delta t} A_i(t')\, dt' . \tag{2.14}$$

Because of property (2.9), the average of Eq. (2.14) gives

$$\langle \Delta\omega_i \rangle = (r_i \omega_j \omega_k - B_i \omega_i)\Delta t . \tag{2.15}$$

If expressions of the form (2.14) are used for both $\Delta\omega_i$ and $\Delta\omega_{i'}$, it follows from property (2.9) that

$$\langle \Delta\omega_i \Delta\omega_{i'} \rangle = O(\Delta t^2) + \int_t^{t+\Delta t} dt' \int_t^{t+\Delta t} dt'' \langle A_i(t') A_{i'}(t'') \rangle . \tag{2.16}$$

The integral can be evaluated by use of property (2.10), giving

$$\langle \Delta\omega_i \Delta\omega_{i'} \rangle = O(\Delta t^2) + 2a_i \delta_{ii'} \Delta t . \tag{2.17}$$

It is apparent that a similar calculation of $\langle \Delta\omega_1{}^\mu \Delta\omega_2{}^\nu \Delta\omega_3{}^\kappa \rangle$, using Eq. (2.14) and properties (2.9)–(2.12), gives a result for which

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \langle \Delta\omega_1{}^\mu \Delta\omega_2{}^\nu \Delta\omega_3{}^\kappa \rangle = 0 \quad \text{if } \mu + \nu + \kappa > 2 . \tag{2.18}$$

If Eq. (2.4) is divided by Δt, the limit $\Delta t \to 0$ is taken, and Eqs. (2.15), (2.17), and (2.18) are used, one obtains the following equation for $P(\vec{\omega}, g, t; \vec{\omega}_0, g_0)$:

$$\frac{\partial}{\partial t} P + \sum_{j=1}^{3} \left(i\omega_j J_j P - \frac{\partial}{\partial \omega_j} [E_j(\vec{\omega}) P] - a_j \frac{\partial^2}{\partial \omega_j{}^2} P \right) = 0 , \tag{2.19}$$

where

$$E_i(\vec{\omega}) \equiv B_i \omega_i - r_i \omega_j \omega_k , \tag{2.20}$$

and i, j, and k are a cyclic permutation of 1, 2, and 3.

Equation (2.19) is the Fokker–Planck equation for rotational motion. It should be remembered that the ω_j which occur in the equation are components of $\vec{\omega}$ along the axes of a principal body-coordinate system S', since Euler's equations have been used in the derivation. Thus the components J_j of the quantum-mechanical angular-momentum operator which occur in Eq. (2.19) must also be the components in S'.

The initial condition on $P(\vec{\omega}, g, t; \vec{\omega}_0, g_0)$ is that

$$P(\vec{\omega}, g, 0; \vec{\omega}_0, g_0) = \delta(\vec{\omega} - \vec{\omega}_0)\delta(g - g_0) , \tag{2.21}$$

where $\delta(g - g_0)$ is zero unless the orientations g and g_0 coincide, and $\int \delta(g - g_0)\, dg = 1$.

III. EXPANSION OF $P(\vec{\omega}, g, t; \vec{\omega}_0, g_0)$

Consider the functions of orientation

$$\psi_{MK}^J(g) \equiv \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{MK}^{J*}(g) , \tag{3.1}$$

which are defined in terms of the rotation matrices

$$D_{m'm}^j(g) = \langle jm' | e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} | jm \rangle , \quad j = 0, 1, \ldots ; \quad -j \le m', m \le j \tag{3.2}$$

that occur in the quantum theory of angular momentum.[19] If the orientation of a rigid body is specified by the Euler angles $g \equiv (\alpha, \beta, \gamma)$ of a principal coordinate system S' fixed in the body with respect to the laboratory coordinate system S, then $\psi_{MK}^J(g)$ is an eigenfunction of the square of the total angular momentum of the body, $\vec{J}^2$, with eigenvalue $J(J+1)$; the z component of $\vec{J}$ in S, J_z, with eigenvalue M; and also the z' component of $\vec{J}$ in S', J_3, with eigenvalue K.[20] These properties are true for a body of arbitrary shape. For the special case of a symmetric top, $\psi^J_{MK}(g)$ is also an eigenfunction of the rotational Hamiltonian, but this fact is irrelevant to its use here. The $\psi^J_{MK}(g)$ form a complete set, in terms of which a function of the Euler angles specifying the orientation of a rigid body may be expanded, no matter what the shape of the body.

The $\psi^J_{MK}(g)$ satisfy the orthonormality relation[21]

$$\int dg\, \psi^{J*}_{MK}(g)\, \psi^{J'}_{M'K'}(g) = \delta_{JJ'}\delta_{MM'}\delta_{KK'} \tag{3.3}$$

and the closure property

$$\delta(g-g_0) = \sum_{J=0}^{\infty} \sum_{M,K=-J}^{J} \psi^{J*}_{MK}(g_0)\, \psi^J_{MK}(g) . \tag{3.4}$$

Now consider the expansion of the probability density in the form

$$P(\vec{\omega}, g, t;\, \vec{\omega}_0, g_0) = \sum_{J=0}^{\infty} \sum_{M,K=-J}^{J} f^J_{KM}(\vec{\omega}, t;\, \vec{\omega}_0,\, g_0)\psi^J_{MK}(g). \tag{3.5}$$

Substitution of (3.5) into Eq. (2.19) and use of (3.3) leads to the following equation for $f^J_{KM}(\vec{\omega}, t;\, \vec{\omega}_0, g_0)$:

$$\left[\frac{\partial}{\partial t} - \sum_{j=1}^{3}\left(\frac{\partial}{\partial \omega_j} E_j(\vec{\omega}) + a_j \frac{\partial^2}{\partial \omega_j^2}\right)\right] f^J_{KM} = -i \sum_{j=1}^{3} \omega_j \sum_{J'M'K'} \langle JMK|J_j|J'M'K'\rangle f^{J'}_{K'M'} , \tag{3.6}$$

where

$$\langle JMK|J_j|J'M'K'\rangle \equiv \int dg \psi^{J*}_{MK}(g) J_j \psi^{J'}_{M'K'}(g) . \tag{3.7}$$

It follows from Eqs. (2.21) and (3.3)–(3.5) that the initial value of f^J_{KM} is

$$f^J_{KM}(\vec{\omega}, 0;\, \vec{\omega}_0, g_0) = \delta(\vec{\omega} - \vec{\omega}_0)\, \psi^{J*}_{MK}(g_0) . \tag{3.8}$$

It is shown in Appendix A that the matrix elements (3.7) are

$$\langle JMK|J_j|J'M'K'\rangle = \delta_{JJ'}\delta_{MM'}\langle JK|J_j|JK'\rangle , \tag{3.9}$$

where

$$\langle JK|J_1 \mp iJ_2|JK'\rangle = \delta_{K,K'\pm 1}[(J\mp K')(J\pm K'+1)]^{1/2} \tag{3.10}$$

and

$$\langle JK|J_3|JK'\rangle = K\delta_{K'K} . \tag{3.11}$$

Hence Eq. (3.6) can be written

$$\left[\frac{\partial}{\partial t} - \sum_{j=1}^{3}\left(\frac{\partial}{\partial \omega_j} E_j(\vec{\omega}) + a_j \frac{\partial^2}{\partial \omega_j^2}\right)\right] f^J_{KM}(\vec{\omega}, t;\, \vec{\omega}_0, g_0) = -\sum_{j=1}^{3} \omega_j \sum_{K'=-J}^{J} \langle JK|J_j|JK'\rangle f^J_{K'M} . \tag{3.12}$$

Let $\underline{J}_1$, $\underline{J}_2$, and $\underline{J}_3$ be square matrices of dimension $2J+1$, whose KK' matrix elements are given by (3.11) and the expressions that follow from (3.10) for $\langle JK|J_1|JK'\rangle$ and $\langle JK|J_2|JK'\rangle$. Also let $\underline{\vec{J}} \equiv (\underline{J}_1, \underline{J}_2, \underline{J}_3)$, which has the properties of a vector whose components are matrices. For a given J, the matrices $\underline{J}_1$ and $\underline{J}_3$ are the usual matrices for the x and z components of angular momentum, but $\underline{J}_2$ is the negative of the usual matrix for the y component of angular momentum. Thus the matrices are Hermitian, and satisfy commutation relations implied by

$$\underline{\vec{J}} \times \underline{\vec{J}} = -i\underline{\vec{J}} . \tag{3.13}$$

The anomalous sign for the matrix $\underline{J}_2$, and hence for the right-hand side of Eq. (3.13), is a consequence of the fact that (3.9) represents matrix elements of the components of the angular momentum with respect to the body-coordinate system S'.[22,23] The anomalous sign of $\underline{J}_2$, of course, does not affect the usual relation

$$\underline{\vec{J}}^2 \equiv \underline{J}_1^2 + \underline{J}_2^2 + \underline{J}_3^2 = J(J+1)\underline{I} . \tag{3.14}$$

Let $\underline{f}(\vec{\omega}, t;\, \vec{\omega}_0, g_0)$ be a square matrix of dimension $2J+1$ whose KMth matrix element for a given J is $f^J_{KM}(\vec{\omega}, t; \vec{\omega}_0, g_0)$. Equation (3.12) can then be expressed conveniently in matrix form for each value of J as

$$\left[\frac{\partial}{\partial t} + \sum_{j=1}^{3}\left(i\omega_j \underline{J}_j - \frac{\partial}{\partial \omega_j} E_j(\vec{\omega}) - a_j \frac{\partial^2}{\partial \omega_j^2}\right)\right] \underline{f}(\vec{\omega}, t;\, \vec{\omega}_0, g_0) = \underline{0} , \tag{3.15}$$

where the derivatives operate on everything to their right.

