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Time Correlations and Conditional Distribution Functions for Classical Ensembles of Free Rotors*

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Explicit expressions are obtained for the classical rotational time-correlation functions for free rotation of the following: the linear, spherical-top, and symmetric-top molecule. This is done by deriving the eigenfunctions and eigenvalues of the potential-free rotational Liouville operator for each case. Conditional distribution functions for orientations and angular momenta are then constructed, and correlation functions are computed by evaluating phase-space averages with the distribution functions. The results obtained agree with those of Sears for the linear molecule and Steele for the spherical top, but differ somewhat from the calculation of Agrawal and Yip for the symmetric top molecule. The reason for this discrepancy is discussed briefly.

I. INTRODUCTION

In classical statistical mechanics the behavior in time of a system point in phase space is governed by Liouville's equation,

$$\frac{dW}{dt} = 0 \tag{1}$$

$$= \frac{\partial W}{\partial t} + i\mathcal{L}W , \tag{2}$$

where W is the probability density for the system, and $\mathcal{L}$ is the Liouville operator. Equation (2) follows since W depends on time both explicitly and implicitly through the phase-space variables, denoted collectively by Γ. If the system is a collection of noninteracting molecules, then W for the system can be written as a product of one-molecule probability densities, and $\mathcal{L}$ becomes a sum of one-molecule operators. We will be concerned here with solving Eqs. (1) and (2) for this case. Furthermore, this paper will be concerned only with rotational degrees of freedom. Consequently Γ will mean the six quantities α, β, γ, p_α, p_β, p_γ, which are the three Eulerian angles defining the orientation of a rigid molecule and their conjugate momenta. We will follow the convention in Rose[1] for rotations. Since these variables form a canonical set, the one-molecule Liouville operator for rotational degrees of freedom is

$$\mathcal{L} = \frac{1}{i}\left\{\frac{\partial H}{\partial p_\alpha}\frac{\partial}{\partial \alpha}+\frac{\partial H}{\partial p_\beta}\frac{\partial}{\partial \beta}+\frac{\partial H}{\partial p_\gamma}\frac{\partial}{\partial \gamma} -\frac{\partial H}{\partial \alpha}\frac{\partial}{\partial p_\alpha}-\frac{\partial H}{\partial \beta}\frac{\partial}{\partial p_\beta}-\frac{\partial H}{\partial \gamma}\frac{\partial}{\partial p_\gamma}\right\}. \tag{3}$$

The Hamiltonian in Eq. (3) is simply the kinetic energy since no potential energy terms are included in the one-molecule problem.

Let L_x, L_y, L_z be the components of the angular momentum vector along the body-fixed principal axes (x, y, z). In the case of the linear molecule the Eulerian momentum $p_\gamma (= L_z)$ is zero, as is also the moment of inertia I_z about the internuclear axis. The angle γ is superfluous and only four variables are needed to span the phase space, namely, α, β, p_α, p_β. Straightforward geometric considerations show that the linear molecule momenta are

$$L_x = I\omega_x = -\csc\beta\, p_\alpha, \quad L_y = I\omega_y = p_\beta, \quad L_z = 0, \tag{4}$$

where $I = I_x = I_y$. Similarly the space-fixed Cartesian components L_X, L_Y, L_Z for this molecule are given by

$$L_X = \sin\alpha\, p_\beta - \cos\alpha \cot\beta\, p_\alpha,$$
$$L_Y = \cos\alpha\, p_\beta - \sin\alpha \cot\beta\, p_\alpha, \quad L_Z = p_\alpha \tag{5}$$

and the Hamiltonian is

$$H = (2I)^{-1}(p_\beta^2 + p_\alpha^2/\sin^2\beta) \tag{6a}$$

$$= (2I)^{-1}(L_x^2 + L_y^2). \tag{6b}$$

It then follows from Eq. (6a) that the Liouville operator becomes

$$\mathcal{L} = \frac{1}{i}\left\{\frac{\partial H}{\partial p_\alpha}\frac{\partial}{\partial \alpha}+\frac{\partial H}{\partial p_\beta}\frac{\partial}{\partial \beta}-\frac{\partial H}{\partial \beta}\frac{\partial}{\partial p_\beta}\right\} \tag{7}$$

for the potential-free linear rotor.