The initial condition (3.8) can be expressed in matrix form

$$\underline{f}(\vec{\omega}, 0;\, \vec{\omega}_0, g_0) = \delta(\vec{\omega} - \vec{\omega}_0)\underline{Q} , \tag{3.16}$$

where $\underline{Q}$ is a square matrix of dimension $2J+1$ whose KMth matrix element is $\psi^{J*}_{MK}(g_0)$.

Rather than dealing with the matrix $\underline{f}$, it is more convenient to introduce another matrix $\underline{F}$ defined by

$$\underline{f}(\vec{\omega}, t;\, \vec{\omega}_0, g_0) \equiv \underline{F}(\vec{\omega}, t; \vec{\omega}_0)\underline{Q} , \tag{3.17}$$

for a given J, so that

$$f^J_{KM}(\vec{\omega}, t;\, \vec{\omega}_0, g_0) = \sum_{N=-J}^{J} F^J_{KN}(\vec{\omega},\, t;\, \vec{\omega}_0)\psi^{J*}_{MN}(g_0) . \tag{3.18}$$

It is apparent that expression (3.17) for $\underline{f}$ will be a solution of Eq. (3.15) if $\underline{F}(\vec{\omega}, t, \vec{\omega}_0)$ is a solution of that equation. But the initial condition on $\underline{F}$ is simpler, since from (3.16) and (3.17),

$$\underline{F}(\vec{\omega}, 0;\, \vec{\omega}_0) = \delta(\vec{\omega} - \vec{\omega}_0)\underline{I} . \tag{3.19}$$

It follows from (3.5) and (3.18) that

$$P(\vec{\omega},g,t;\vec{\omega}_0,g_0) = \sum_{J=0}^{\infty}\sum_{K,M,N=-J}^{J} F^J_{KN}(\vec{\omega},t;\vec{\omega}_0)\,\psi^{J*}_{MN}(g_0)\,\psi^J_{MK}(g)\ . \tag{3.20}$$

It is useful to introduce the Fourier transform of $F^J_{KN}(\vec{\omega},t;\vec{\omega}_0)$ with respect to $\vec{\omega}$, which we denote by $G^J_{KN}(\vec{k},t;\vec{\omega}_0)$ and define in matrix form

$$\underline{G}(\vec{k},t;\vec{\omega}_0)\equiv\int d^3\omega\, e^{-i\vec{k}\cdot\vec{\omega}}\,\underline{F}(\vec{\omega},t;\vec{\omega}_0)\ . \tag{3.21}$$

$\underline{F}$ is then given in terms of $\underline{G}$ by

$$\underline{F}(\vec{\omega},t;\vec{\omega}_0)=(2\pi)^{-3}\int d^3k\, e^{i\vec{k}\cdot\vec{\omega}}\,\underline{G}(\vec{k},t;\vec{\omega}_0)\ . \tag{3.22}$$

It follows from Eqs. (2.20), (3.21), and the fact that $\underline{F}$ satisfies Eq. (3.15) that the Fourier-transform matrix $\underline{G}(\vec{k},t;\vec{\omega}_0)$ satisfies

$$\left[\frac{\partial}{\partial t}+\sum_{j=1}^{3}\left(-\underline{J}_j\frac{\partial}{\partial k_j}+B_jk_j\frac{\partial}{\partial k_j} - ir_jk_j\frac{\partial^2}{\partial k_k\,\partial k_i}+a_jk_j^2\right)\right]\underline{G}=0\ , \tag{3.23}$$

where the subscripts i, j, k are a cyclic permutation of 1, 2, 3.

Equations (3.19) and (3.21) give the initial condition

$$\underline{G}(\vec{k},0;\vec{\omega}_0)=e^{-i\vec{k}\cdot\vec{\omega}_0}\,\underline{I}. \tag{3.24}$$

IV. DISTRIBUTION OF ANGULAR VELOCITY

Let $P(\vec{\omega},t;\vec{\omega}_0)$ be the conditional probability density that a body has angular velocity $\vec{\omega}$ at time $t\geq 0$ if it has angular velocity $\vec{\omega}_0$ at $t=0$. As before, $\vec{\omega}$ and $\vec{\omega}_0$ represent components in the principal body-coordinate system S'. $P(\vec{\omega},t;\vec{\omega}_0)$ can be obtained from $P(\vec{\omega},g,t;\vec{\omega}_0,g_0)$ by integrating over all values of g and averaging over g_0. If it is assumed that all initial orientations g_0 are equally probable, so that the probability of g_0 in dg_0 is $dg_0/8\pi^2$, then

$$P(\vec{\omega},t;\vec{\omega}_0)=\int dg\int dg_0\,P(\vec{\omega},g,t;\vec{\omega}_0,g_0)/8\pi^2. \tag{4.1}$$

It follows from definition (2.2) that $D^0_{00}(g)=1$, so that (2.1) gives $\psi^0_{00}(g)=(8\pi^2)^{-1/2}$. Hence the orthogonality relation (2.3) gives

$$\int dg\,\psi^J_{MK}(g)=(8\pi^2)^{1/2}\,\delta_{J0}\delta_{M0}\delta_{K0}\ . \tag{4.2}$$

Therefore, use of expression (3.20) in Eq. (4.1) gives

$$P(\vec{\omega},t;\vec{\omega}_0)=F^0_{00}(\vec{\omega},t;\vec{\omega}_0)\ . \tag{4.3}$$

With $J=0$, Eq. (3.15) for $\underline{F}$ gives

$$\left[\frac{\partial}{\partial t}-\sum_{j=1}^{3}\left(\frac{\partial}{\partial\omega_j}E_j(\vec{\omega})+a_j\frac{\partial^2}{\partial\omega_j^2}\right)\right]P(\vec{\omega},t;\vec{\omega}_0)=0\ , \tag{4.4}$$

and Eq. (3.23) gives

$$\left[\frac{\partial}{\partial t}+\sum_{j=1}^{3}\left(B_jk_j\frac{\partial}{\partial k_j} - ir_jk_j\frac{\partial^2}{\partial k_k\,\partial k_i}+a_jk_j^2\right)\right]G^0_{00}(\vec{k},t;\vec{\omega}_0)=0 \tag{4.5}$$

for the Fourier transform G^0_{00} of F^0_{00}, and hence of $P(\vec{\omega},t;\vec{\omega}_0)$.

It is reasonable to expect that, as $t\to\infty$, $P(\vec{\omega},t;\vec{\omega}_0)$ should approach the Maxwell–Boltzmann expression

$$P_0(\vec{\omega})=C\exp[-(I_1\omega_1^2+I_2\omega_2^2+I_3\omega_3^2)/2k_BT]\ , \tag{4.6}$$

where k_B is the Boltzmann constant, T is the temperature, and C is a normalization constant having the value

$$C=(I_1I_2I_3)^{1/2}/(2\pi k_BT)^{3/2}\ . \tag{4.7}$$

Substitution of $P_0(\vec{\omega})$ into Eq. (4.4) reveals that it is a solution of that equation if

$$a_i=B_ik_BT/I_i\ . \tag{4.8}$$

Hence, if it is required that $P(\vec{\omega},t;\vec{\omega}_0)$ approach $P_0(\vec{\omega})$ as $t\to\infty$, then a_i and B_i must be related by Eq. (4.8). We shall henceforth suppose that relation (4.8) is satisfied.

The solution of Eqs. (4.4) or (4.5) is simple only for the special case of a spherical top, for which $I_1=I_2=I_3\equiv I$. In this case, $r_i\equiv(I_j-I_k)/I_i=0$, so Eq. (4.5) reduces to a linear first-order partial differential equation, which can be solved by standard procedures. The solution which satisfies the initial condition (3.24) is

$$G^0_{00}(\vec{k},t;\vec{\omega}_0)=\exp\left\{-\sum_{j=1}^{3}\left[\left(\frac{k_BT}{2I}\right)k_j^2(1-e^{-2B_jt}) + i\omega_{0j}k_je^{-B_jt}\right]\right\}\ , \tag{4.9}$$

in which the relations (4.8) have been used. It then follows from Eqs. (4.9), (3.22), and (4.3) that[24]

$$P(\vec{\omega},t;\vec{\omega}_0)=\prod_{j=1}^{3}\left(\frac{I}{2\pi k_BT(1-e^{-2B_jt})}\right)^{1/2} \times\exp\left(-\frac{I(\omega_j-\omega_{0j}e^{-B_jt})^2}{2k_BT(1-e^{-2B_jt})}\right). \tag{4.10}$$

It is apparent that the limit of this result as $t\to\infty$ is indeed $P_0(\vec{\omega})$, Eq. (4.6), when $I_1=I_2=I_3\equiv I$.

V. DISTRIBUTION OF ORIENTATION

Let $W(g,t;g_0)\,dg$ be the probability that a body has orientation g within dg at time $t\geq 0$ if the body has orientation g_0 at $t=0$. The conditional probability density $W(g,t;g_0)$ can be obtained from $P(\vec{\omega},g,t;\vec{\omega}_0,g_0)$ by integrating over $\vec{\omega}$ and averaging over $\vec{\omega}_0$ using the Maxwell–Boltzmann distribution $P_0(\vec{\omega}_0)$ for $\vec{\omega}_0$. Thus, using Eq. (3.20),

$$W(g,t;g_0)=\int d^3\omega\int d^3\omega_0 P_0(\vec{\omega}_0)P(\vec{\omega},g,t;\vec{\omega}_0,g_0)$$
$$=\sum_{J=0}^{\infty}\sum_{K,M,N=-J}^{J} w^J_{KN}(t)\psi^{J*}_{MN}(g_0)\psi^J_{MK}(g)\ , \quad (5.1)$$

where

$$w^J_{KN}(t)\equiv\int d^3\omega\int d^3\omega_0 P_0(\vec{\omega}_0)F^J_{KN}(\vec{\omega},t:\vec{\omega}_0)\ , \quad (5.2)$$

and $P_0(\vec{\omega})$ is given by Eq. (4.6).

It is apparent from Eq. (5.2), and from the definition (3.21) of the Fourier-transform matrix $\underline{G}(\vec{k},t;\vec{\omega}_0)$ of $\underline{F}(\vec{\omega},t;\vec{\omega}_0)$, that

$$\underline{w}(t)=\int d^3\omega_0 P_0(\vec{\omega}_0)\underline{G}(0,t;\vec{\omega}_0)\ , \quad (5.3)$$

where $\underline{w}(t)$ is the square matrix of dimension $2J+1$ whose $\overline{KN}$th element is $w^J_{KN}(t)$ for a given J. The relation (5.3) is used in Sec. VI to determine $\underline{w}(t)$, and thus determine $W(g,t;g_0)$.

VI. SPHERICAL BODY

In this section we consider the determination of the distribution of orientation $W(g,t;g_0)$ for a body for which $I_1=I_2=I_3\equiv I$. In this case, $r_i\equiv(I_j-I_k)/I_i=0$, so that Eq. (3.21) reduces to a first-order partial differential equation for the Fourier-transform matrix $\underline{G}(\vec{k},t;\vec{\omega}_0)$, which is a considerable simplification. We shall also suppose that the friction constants about the three principal axes are equal: $B_1=B_2=B_3=B$. The calculations can be carried out without assuming the B_i's are equal, but it seems likely on physical grounds that in most cases in which the I_i's are equal, the B_i's will also be equal. Furthermore, if the B_i's are equal, the equations can be written concisely by use of vector notation. In particular, Eq. (3.15) for $\underline{F}$ can be written

$$\left(\frac{\partial}{\partial t}+i\vec{\omega}\cdot\underline{\vec{J}}-3B-B\vec{\omega}\cdot\nabla_\omega-B\alpha\nabla_\omega{}^2\right)\underline{F}(\vec{\omega},t;\vec{\omega}_0)=\underline{0}\ , \quad (6.1)$$

where $\underline{\vec{J}}$ is the vector whose components are the matrices $\underline{J}_1$, $\underline{J}_2$, and $\underline{J}_3$;

$$\vec{\omega}\equiv(\omega_1,\omega_2,\omega_3)\ ;\ \nabla_\omega\equiv(\partial/\partial\omega_1,\partial/\partial\omega_2,\partial/\partial\omega_3)\ ;$$

and

$$\alpha\equiv k_BT/I\ . \quad (6.2)$$

Similarly, Eq. (3.23) becomes

$$\left(\frac{\partial}{\partial t}-\underline{\vec{J}}\cdot\nabla_k+B\vec{k}\cdot\nabla_k+B\alpha k^2\right)\underline{G}(\vec{k},t;\vec{\omega}_0)=\underline{0}\ . \quad (6.3)$$

Equations (6.1) and (6.3) are still quite complicated. Since they are matrix equations, each represents a system of coupled partial differential equations. Even for the simplest special case of a spherical body we have been unable to obtain an exact solution in closed form of either Eq. (6.1) or (6.3). However, we derive below two iterative solutions, one of which provides a good approximation for small values of B, and the other of which provides a good approximation for large values of B. But first, for purposes of later reference and to develop some useful techniques, we consider the case of a free spherical body.

A. Free Spherical Body

If a spherical body experiences no interactions with its surroundings, then $B=0$ in Eqs. (6.1) and (6.3), so that

$$\left(\frac{\partial}{\partial t}+i\vec{\omega}\cdot\underline{\vec{J}}\right)\underline{F}(\vec{\omega},t;\vec{\omega}_0)=\underline{0} \quad (6.4)$$

and

$$\left(\frac{\partial}{\partial t}-\underline{\vec{J}}\cdot\nabla_k\right)\underline{G}(\vec{k},t;\vec{\omega}_0)=\underline{0}\ . \quad (6.5)$$

The solution of Eq. (6.4) that satisfies the initial condition (3.19) is obviously

$$\underline{F}(\vec{\omega},t;\vec{\omega}_0)=e^{-i\vec{\omega}_0\cdot\underline{\vec{J}}t}\,\delta(\vec{\omega}-\vec{\omega}_0)\ , \quad (6.6)$$

so that, from (4.3) and (6.6), $P(\vec{\omega},t;\vec{\omega}_0)=\delta(\vec{\omega}-\vec{\omega}_0)$, as expected. The Fourier transform (3.21) of expression (6.6) is

$$\underline{G}(\vec{k},t;\vec{\omega}_0)=e^{-i\vec{k}\cdot\vec{\omega}_0}e^{-i\vec{\omega}_0\cdot\underline{\vec{J}}t}\ . \quad (6.7)$$

It is easily verified that expression (6.7) is the solution of Eq. (6.5) which satisfies initial condition (3.24).

Substitution of (6.7) in Eq. (5.3) gives

$$\underline{w}(t)=\int d^3\omega\,P_0(\omega)e^{-i\vec{\omega}\cdot\underline{\vec{J}}t}\ , \quad (6.8)$$

where we have omitted the subscript on the variable of integration $\vec{\omega}_0$, and have used the fact that $P_0(\vec{\omega})=P_0(\omega)$ for a spherical body.

In order to evaluate the integral in (6.8), it is useful to introduce the spherical coordinates ω, θ, ϕ of $\vec{\omega}$. It is shown in Appendix B that, as a consequence of the commutation relations satisfied by the matrices $\underline{J}_1$, $\underline{J}_2$, $\underline{J}_3$,

$$e^{-i\vec{\omega}\cdot\underline{\vec{J}}t}=e^{i\phi\underline{J}_3}e^{i\theta\underline{J}_2}e^{-i\omega t\underline{J}_3}e^{-i\theta\underline{J}_2}e^{-i\phi\underline{J}_3}\ . \quad (6.9)$$

Since $\underline{J}_3$ is the diagonal matrix (3.11), then $(e^{i\phi\underline{J}_3})_{KL}=\delta_{KL}e^{i\phi K}$, so use of (6.9) in (6.8) gives for the KN matrix element

$$w^J_{KN}(t)=\sum_{L=-J}^{J}\int_0^{2\pi}e^{i\phi(K-N)}\,d\phi\int_0^{\pi}(e^{i\theta\underline{J}_2})_{KL}(e^{-i\theta\underline{J}_2})_{LN}\times\sin\theta\,d\theta\,I^0_L(t)/4\pi$$
$$=\tfrac{1}{2}\,\delta_{KN}\sum_{L=-J}^{J}\int_0^{\pi}(e^{i\theta\underline{J}_2})_{KL}(e^{-i\theta\underline{J}_2})_{LK}\sin\theta\,d\theta\,I^0_L(t)\ , \quad (6.10)$$

where

$$I^0_L(t)=4\pi\int_0^{\infty}d\omega\,\omega^2P_0(\omega)e^{-i\omega tL}\ . \quad (6.11)$$

This integral can be evaluated in a straighforward manner, using for $P_0(\omega)$ expression (4.6) with $I_1=I_2=I_3=I$. The result is

$$I_L^0(t)=[1-L^2\alpha t^2-iLt(8\alpha/\pi)^{1/2}]e^{-L^2\alpha t^2/2} . \tag{6.12}$$

It follows from definition (3.2) that

$$D^j_{m'm}(g)=e^{-i\alpha m'}d^j_{m'm}(\beta)e^{-im\gamma} , \tag{6.13}$$

where

$$d^j_{m'm}(\beta)\equiv\langle jm'|e^{-i\beta J_y}|jm\rangle . \tag{6.14}$$

Definition (3.1) and orthogonality relation (3.3) then give

$$\int_0^\pi d^J_{KL}(\beta)\,d^{J'*}_{KL}(\beta)\sin\beta\,d\beta=\delta_{JJ'}[2/(2J+1)] . \tag{6.15}$$

Because the matrix $\underline{J}_2$ is opposite in sign to the corresponding matrix of the component J_y in the laboratory coordinate system, it follows from (6.14) that

$$(e^{i\theta\underline{J}_2})_{KL}=d^J_{KL}(\theta) . \tag{6.16}$$

Since $\underline{J}_2$ is Hermitian,

$$(e^{-i\theta\underline{J}_2})_{LK}=(e^{i\theta\underline{J}_2})^*_{KL}=d^{J*}_{KL}(\theta) . \tag{6.17}$$

Use of Eqs. (6.15)–(6.17) gives for the integral over θ in Eq. (6.10) the value $2/(2J+1)$. Using also (6.12), Eq. (6.10) then gives

$$w^J_{KN}(t)=\delta_{KN}(2J+1)^{-1}\sum_{L=-J}^{J}(1-L^2\alpha t^2)e^{-L^2\alpha t^2/2} . \tag{6.18}$$

This result and Eq. (5.1) give the conditional probability density for the orientation of a free spherical body.