For the spherical-top $(I_x = I_y = I_z)$ and the symmetric-top molecule $(I_x = I_y \neq I_z)$ the body-fixed angular momentum components L_j $(j = x, y, z)$ are related to the Eulerian momenta as follows:

$$L_x = \cos\gamma \cot\beta\, p_\gamma + \sin\gamma\, p_\beta - \frac{\cos\gamma}{\sin\beta} p_\alpha,$$
$$L_y = -\sin\gamma \cot\beta\, p_\gamma + \cos\gamma\, p_\beta + \frac{\sin\gamma}{\sin\beta} p_\alpha, \tag{8}$$
$$L_z = p_\gamma .$$

Similarly, for the space-fixed components we have

$$L_X = -\cos\alpha \cot\beta\, p_\alpha - \sin\alpha\, p_\beta + \frac{\cos\alpha}{\sin\beta} p_\gamma,$$
$$L_Y = \sin\alpha \cot\beta\, p_\alpha + \cos\alpha\, p_\beta + \frac{\sin\alpha}{\sin\beta} p_\gamma, \tag{9}$$
$$L_Z = p_\alpha .$$

The Hamiltonian for the symmetric-top molecule will be written as

$$H = \frac{1}{2I}(L_x^2 + L_y^2) + \frac{1}{2I_z} L_z^2 . \tag{10}$$

For the spherical top, H is of course given by Eq. (10) with $I_z = I$. We will not write down the corresponding expressions for H in the Eulerian representation. It is sufficient to point out that these expressions are independent of the angles α and γ. Consequently the Liouville operator becomes

$$\mathcal{L} = \frac{1}{i}\left(\frac{\partial H}{\partial p_\alpha}\frac{\partial}{\partial \alpha}+\frac{\partial H}{\partial p_\beta}\frac{\partial}{\partial \beta}+\frac{\partial H}{\partial p_\gamma}\frac{\partial}{\partial \gamma}-\frac{\partial H}{\partial \beta}\frac{\partial}{\partial p_\beta}\right) \tag{11}$$

for these potential-free rotors.

We now write the probability density W as

$$W(\Gamma, t) = \sum_n a_n(t) w_n(\Gamma), \tag{12}$$

where the $w_n(\Gamma)$ are a complete orthogonal set of eigenfunctions of the operator $\mathcal{L}$ spanning phase space. Substituting Eq. (12) into Eq. (2) and separating variables, we obtain

$$a_n(t) = c_n \exp(-i\Lambda_n t), \tag{13}$$

$$\mathcal{L} w_n(\Gamma) = \Lambda_n w_n(\Gamma), \tag{14}$$

where Λ_n is the eigenvalue to which the eigenfunction w_n corresponds. Of course, the explicit form of these eigenfunctions and eigenvalues will depend on the detailed form of the Liouville operator $\mathcal{L}$. Equation (14) is the time-independent version of the Liouville equation, the solution of which comprises most of Sec. II below.

Consider the function $W^c(\Gamma, t; \Gamma^0, t^0)$. This is the conditional probability density that the phase-space coordinates and momenta are Γ at time t given that they were Γ^0 at time t^0. Sometimes called the propagator, W^c is functionally related to the probability density, W, as follows:

$$W(\Gamma, t) = \int W^c(\Gamma, t; \Gamma^0, t^0) W(\Gamma^0, t^0) d\Gamma^0. \tag{15}$$

It obeys the same equation of motion

$$\partial W^c/\partial t = -i\mathcal{L}W^c \tag{16}$$

and satisfies the initial condition

$$W^c(\Gamma, t^0; \Gamma^0, t^0) = \delta(\Gamma - \Gamma^0). \tag{17}$$

If the system is stationary, then W^c is a function only of the time interval, $t - t^0$, and not the initial time t^0. Thus $W(\Gamma^0, t^0)$ will be dependent on Γ^0 only, and one can arbitrarily set t^0 equal to zero.

These propagators are particularly suited for calculating correlation functions. For instance, let $\vec{V}(t)$ be some physical vector of interest at rest in the body-fixed frame of a symmetric-top molecule. The averaging operation in the definition of the correlation function $\langle \vec{V}(t) \cdot \vec{V}(0) \rangle$ can be performed in two steps. We will divide by $\langle V^2 \rangle$, thereby making the quantity $\langle \vec{V}(t) \cdot \vec{V}(0) \rangle / \langle \vec{V}^2 \rangle$ a function only of the angles $\delta\Omega$ between the vector at time t and at time 0 (as measured by a space-fixed observer). The physically relevant functions of the angles of reorientation, $\delta\Omega$, can generally be expressed in terms of the D functions of Wigner (cf. Rose[1]) given by

$$D_{k,m}^{\;j}(\alpha, \beta, \gamma) = e^{-ik\alpha} d_{k,m}^{\;j}(\beta) e^{-im\gamma}. \tag{18}$$