B. Weak Interactions

It is useful to introduce dimensionless variables $\vec{p}$, s, and $\vec{\omega}_1$ defined by

$$\vec{p}\equiv\alpha^{1/2}\vec{k} ,\quad s\equiv\alpha^{1/2}t ,\quad \vec{\omega}_1\equiv\vec{\omega}_0/\alpha^{1/2} . \tag{6.19}$$

Equation (6.3) in terms of these variables is

$$\left(\frac{\partial}{\partial s}-\vec{\underline{J}}\cdot\nabla_p+b\vec{p}\cdot\nabla_p+bp^2\right)\underline{U}(\vec{p},s;\vec{\omega}_1)=\underline{0} , \tag{6.20}$$

where

$$\underline{U}(\vec{p},s;\vec{\omega}_1)\equiv\underline{G}(\vec{k},t;\vec{\omega}_0) \tag{6.21}$$

and

$$b\equiv B/\alpha^{1/2}=B(I/k_BT)^{1/2} . \tag{6.22}$$

The initial condition (3.24) gives

$$\underline{U}(\vec{p},0;\vec{\omega}_1)=e^{-i\vec{p}\cdot\vec{\omega}_1}\underline{I} . \tag{6.23}$$

We now seek a solution of Eqs. (6.20) and (6.23) which is valid for small values of the dimensionless parameter b. Let

$$\underline{U}(\vec{p},s;\vec{\omega}_1)\equiv\underline{U}_0(\vec{p},s;\vec{\omega}_1)e^{\underline{H}(\vec{p},s;\vec{\omega}_1)} , \tag{6.24}$$

where $\underline{U}_0(\vec{p},s;\vec{\omega}_1)$ is the solution of Eq. (6.20) when $b=0$ which satisfies the initial condition (6.23):

$$\underline{U}_0(\vec{p},s;\vec{\omega}_1)=e^{-i\vec{p}\cdot\vec{\omega}_1-i\vec{\omega}_1\cdot\vec{\underline{J}}s} . \tag{6.25}$$

Substitution of (6.24) in (6.20), followed by multiplication on the left-hand side by $\underline{U}_0^{-1}$, results in the following equation for $e^{\underline{H}(\vec{p},s;\vec{\omega}_1)}$:

$$\left(\frac{\partial}{\partial s}-\vec{\underline{J}}(s)\cdot\nabla_p-bi\vec{\omega}_1\cdot\vec{p}+b\vec{p}\cdot\nabla_p+bp^2\right)e^{\underline{H}}=0 , \tag{6.26}$$

where

$$\vec{\underline{J}}(s)\equiv\underline{U}_0^{-1}\vec{\underline{J}}\,\underline{U}_0=e^{i\vec{\omega}_1\cdot\vec{\underline{J}}s}\vec{\underline{J}}e^{-i\vec{\omega}_1\cdot\vec{\underline{J}}s} . \tag{6.27}$$

Since $e^{\underline{H}}=\underline{I}$ if $b=0$, $\underline{H}$ has the following form as a power series in b:

$$\underline{H}(\vec{p},s;\vec{\omega}_1)=\sum_{n=1}^{\infty}b^n\underline{R}_n(\vec{p},s;\vec{\omega}_1) . \tag{6.28}$$

Since it must be that $\underline{H}(\vec{p},0;\vec{\omega}_1)=\underline{0}$, it follows that

$$\underline{R}_n(\vec{p},0;\vec{\omega}_1)=\underline{0} . \tag{6.29}$$

An expression for the derivative of an exponential operator or matrix is[25]

$$\frac{\partial}{\partial s}e^{\underline{H}}=\int_0^1 dx\,e^{x\underline{H}}\left(\frac{\partial\underline{H}}{\partial s}\right)e^{-x\underline{H}}e^{\underline{H}} . \tag{6.30}$$

Hence, from Eq. (6.28) for $\underline{H}$,

$$\frac{\partial}{\partial s}e^{\underline{H}}=\sum_{n=1}^{\infty}b^n\int_0^1 dx\,e^{x\underline{H}}\frac{\partial\underline{R}_n}{\partial s}e^{-x\underline{H}}e^{\underline{H}} . \tag{6.31}$$

The familiar expansion of $e^{x\underline{H}}\underline{Q}e^{-x\underline{H}}$ in powers of x can be written[26]

$$e^{x\underline{H}}\underline{Q}e^{-x\underline{H}}=\sum_{j=0}^{\infty}x^j(j!)^{-1}\{\underline{H}^j,\underline{Q}\} , \tag{6.32}$$

where the repeated commutator bracket is defined by

$$\{\underline{H}^0,\underline{Q}\}\equiv\underline{Q} ,\quad \{\underline{H}^{n+1},\underline{Q}\}\equiv[\underline{H},\{\underline{H}^n,\underline{Q}\}] . \tag{6.33}$$

If expression (6.32) with $\underline{Q}=\partial\underline{R}_n/\partial s$ is used in Eq. (6.31), and the integral over x is performed, one obtains

$$\begin{aligned}\frac{\partial}{\partial s}e^{\underline{H}}&=\sum_{n=1}^{\infty}b^n\sum_{j=0}^{\infty}\frac{1}{(j+1)!}\left\{\left(\sum_{m=1}^{\infty}b^m\underline{R}_m\right)^j,\ \frac{\partial}{\partial s}\underline{R}_n\right\}e^{\underline{H}}\\&=\Bigg[b\frac{\partial\underline{R}_1}{\partial s}+b^2\left(\frac{\partial\underline{R}_2}{\partial s}+\frac{1}{2}\left[\underline{R}_1,\ \frac{\partial\underline{R}_1}{\partial s}\right]\right)\\&\quad+b^3\left(\frac{\partial\underline{R}_3}{\partial s}+\frac{1}{2}\left[\underline{R}_2,\ \frac{\partial\underline{R}_1}{\partial s}\right]+\frac{1}{2}\left[\underline{R}_1,\frac{\partial\underline{R}_2}{\partial s}\right]\right.\\&\quad\left.+\frac{1}{6}\left[\underline{R}_1,\left[\underline{R}_1,\ \frac{\partial\underline{R}_1}{\partial s}\right]\right]\right)+O(b^4)\Bigg]e^{\underline{H}} .\end{aligned} \tag{6.34}$$

There is a similar expression for $\nabla_pe^{\underline{H}}$ given by Eq. (6.34) with $\partial/\partial s$ replaced everywhere by ∇_p. If this expression and Eq. (6.34) are used in Eq. (6.26), and the equation is then multiplied on the right-hand side by $e^{-\underline{H}}$, the resulting equation is a power series in b equal to zero, so the coefficient of each power of b must be zero. The requirement that the coefficients of the first two powers of b be zero gives the following equations:

$$\frac{\partial \underline{R}_1}{\partial s} - \underline{\vec{J}}(s)\cdot \nabla_p \underline{R}_1 = (i\vec{\omega}_1\cdot\vec{p} - p^2)\underline{I} \ , \tag{6.35a}$$

$$\frac{\partial \underline{R}_2}{\partial s} - \underline{\vec{J}}(s)\cdot \nabla_p \underline{R}_2 = \frac{1}{2}\left[\frac{\partial \underline{R}_1}{\partial s}, \underline{R}_1\right] + \tfrac{1}{2}\underline{\vec{J}}(s)\cdot[\underline{R}_1, \nabla_p \underline{R}_1] - \vec{p}\cdot\nabla_p\underline{R}_1 \ . \tag{6.35b}$$

In order to solve Eq. (6.35a), let

$$\underline{R}_1(\vec{p}, s; \vec{\omega}_1) = \underline{I}(i\vec{\omega}_1\cdot\vec{p} - p^2)s + \underline{e}(\vec{p}, s; \vec{\omega}_1) \ . \tag{6.36}$$

Substitution of this expression into Eq. (6.35a) reveals that it is a solution of that equation if the matrix $\underline{e}(\vec{p}, s; \vec{\omega}_1)$ satisfies

$$\frac{\partial \underline{e}}{\partial s} - \underline{\vec{J}}(s)\cdot\nabla_p\underline{e} = (i\vec{\omega}_1 - 2\vec{p})\cdot\underline{\vec{J}}(s)s \ . \tag{6.37}$$

Let

$$\underline{e}(\vec{p}, s; \vec{\omega}_1) = (i\vec{\omega}_1 - 2\vec{p})\cdot\underline{\vec{V}}(s) + \underline{g}(s, \vec{\omega}_1) \ , \tag{6.38}$$

where

$$\underline{\vec{V}}(s) \equiv \int_0^s ds'\,\underline{\vec{J}}(s')s' \ . \tag{6.39}$$

Expression (6.38) is a solution of Eq. (6.37) if

$$\frac{\partial \underline{g}}{\partial s} - \underline{\vec{J}}(s)\cdot\nabla_p\underline{g} = -2\underline{\vec{J}}(s)\cdot\underline{\vec{V}}(s) \ . \tag{6.40}$$

The solution of Eq. (6.40) which satisfies $\underline{g}(0, \vec{\omega}_1) = \underline{0}$ is clearly

$$\underline{g}(s, \vec{\omega}_1) = -2\int_0^s ds'\,\underline{\vec{J}}(s')\cdot\underline{\vec{V}}(s') \ . \tag{6.41}$$

Therefore, the solution of Eq. (6.35a) satisfying the initial condition $\underline{R}_1(\vec{p}, 0; \vec{\omega}_1) = \underline{0}$ is

$$\underline{R}_1(\vec{p}, s; \vec{\omega}_1) = \underline{I}(i\vec{\omega}_1\cdot\vec{p} - p^2)s + (i\vec{\omega}_1 - 2\vec{p})\cdot\underline{\vec{V}}(s) + \underline{g}(s, \vec{\omega}_1) \ , \tag{6.42}$$

where $\underline{\vec{V}}(s)$ is given by (6.39) and $\underline{g}(s, \vec{\omega}_1)$ is given by (6.41).

It is shown in Appendix C that, as a consequence of definition (6.27) and the commutation relations $\underline{\vec{J}}\times\underline{\vec{J}} = -i\underline{\vec{J}}$, $\underline{\vec{J}}(s)$ can be expressed as

$$\underline{\vec{J}}(s) = \underline{\vec{J}} - [\underline{\vec{J}} - \hat{n}(\hat{n}\cdot\underline{\vec{J}})](1 - \cos\omega_1 s) - (\hat{n}\times\underline{\vec{J}})\sin\omega_1 s \ , \tag{6.43}$$

where $\hat{n} \equiv \vec{\omega}_1/\omega_1$. By use of (6.43), the integrals in (6.39) and (6.41) can be evaluated, with the results

$$\underline{\vec{V}}(s) = \tfrac{1}{2}\underline{\vec{J}}s^2 - [\underline{\vec{J}} - \hat{n}(\hat{n}\cdot\underline{\vec{J}})] \times[\tfrac{1}{2}s^2 + \omega_1^{-2}(1 - \cos\omega_1 s - \omega_1 s\sin\omega_1 s)] + (\hat{n}\times\underline{\vec{J}})\omega_1^{-2}(\omega_1 s\cos\omega_1 s - \sin\omega_1 s) \tag{6.44}$$

and

$$\underline{g}(s, \vec{\omega}_1) = -2\{\tfrac{1}{6}(\hat{n}\cdot\underline{\vec{J}})^2 s^3 + [\underline{\vec{J}}^2 - (\hat{n}\cdot\underline{\vec{J}})^2]\omega_1^{-3}(\omega_1 s - \sin\omega_1 s) + i(\hat{n}\cdot\underline{\vec{J}})\omega_1^{-3}(\tfrac{1}{2}\omega_1^2 s^2 + \cos\omega_1 s - 1)\} \ . \tag{6.45}$$

Equation (6.35b) can be solved for $\underline{R}_2(\vec{p}, s; \vec{\omega}_1)$ in a manner similar to the calculation of $\underline{R}_1$, but the calculation and the result are complicated, and will not be presented here.

If the number b defined by Eq. (6.22) is small, it is plausible to expect that (6.24) is obtained to good approximation by retaining only the first term in (6.28), which gives

$$\underline{U}(\vec{p}, s; \vec{\omega}_1) = \underline{U}_0(\vec{p}, s; \vec{\omega}_1)\,e^{b\underline{R}_1(\vec{p}, s; \vec{\omega}_1)} \ . \tag{6.46}$$

It will be assumed that this expression is valid for small values of b, and it will be used to calculate this distribution of orientation of a spherical body.

From Eqs. (6.46), (6.25), (6.42), and (6.44), it follows that

$$\underline{U}(0, s; \vec{\omega}_1) = \exp\{-i\omega_1\hat{n}\cdot\underline{\vec{J}}s + b[\tfrac{1}{2}i\omega_1\hat{n}\cdot\underline{\vec{J}}s^2 + \underline{g}(s, \vec{\omega}_1)]\} \ . \tag{6.47}$$

From (5.3), (4.6), and (6.19),

$$w_{KN}^J(t) = (2\pi)^{-3/2}\int d^3\omega_1\,e^{-\omega_1^2/2}\,U_{KN}(0, s; \vec{\omega}_1) \ , \tag{6.48}$$

where U_{KN} is the KNth matrix element of $\underline{U}$ and $s = \alpha^{1/2}t$. It is convenient to use the spherical coordinates ω_1, θ, ϕ of $\vec{\omega}_1$ as variables of integration in (6.48). If (6.45) is used in (6.47), the result substituted in (6.48), and (6.9) employed, the integrals over the angles θ and ϕ can be evaluated as in (6.10) and (6.15), giving

$$w_{KN}^J(t) = \delta_{KN}(2J+1)^{-1}\sum_{L=-J}^{J} I_L(t) \ , \tag{6.49}$$

where

$$I_L(t) = (2/\pi)^{1/2}\int_0^\infty d\omega\,\omega^2 e^{-(\omega^2/2) - iL\omega s} \times\exp(-2b\{J(J+1)\omega^{-3}(\omega s - \sin\omega s) + L^2[\tfrac{1}{6}s^3 - \omega^{-3}(\omega s - \sin\omega s)] + iL[\omega^{-3}(\tfrac{1}{2}\omega^2 s^2 + \cos\omega s - 1) - \tfrac{1}{4}\omega s^2]\}) \ . \tag{6.50}$$

When $b = 0$, $I_L(t)$ reduces to the $I_L^0(t)$ of Eqs. (6.11) and (6.12).

Consider (6.50) for $L = 0$:

$$I_0(t) = (2/\pi)^{1/2}\int_0^\infty d\omega\,\omega^2 e^{-\omega^2/2} \times\exp[-2bJ(J+1)\omega^{-3}(\omega s - \sin\omega s)] \ . \tag{6.51}$$

The behavior of the integrands of both (6.50) and (6.51) is determined primarily by $\omega^2 e^{-\omega^2/2}$, which increases from zero at $\omega = 0$ to a maximum of $2/e$ at $\omega = 2^{1/2}$, and then decays rapidly as ω increases. As a consequence, the entire integrands have appreciable values only for $0 \leq \omega \lesssim 1$. Thus, if $s \ll 1$, the approximation $\omega s - \sin\omega s \approx \frac{1}{6}(\omega s)^3$ can be used in the integrand of (6.51), with the result

$$I_0(t) = e^{-bJ(J+1)s^3/3} . \tag{6.52}$$

But this approximation is not very useful since it does not show how $I_0(s)$ decays as s becomes large, because it is valid only for $s \ll 1$, and because also we are considering $b \ll 1$.

A more useful approximation can be obtained as follows. The integral $I_0^{(1)}(t)$ obtained by omitting $\sin\omega s$ in the integrand of (6.51) can be evaluated exactly, with the result[27]

$$I_0^{(1)}(t) = \{1 + 2[bJ(J+1)s]^{1/2}\} \exp\{-2[bJ(J+1)s]^{1/2}\} . \tag{6.53}$$

From the definitions it is apparent that $I_0^{(1)}(0) = 1 = I_0(0)$. Since $\omega s - \sin\omega s \approx \omega s$ for $\omega s \gg 1$, or saying it another way $\omega s - \sin\omega s \sim \omega s$ as $s \to \infty$ if $\omega \neq 0$, and since the integrand of $I_0(t)$ is zero at $\omega = 0$ because of the factor ω^2, it can be expected that $I_0^{(1)}(t)$ is a good approximation to $I_0(t)$ for large values of s, as well as agreeing exactly at $t = 0$. Hence, we shall approximate $I_0(t)$ by $I_0^{(1)}(t)$.

Now consider $I_L(t)$ for $L \neq 0$. If $b = 0$, Eq. (6.50) for $I_L(t)$ reduces to Eq. (6.11) for $I_L^0(t)$. According to (6.12), $I_L^0(t)$ decays in a time $s \equiv \alpha^{1/2} t \approx 1$ if $L \neq 0$. But for $0 \leq s \lesssim 1$, the factor involving b in the integrand of (6.50) is approximately unity if $bJ(J+1) \ll 1$. Thus, if $bJ(J+1) \ll 1$, and if $L \neq 0$, $I_L(t)$ decays in approximately the same manner as $I_L^0(t)$.

Therefore, if $I_L^0(t)$ is used for $I_L(t)$ when $L \neq 0$, and (6.53) is used for $I_0(t)$, Eq. (6.49) becomes

$$w_{KN}^J(t) = \delta_{KN}(2J+1)^{-1}\Big(\{1 + 2[bJ(J+1)s]^{1/2}\} \times \exp\{-2[bJ(J+1)s]^{1/2}\} + 2\sum_{L=1}^{J}(1 - L^2 s^2)\, e^{-L^2 s^2/2}\Big), \tag{6.54}$$

where $s \equiv \alpha^{1/2} t$. Expression (6.54) can be expected to be a good approximation if $bJ(J+1) \ll 1$.

C. Strong Interactions

It is useful to introduce dimensionless variables

$$\vec{q} \equiv B\vec{k} e^{-Bt} , \quad \tau \equiv Bt . \tag{6.55}$$

Since $\partial/\partial t = B\partial/\partial\tau - B\vec{q} \cdot \nabla_q$ and $\nabla_k = Be^{-\tau}\nabla_q$, Eq. (6.3) gives

$$\left(\frac{\partial}{\partial\tau} - e^{-\tau}\underline{\vec{J}} \cdot \nabla_q + Aq^2 e^{2\tau}\right)\underline{X}(\vec{q}, \tau; \vec{\omega}_0) = \underline{0} , \tag{6.56}$$

where

$$\underline{X}(\vec{q}, \tau; \vec{\omega}_0) \equiv \underline{G}(\vec{k}, t; \vec{\omega}_0) \tag{6.57}$$

and

$$A \equiv \alpha/B^2 = (k_B T/IB^2) = 1/b^2 . \tag{6.58}$$

The primary objective of this paper is the calculation of the orientation distribution. Thus it follows from (5.3) that it is sufficient to calculate

$$\int d^3\omega_0 P_0(\omega_0)\underline{G}(\vec{k}, t; \vec{\omega}_0) = \int d^3\omega_0 P_0(\omega_0)\underline{X}(\vec{q}, \tau; \vec{\omega}_0) \equiv e^{-Aq^2 e^{2\tau}/2}\, \underline{Z}(\vec{q}, \tau) , \tag{6.59}$$

since, from (5.3), $\underline{w}(t) = \underline{Z}(0, Bt)$.

If Eq. (6.56) is multiplied by $P_0(\omega_0)$ and integrated over $d^3\omega_0$, one obtains the following equation for the matrix $\underline{Z}(\vec{q}, \tau)$ defined by (6.59):

$$\left(\frac{\partial}{\partial\tau} - e^{-\tau}\underline{\vec{J}} \cdot \nabla_q + Ae^{\tau}\vec{q} \cdot \underline{\vec{J}}\right)\underline{Z}(\vec{q}, \tau) = \underline{0} . \tag{6.60}$$

From (3.24), (4.6), (6.57), and (6.59), it follows that

$$\underline{Z}(\vec{q}, 0) = \underline{I} . \tag{6.61}$$

We now seek a solution of Eqs. (6.60) and (6.61) in the form

$$\underline{Z}(\vec{q}, \tau) = \exp\left(\sum_{n=1}^{\infty} A^n \underline{S}_n(\vec{q}, \tau)\right) . \tag{6.62}$$

The sum in (6.33) begins with $n = 1$, since it is apparent that, if $A = 0$, the solution of (6.60) and (6.61) is $\underline{Z} = \underline{I}$. In view of initial condition (6.61),

$$\underline{S}_n(\vec{q}, 0) = \underline{0} . \tag{6.63}$$

Equations for the matrices $\underline{S}_n(\vec{q}, \tau)$ can be derived by the same procedure used to obtain Eqs. (6.35). The equations governing the first three $\underline{R}_n$ are

$$\frac{\partial\underline{S}_1}{\partial\tau} - e^{-\tau}\underline{\vec{J}} \cdot \nabla_q \underline{S}_1 = -e^{\tau}\vec{q} \cdot \underline{\vec{J}} , \tag{6.64a}$$

$$\frac{\partial\underline{S}_2}{\partial\tau} - e^{-\tau}\underline{\vec{J}} \cdot \nabla_q \underline{S}_2 = \frac{1}{2}\left[\frac{\partial\underline{S}_1}{\partial\tau}, \underline{S}_1\right] + \tfrac{1}{2}e^{-\tau}\underline{\vec{J}} \cdot [\underline{S}_1, \nabla_q\underline{S}_1] , \tag{6.64b}$$

$$\frac{\partial\underline{S}_3}{\partial\tau} - e^{-\tau}\underline{\vec{J}} \cdot \nabla_q\underline{S}_3 = \frac{1}{2}\left[\frac{\partial\underline{S}_1}{\partial\tau}, \underline{S}_2\right] + \frac{1}{2}\left[\frac{\partial\underline{S}_2}{\partial\tau}, \underline{S}_1\right] + \frac{1}{6}\left[\underline{S}_1, \left[\frac{\partial\underline{S}_1}{\partial\tau}, \underline{S}_1\right]\right] + e^{-\tau}\underline{\vec{J}} \cdot \{\tfrac{1}{2}[\underline{S}_2, \nabla_q\underline{S}_1] + \tfrac{1}{2}[\underline{S}_1, \nabla_q\underline{S}_2] + \tfrac{1}{6}[\underline{S}_1, [\underline{S}_1, \nabla_q\underline{S}_1]]\} . \tag{6.64c}$$

These equations can be solved by the same procedure used to solve Eq. (6.35a). The results are

$$\underline{S}_1(\vec{q}, \tau) = \vec{q} \cdot \underline{\vec{J}} h_{11}(\tau) - J(J+1)h_{10}(\tau)\underline{I} , \tag{6.65}$$

where

$$h_{11}(\tau) \equiv (1 - e^{\tau}) , \quad h_{10}(\tau) \equiv (\tau + e^{-\tau} - 1) ; \tag{6.66}$$

$$\underline{S}_2(\vec{q}, \tau) = \vec{q} \cdot \underline{\vec{J}} h_{21}(\tau) - J(J+1)h_{20}(\tau)\underline{I} , \tag{6.67}$$

where

$$h_{21}(\tau) \equiv -\tfrac{1}{2}(e^{\tau} - 2\tau - e^{-\tau}), \tag{6.68}$$

$$h_{20}(\tau) \equiv \tfrac{1}{4}[2\tau - 5 + 4(\tau+1)e^{-\tau} + e^{-2\tau}]; \tag{6.69}$$

$$\underline{S}_3(\vec{q}, \tau) = -J(J+1)h_{30}(\tau)\underline{I} + \vec{q}\cdot\vec{\underline{J}}h_{31}(\tau) + h_{32}(\tau)[J(J+1)q^2\underline{I} - (\vec{q}\cdot\vec{\underline{J}})^2], \tag{6.70}$$

where

$$h_{30}(\tau) \equiv \tfrac{1}{36}[21\tau - 76 + (18\tau^2 + 72\tau + 36)e^{-\tau} + 36e^{-2\tau} + 4e^{-3\tau}], \tag{6.71}$$

$$h_{31}(\tau) \equiv -\tfrac{1}{12}[7e^{\tau} - 6\tau^2 - 12\tau + 12 - (18\tau + 15)e^{-\tau} - 4e^{-2\tau}], \tag{6.72}$$

$$h_{32}(\tau) \equiv -\tfrac{1}{12}[e^{2\tau} - 6e^{\tau} + 6\tau + 3 + 2e^{-\tau}]. \tag{6.73}$$

Since from (5.3), $\underline{w}(t) = \underline{Z}(0, Bt)$, it follows from (6.62) and (6.65)–(6.73) that

$$\underline{w}(t) = \exp\Big(\sum_{n=1}^{\infty} A^n \underline{S}_n(0, Bt)\Big) = \underline{I}\exp\{-J(J+1)[Ah_{10}(Bt) + A^2h_{20}(Bt) + A^3h_{30}(Bt)] + O(A^4)\}. \tag{6.74}$$

It appears from expressions (6.66) for $h_{10}(\tau)$, (6.69) for $h_{20}(\tau)$, and (6.71) for $h_{30}(\tau)$, that the series in the exponent of (6.74) converges rapidly if $A \ll 1$. In this case, $\underline{w}(t)$ is obtained to good approximation by retaining just the first term in the exponent of (6.74):

$$\underline{w}(t) = \underline{I}\exp[-J(J+1)A(Bt + e^{-Bt} - 1)] \quad \text{if } A \ll 1. \tag{6.75}$$

If expression (6.75) is used in Eq. (5.1) for the conditional probability density for orientation, one obtains the same time dependence previously given by Steele for the case of a spherical body with equal principal moments of inertia and equal frictional constants about the three principal axes.[28] It is clear from the present derivation that this result is correct only if $A \ll 1$.

If, in addition to $A \ll 1$, it is also the case that $J(J+1)A \ll 1$, then it follows from (6.75) that, to good approximation,

$$\underline{w}(t) = \underline{I}\, e^{-J(J+1)ABt} \quad \text{if } J(J+1)A \ll 1. \tag{6.76}$$

Expression (6.76) is the result obtained in theories of rotational diffusion of a spherical body.[5–10] The present derivation shows that such theories are valid only if $J(J+1)A \ll 1$.

Since Steele discusses the limit of expression (6.75) as $B \to 0$,[29] it is of some interest to consider the behavior of the more general result (6.74) as $B \to 0$. It can be shown from expressions (6.66), (6.69), and (6.71) that

$$h_{10}(\tau) = \tfrac{1}{2}\tau^2 + O(\tau^3), \tag{6.77}$$

$$h_{20}(\tau) = \tfrac{1}{24}\tau^4 + O(\tau^5), \tag{6.78}$$

$$h_{30}(\tau) = \tfrac{1}{144}\tau^6 + O(\tau^7). \tag{6.79}$$

Since $A \equiv \alpha/B^2$ and $\tau \equiv Bt$, it then follows that the limit of expression (6.74) for $\underline{w}(t)$ as $B \to 0$ is

$$\underline{w}(t) = \underline{I}\exp\{-J(J+1)[\tfrac{1}{2}(\alpha t^2) + \tfrac{1}{24}(\alpha t^2)^2 + \tfrac{1}{144}(\alpha t^2)^3]\cdots\}. \tag{6.80}$$

From the manner in which the $\underline{S}_n(\vec{q}, \tau)$ in (6.62) are calculated, it is apparent that the omitted terms in the exponent in (6.80) will involve t^n where $n \geq 8$.

The exact expression for $\underline{w}(t)$ for a free body ($B=0$), Eq. (6.18), approaches $\underline{w}(t) = \underline{I}(2J+1)^{-1}$ as $t \to \infty$. But expression (6.80) apparently approaches zero as $t \to \infty$. Thus (6.80) cannot be correct for large values of t, presumably because the series in the exponent does not then converge.

On the other hand, the omitted terms in the exponent of (6.80) are of order $(\alpha t^2)^4$. Hence, the expansion of (6.80) itself (not the exponent) to third power in (αt^2) can be obtained by using just the terms in the exponent to $O((\alpha t^2)^3)$. It can be shown that the expansion of (6.80) obtained in this manner agrees with the expansion of the exact expression (6.18) for a free body to the third power in (αt^2).

Thus, while the exponent in (6.74) is finite as $B \to 0$, the resulting expression is not correct except for small values of t. However, as we have noted above, Eqs. (6.74) and (6.75) appear to provide a good approximation for all $t \geq 0$ if B is sufficiently large that $A \equiv \alpha/B^2 \ll 1$.

VII. CORRELATION FUNCTIONS

The results obtained above can be used to calculate time-dependent correlation functions of functions of the orientation of a body. The functions that occur in practice can be expressed as linear combinations of irreducible spherical tensors, so it is sufficient to calculate the correlation function of two such tensors. A spherical tensor of rank k has $2k+1$ components T_{km}, where $m = -k, -k+1, \ldots, k$. The tensors considered here have the property $T^*_{km} = (-1)^m T_{k,-m}$. As before, suppose that S' is a principal body-coordinate system whose Euler angles with respect to the laboratory coordinate system S are $g \equiv (\alpha\beta\gamma)$. Components T_{km} in S are related to components T'_{kn} in S' by[30]

$$T_{km} = \sum_{n=-k}^{k} D^{k\,*}_{mn}(g)\, T'_{kn}. \tag{7.1}$$

We consider here spherical tensors that depend on the orientation of a body, but not on its angular velocity. In this case, the components T'_{kn} in the body system are constant, and the time dependence of the components T_{km} in the laboratory system is due to the time dependence of the Euler angles. The correlation function of two such tensors, say T_{km} and $S_{k'm'}$, is then

$$\langle T^*_{km}(t)\, S_{k'm'}(0)\rangle = \sum_{n=-k}^{k} \sum_{n'=-k'}^{k'} \langle D^k_{mn}(g(t))\, D^{k'*}_{m'n'}(g(0))\rangle\, T'^*_{kn} S'_{k'n'} \; . \tag{7.2}$$

The joint probability density that a body has orientation g at t and orientation g_0 at the earlier time $t=0$ is $W(g,t;g_0)/8\pi^2$, where $W(g,t;g_0)$ is the conditional probability density discussed in Sec. V, and $1/8\pi^2$ is the probability density for g_0, assuming that initially all orientations are equally probable. Hence, for $t\geq 0$,

$$\langle D^k_{mn}(g(t))\, D^{k'*}_{m'n'}(g(0))\rangle = \int dg \int dg_0\, D^k_{mn}(g)\, D^{k'*}_{m'n'}(g_0)\, W(g,t;g_0)/8\pi^2 \; . \tag{7.3}$$

If expression (5.1) is used, and also definition (3.1), the integrals over dg and dg_0 in (7.3) can be performed by use of (3.3), with the result

$$\langle D^k_{mn}(g(t))\, D^{k'*}_{m'n'}(g(0))\rangle = \delta_{k'k}\delta_{m'm} w^k_{nn'}(t)/(2k+1) \; , \tag{7.4}$$

where $w^k_{nn'}(t)$ is defined by (5.2).

Use of (7.4) in (7.2) gives, for $t\geq 0$,

$$\langle T^*_{km}(t)\, S_{k'm'}(0)\rangle = \delta_{kk'}\delta_{mm'}(2k+1)^{-1} \times \sum_{n,n'=-k}^{k} w^k_{nn'}(t)\, T'^*_{kn}\, S'_{kn'} \; . \tag{7.5}$$

The equations given above in this section are valid for a body of arbitrary shape. In the special case of a spherical body, it can be shown that[31]

$$w^k_{nn'}(t) = \delta_{nn'}\, w^k(t) \; . \tag{7.6}$$

The specific expressions calculated in Sec. VI all satisfy this relation, as can be seen from Eqs. (6.18), (6.49), (6.54), and (6.74)–(6.76). Thus, for a spherical body,

$$\langle T^*_{km}(t) S_{k'm'}(0)\rangle = \delta_{kk'}\delta_{mm'}(2k+1)^{-1} w^k(t) \sum_{n=-k}^{k} T'^*_{kn} S'_{kn} \; . \tag{7.7}$$

A spherical tensor that occurs frequently in applications is the spherical harmonic $Y_{kn}(\Omega_i)$, whose spherical angles $\Omega_i \equiv \theta_i, \phi_i$ specify the orientation in the laboratory coordinate system S of a vector $\vec{r}_i$ that is fixed in a body undergoing rotational motion. Thus $T_{km}(t) = Y_{km}(\Omega_i(t))$ and $T'_{kn} = Y_{kn}(\Omega'_i)$, where $\Omega'_i \equiv \theta'_i, \phi'_i$ are the constant spherical angles of $\vec{r}_i$ with respect to the body-coordinate system in which $\vec{r}_i$ is fixed. The correlation function of two such spherical harmonics is given by (7.5) for a body of arbitrary shape, and by (7.7) for a spherical body. Since the addition theorem for spherical harmonics gives[32]

$$\sum_{n=-k}^{k} Y^*_{kn}(\Omega'_i)\, Y_{kn}(\Omega'_j) = \frac{(2k+1)}{4\pi}\, P_k(\cos\theta_{ij}) \; , \tag{7.8}$$

where P_k is a Legendre polynomial and θ_{ij} is the constant angle between $\vec{r}_i$ and $\vec{r}_j$ fixed in the body, it follows from (7.7) that

$$\langle Y^*_{km}(\Omega_i(t))\, Y_{k'm'}(\Omega_j(0))\rangle = \delta_{kk'}\delta_{mm'}\; w^k(t)\, P_k(\cos\theta_{ij})/4\pi \; . \tag{7.9}$$

In Eqs. (7.7) and (7.9), which apply to a spherical body, $w^k(t)$ is given by (7.6) combined with (6.18) for a free spherical body, with (6.54) if $bk(k+1) \ll 1$, and with (6.75) if $A \ll 1$.

APPENDIX A

The components of the angular-momentum operator $\vec{J}$ with respect to the laboratory coordinate system S are J_x, J_y, and J_z, and with respect to the body coordinate system S' are J_1, J_2, and J_3. The $\psi^J_{MK}(g)$ defined by (3.1) are eigenfunctions of $\vec{J}^2$, J_z, and J_3, with eigenvalues $J(J+1)$, M, and K, respectively.[20] From the explicit expressions for the operators J_x, J_y, J_z, and J_3 given in Sec. 2.5 of Ref. 17, it is clear that J_x, J_y, and J_z commute with J_3. Hence the matrix elements of J_x, J_y, and J_z between two ψ's are diagonal in K, and have the usual expressions with regard to J and M:

$$\langle JMK|\, J_z\, |J'M'K'\rangle = \delta_{JJ'}\,\delta_{MM'}\,\delta_{KK'}\, M \; , \tag{A1}$$

$$\langle JMK|\, J_x \pm iJ_y\, |J'M'K'\rangle = \delta_{JJ'}\,\delta_{M,M'\pm 1}\delta_{KK'}[(J\mp M')(J\pm M'+1)]^{1/2} \; . \tag{A2}$$

The spherical components of $\vec{J}$ in S are[33]

$$T_{\pm 1} \equiv \mp (2)^{-1/2}(J_x \pm iJ_y), \quad T_0 \equiv J_z \; , \tag{A3}$$

and the spherical components with respect to S' are

$$T'_{\pm 1} \equiv \mp (2)^{-1/2}(J_1 \pm iJ_2) \; , \quad T'_0 \equiv J_3 \; . \tag{A4}$$

Since the spherical components are irreducible spherical-tensor operators of rank one,[34]

$$T'_m = \sum_{n=-1}^{1} T_n D^1_{nm}(g) \; , \tag{A5}$$

where $g \equiv (\alpha\beta\gamma)$ are the Euler angles of S' with respect to S. These same Euler angles are the arguments of the $\psi^J_{MK}(g)$, so that from (A5)

$$\langle JMK|\, T'_m\, |J'M'K'\rangle = \sum_{n=-1}^{1} \langle JKM|\, T_n D^1_{nm}(g)\, |J'M'K'\rangle = \sum_{n=-1}^{1} \sum_{J''M''K''} \langle JMK|\, T_n\, |J''M''K''\rangle \times \langle J''M''K''|\, D^1_{nm}(g)\, |J'M'K'\rangle \; . \tag{A6}$$

It follows from (A1), (A2), and Eq. (5.19c) of Ref. 18 that

$$\langle JMK|\, T_n\, |J''M''K''\rangle = \delta_{JJ''}\delta_{KK''}[J(J+1)]^{1/2}\, C(J1J;\, M''nM) \; , \tag{A7}$$

where the C is a Clebsch–Gordan coefficient.[18] Use of (A7) in (A6) gives

$$\langle JMK|\, T'_m\, |J'M'K'\rangle$$

$$= [J(J+1)]^{1/2} \sum_{n,M''} C(J1J;\, M''nM) \times \langle JM''K|\, D^1_{nm}(g)\,|J'M'K'\rangle \;. \quad (A8)$$

From the expression for the integral of three D's,[35]

$$\langle JM''K|\, D^1_{nm}(g)\,|J'M'K'\rangle = \left(\frac{2J+1}{2J'+1}\right)^{1/2} C(J1J';\, M''nM')\, C(J1J';\, KmK') \;. \quad (A9)$$

If (A9) is substituted in (A8), the sum over n can be performed by using the property

$$C(J1J';\, M''nM') = C(J1J';\, M'n)\, \delta_{M',M''+n} \;. \quad (A10)$$

If one also uses the fact that[36]

$$\sum_{M''} C(J1J;\, M'',\, M-M'')\, C(J1J';\, M'',\, M-M'') = \delta_{JJ'} \;, \quad (A11)$$

the result is

$$\langle JMK|\, T'_m\,|J'M'K'\rangle = \delta_{JJ'}\delta_{MM'}[J(J+1)]^{1/2}\, C(J1J;\, KmK') \;. \quad (A12)$$

Since $T'^{\dagger}_m = (-1)^m T'_{-m}$, and since

$$C(J1J;\, KmK') = (-1)^{-m}\, C(J1J;\, K',\, -m,\, K) \;, \quad (A13)$$

it follows from (A12) that

$$\langle JMK|\, T'^{\dagger}_m\,|J'M'K'\rangle = \delta_{JJ'}\delta_{MM'}[J(J+1)]^{1/2}\, C(J1J;\, K'mK) \;. \quad (A14)$$

Comparison of (A14) and (A7) shows that

$$\langle JMK|\, T'^{\dagger}_m\,|J'M'K'\rangle = \langle JKM|\, T_m\,|J'K'M'\rangle \;. \quad (A15)$$

The matrix elements (3.9)–(3.11) in the text follow from (A15), definitions (A3) and (A4), and matrix elements (A1) and (A2).

It is worth noting that result (A15) is also obtained if the transformation equation (A5) is written

$$T'_m = \sum_{n=-1}^{1} D^1_{nm}(g)\, T_n \;. \quad (A16)$$

APPENDIX B

Consider the matrix function of ϕ:

$$\underline{f}(\phi) \equiv e^{i\phi \underline{J}_3}\, \underline{J}_{\pm}\, e^{-i\phi \underline{J}_3} \;, \quad (B1)$$

where $\underline{J}_{\pm} \equiv \underline{J}_1 \pm i\underline{J}_2$. Differentiation of $\underline{f}(\phi)$ with respect to ϕ gives

$$\underline{f}'(\phi) = i e^{i\phi \underline{J}_3}\, [\underline{J}_3,\, \underline{J}_1 \pm i\underline{J}_2]\, e^{-i\phi \underline{J}_3} \;. \quad (B2)$$

But the commutation relation (3.13) can be written

$$[\underline{J}_i,\, \underline{J}_j] = -i\underline{J}_k \;, \quad (B3)$$

where the subscripts i, j, and k are a cyclic permutation of 1, 2, 3. Hence

$$[\underline{J}_3,\, \underline{J}_1 \pm i\underline{J}_2] = \mp(\underline{J}_1 \pm i\underline{J}_2) \;, \quad (B4)$$

so

$$\underline{f}'(\phi) = \mp i \underline{f}(\phi) \;.$$

The solution of this equation which satisfies the condition $\underline{f}(0) = \underline{J}_1 \pm i\underline{J}_2$ implied by definition (B1) is

$$e^{i\phi \underline{J}_3}(\underline{J}_1 \pm i\underline{J}_2)\, e^{-i\phi \underline{J}_3} = (\underline{J}_1 \pm i\underline{J}_2)\, e^{\mp i\phi} \;. \quad (B5)$$

By adding and subtracting the two equations (B5), one obtains

$$e^{i\phi \underline{J}_3}\underline{J}_1 e^{-i\phi \underline{J}_3} = \underline{J}_1 \cos\phi + \underline{J}_2 \sin\phi \quad (B6)$$

and

$$e^{i\phi \underline{J}_3}\underline{J}_2 e^{-i\phi \underline{J}_3} = \underline{J}_2 \cos\phi - \underline{J}_1 \sin\phi \;. \quad (B7)$$

The equations obtained by cyclic permutation of the subscripts 1, 2, and 3 in Eqs. (B6) and (B7) are also correct, since (B6) and (B7) depend just on the cyclic commutation relations (B3).

Now consider

$$\vec{\omega} \cdot \vec{\underline{J}} = \omega[\sin\theta(\cos\phi\, \underline{J}_1 + \sin\phi\, \underline{J}_2) + \cos\theta\, \underline{J}_3] \;. \quad (B8)$$

Using (B6), and then a cyclic permutation of (B6), one obtains

$$\vec{\omega} \cdot \vec{\underline{J}} = \omega e^{i\phi \underline{J}_3}[\sin\theta\, \underline{J}_1 + \cos\theta\, \underline{J}_3]\, e^{-i\phi \underline{J}_3} = \omega e^{i\phi \underline{J}_3} e^{i\theta \underline{J}_2}\, \underline{J}_3\, e^{-i\theta \underline{J}_2}\, e^{-i\phi \underline{J}_3} \;. \quad (B9)$$

Equation (6.9) then follows from (B9) and the power-series definition of $e^{-i\vec{\omega}\cdot\vec{\underline{J}}t}$.

APPENDIX C

If follows from the relation $\vec{\underline{J}} \times \vec{\underline{J}} = -i\vec{\underline{J}}$, Eq. (3.13), that

$$[\vec{\omega} \cdot \vec{\underline{J}},\, \vec{\underline{J}}] = i(\vec{\omega} \times \vec{\underline{J}}) \;. \quad (C1)$$

Thus, if the expression $\vec{\underline{J}}(s)$ given by (6.27) is differentiated with respect to s, one obtains

$$\vec{\underline{J}}'(s) = -\vec{\omega}_1 \times \vec{\underline{J}}(s) \;. \quad (C2)$$

A second differentiation then leads to

$$\vec{\underline{J}}''(s) + \omega_1^2\, \vec{\underline{J}}(s) = \vec{\omega}_1(\vec{\omega}_1 \cdot \vec{\underline{J}}) \;. \quad (C3)$$

The solution of Eq. (C3) which satisfies the initial conditions implied by the definition of $\vec{\underline{J}}(s)$ and by (C2) is Eq. (6.44).

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[17]D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Oxford U. P., London, 1968), Secs. 1.4–1.7 provide the justification for this use of the angular-momentum operator.
[18]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
[19]The $D^{J}_{MK}(g)$ defined by Eq. (2.2) is identical to the $D^{J}_{MK}(\alpha\beta\gamma)$ of Ref. 18 and the $\mathfrak{D}^{J}_{MK}(\alpha\beta\gamma)$ of Ref. 17.
[20]Reference 17, Sec. 2.5; a complex-conjugate sign is omitted from the $\mathfrak{D}$ in the first line of this section, but it is clear from the subsequent derivation that it should be there. Our Eq. (3.1) is also consistent with the expression given on p. 55 of Ref. 18, which can be shown to differ only by an irrelevant sign.
[21]Equation (3.3) follows from definition (3.1) and Eq. (4.60) of Ref. 18, or Appendix V or Ref. 17.
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[23]J. H. Van Vleck, Rev. Mod. Phys. 23, 213 (1951).
[24]This result has previously been given by W. A. Steele, Ref. 11, Eq. (4.1).
[25]Reference 15, Eq. (4.1).
[26]Reference 15, Eq. (4.5).
[27]W. Gröbner and N. Hofreiter, *Integraltafel, Zweiter Teil, Bestimmte Integrale* (Springer-Verlag, Vienna, 1950), Eq. 031.12c.
[28]Reference 11, Eq. (4.21) with $\xi_x=\xi_y=\xi_z=IB$.
[29]W. A. Steele, J. Chem. Phys. 38, 2411 (1963), Eqs. (3.12) and (3.13).
[30]This is the inverse of the usual relation, Eq. (4.5) of Ref. 17; it follows from Eq. (4.5) and p. 147 or Ref. 17.
[31]The proof is the same as that given in connection with Eqs. (17)–(19) or Ref. 9.
[32]Reference 18, Eq. (4.28).
[33]Reference 18, Eqs. (5.9).
[34]Reference 17, Eq. (4.8), or Ref. 18, Eq. (5.1).
[35]Reference 18, Eq. (4.62), corrected for a missing factor of $4\pi^2$.
[36]Reference 18, Eq. (3.7).

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Higher-Multipole Contributions to the Retarded van der Waals Potential*

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We calculate the two-photon exchange (retarded van der Waals) potential between neutral spinless systems, including the effects of higher partial waves in the atom-photon scattering amplitude. This is equivalent to including higher multipoles in the interaction of the charges in the atoms. We show that this potential can be expressed as an infinite series of terms, with coefficients that can, in principle, be measured in atom-photon scattering. The behavior of the various terms, at small separation and large separation of the system, is discussed. We show that the leading term in the contribution of each multipole has the property that it has one more power of R^{-1} in its large-R behavior than in its small-R behavior.

I. INTRODUCTION

A recent analysis[1] has shown that the two-photon exchange (retarded van der Waals) potential between spinless atoms can be expressed in terms of the scattering amplitudes for photon-atom scattering by the individual atoms. An exact expression for this potential has been given, involving an integral over these amplitudes, evaluated at positive photon energy, and at positive, and therefore unphysical, momentum transfers. In the previous analysis, it was shown that when the dependence of the scattering amplitude on momentum transfer was neglected, the potential could be expressed in terms of the atomic polarizability evaluated at real frequencies, a quantity directly measurable in photon-atom scattering. The approximation so made is equivalent to neglecting all partial waves other than s wave in the photon-atom scattering amplitude. The result obtained is an extension of the retarded van der Waals interaction of Casimir and Polder,[2] generalized to include magnetic effects and relativistic effects.

In the present work, we shall retain the depen-