The first step in calculating a correlation function is to carry out the conditional average by integrating over the phase-space variables at time t

$$\langle D_{k,m}^{\;j}(\delta\Omega) \rangle_{\Gamma^0} = \int W^c(\Gamma(t), t; \Gamma^0) D_{k,m}^{\;j}(\delta\Omega) d\Gamma(t). \tag{19}$$

This is then followed by an average over the distribution of initial orientations and momenta

$$\langle D_{k,m}^{\;j}(\delta\Omega) \rangle = \int \langle D_{k,m}^{\;j}(\delta\Omega) \rangle_{\Gamma^0} W(\Gamma^0) d\Gamma^0. \tag{20}$$

In performing the integration in Eq. (19), the function $D_{k,m}^{\;j}(\delta\Omega)$ can be expanded in terms of other D functions of the orientation angles at time t, $\Omega(t)$, and of the initial orientation angles Ω^0. An alternative procedure is to invoke the property[2] of the conditional probabilities W^c which states that these functions actually do not depend on the initial orientation angles, but only upon $\delta\Omega$. Then in place of Eqs. (19) and (20) we have

$$\langle D_{k,m}^{\;j}(\delta\Omega) \rangle_{\vec{L}^0} = \int W^c(\delta\Omega, \vec{L}(t), t; \vec{L}^0) \times D_{k,m}^{\;j}(\delta\Omega) d(\delta\Omega) d\vec{L}(t) \tag{21}$$

and

$$\langle D_{k,m}^{\;j}(\delta\Omega) \rangle = \int \langle D_{k,m}^{\;j}(\delta\Omega) \rangle_{\vec{L}^0} W(\vec{L}^0) d\vec{L}^0. \tag{22}$$

In Sec. III correlation functions are explicitly evaluated for several choices of the indices k, m, j.

II. LIOUVILLE EQUATION

A. Linear Molecule

In general, a potential-free linear rotor undergoes uniform rotation in a plane about an axis perpendicular to that plane. The direction of the axis is the direction both of the angular momentum ($\vec{L}$) and angular velocity ($\vec{\omega}$) vectors. The internuclear axis, always lying in the plane, defines the body-fixed z axis.

The components of the angular momentum along the laboratory axes (L_X, L_Y, L_Z) are constant. This suggests the following separation of variables for the eigenfunctions $w_n(\Gamma)$:

$$w_m^{\;j}(\Gamma) = g_m^{\;j}(\alpha, \beta) \delta(L_X - L_X^{\;0}) \times \delta(L_Y - L_Y^{\;0}) \delta(L_Z - L_Z^{\;0}). \tag{23}$$

An explicit form for the function $g_m^{\;j}$ will be derived below. It is the eigenfunction of the configurational part of the Liouville operator, and is a function only of the angles. Of course, we could also write

$$\delta(L_x - L_x^{\;0}) \delta(L_y - L_y^{\;0}) \delta(L_z)$$

or $\delta(p_\alpha - p_\alpha^{\;0})(p_\beta - p_\beta^{\;0}) \delta(p_\gamma)$

in place of the space-fixed arguments in Eq. (23) but choose not to do so for the present. The appearance of three momentum δ functions is not inconsistent with the dimensionality of the phase space, $\Gamma \sim \alpha, \beta, p_\alpha, p_\beta$. This is because the component of $\vec{L}$ along the internuclear axis is always zero. Thus integrations over phase space can alternately be written as

$$\begin{aligned} \int d\Gamma &= \int d\alpha \sin\beta d\beta d L_x dL_y \delta(L_z) dL_z \\ &= \int d\alpha d\beta dp_\alpha dp_\beta \delta(p_\gamma) dp_\gamma . \end{aligned} \tag{24}$$

If Eq. (23) is substituted into

$$\mathcal{L} w_m^{\;j}(\Gamma) = \Lambda_m^{\;j} w_m^{\;j}(\Gamma) \tag{25}$$

with the operator $\mathcal{L}$ given by Eq. (7), both sides can be integrated over the momentum variables to give

$$\frac{1}{i}\left(\frac{\partial H}{\partial p_\partial}\right)_0 \frac{\partial}{\partial \alpha} + \left(\frac{\partial H}{\partial p_\beta}\right)_0 \frac{\partial}{\partial \beta} g_m{}^j = \Lambda_m{}^j g_m{}^j \ , \tag{26}$$

where the subscript 0 indicates that the momenta are assigned their initial values. It is thus seen that the effect of the term $(\partial H/\partial\beta)\,(\partial/\partial p_\beta)$ in the Liouville operator operating on the δ functions, yields zero after integrating over the momenta. The operator on the left-hand side of Eq. (26) will be denoted by $\mathcal{L}\Omega$, and will be called the configurational Liouville operator. With the aid of Eq. (6) for the linear molecule Hamiltonian, this operator can be written as follows:

$$\mathcal{L}_\Omega = \omega_X{}^0 l_X + \omega_Y{}^0 l_Y + \omega_Z{}^0 l_Z, \tag{27}$$

where
$$l_X = \frac{1}{i}\left(-\cos\alpha \cot\beta \frac{\partial}{\partial\alpha} - \sin\alpha \frac{\partial}{\partial\beta}\right),$$
$$l_Y = \frac{1}{i}\left(-\sin\alpha \cot\beta \frac{\partial}{\partial\alpha} + \cos\alpha \frac{\partial}{\partial\beta}\right), \tag{28}$$
$$l_Z = \frac{1}{i}\,\frac{\partial}{\partial\alpha}$$

The operators of Eq. (28) are also the space-fixed components of the quantum-mechanical angular momentum operator, apart from a factor of $\hbar$. Dropping the superscript 0, the right-hand side of Eq. (27) can be written as

$$\mathcal{L}_\Omega = \sum_{\mu=-1,0,+1} (-1)^\mu \omega_\mu l_{-\mu}, \tag{29}$$

where
$$\omega_{\pm 1} = \mp 2^{-1/2}(\omega_X \pm i\omega_Y)$$
$$= \mp 2^{-1/2}\omega \sin\theta_{\omega s} \exp(\pm i\phi_{\omega s}), \tag{30}$$
$$\omega_0 = \omega_Z = \omega \cos\theta_{\omega s},$$

and
$$l_{\pm 1} = \mp 2^{-1/2}(l_X \pm i l_Y), \quad l_0 = l_Z . \tag{31}$$

In Eqs. 30) the polar and azimuthal angles $\theta_{\omega s}$, $\phi_{\omega s}$ of the vector $\vec{\omega}$ are measured relative to the space-fixed frame (X, Y, Z) and of course are constant in time. The eigenvalue equation now becomes

$$\omega \sum_{m=-1}^{+1} D_{m,0}{}^1(\phi_{\omega s}, \theta_{\omega s}) l_m g_m{}^j = \Lambda_m{}^j g_m{}^j . \tag{32}$$

Equation (32) is solved most directly by observing that the operator on the left-hand side is a linear combination of irreducible vector operators, l_m. Consequently these operators transform as follows [Rose,[1] Eq. (5.1)]:

$$R l_m R^{-1} = \sum_{m'} D_{m',m}{}^1(\delta\Omega_\omega) l_{m'}, \tag{33}$$

where $\delta\Omega_\omega$ represents the angles of the transformation $\delta\alpha_\omega$, $\delta\beta_\omega$, $\delta\gamma_\omega$. If these angles are such as to diagonalize the configurational Liouville operator, one can write

$$\mathcal{L}_{\Omega'} = R l_\Omega R^{-1} = \omega_0 l_0(\Omega'), \tag{34}$$

where $\Omega'(=\alpha', \beta')$ are the angular variables in the transformed operator. Since

$$l_0(\Omega') Y_{j,m}(\Omega') = m Y_{j,m}(\Omega'), \tag{35}$$

one finds that the solutions to the eigenvalue problem are

$$\Lambda_m{}^j = m\omega, \tag{36}$$

$$g_m{}^j(\Omega) = R^{-1} Y_{j,m}(\Omega'). \tag{37}$$

The functions $Y_{j,m}$ are the spherical harmonics. In order to determine the angles $\delta\Omega_\omega$ we note

$$R\mathcal{L}_\Omega R^{-1} = \omega \sum_{m,m'} D_{m,0}{}^1(\phi_{\omega s}, \theta_{\omega s})$$
$$\times D_{m',m}{}^1(\delta\Omega_\omega) l_m . \tag{38}$$

The diagonalization is accomplished if

$$\sum_m D_{m,0}{}^1(\phi_{\omega s}, \theta_{\omega s}) D_{m',m}{}^1(\delta\Omega_\omega) = \delta_{m',0}, \tag{39}$$

but

$$D_{m',m}{}^1(\delta\alpha_\omega, \delta\beta_\omega, \delta\gamma_\omega)$$
$$= D^*_{m,m'}{}^1(-\delta\gamma_\omega, -\delta\beta_\omega, -\delta\alpha_\omega).$$

It is thus necessary to choose the angles of $\delta\Omega_\omega$ such that

$$\sum_m D_{m,0}{}^1(\phi_{\omega s}, \theta_{\omega s})$$
$$\times D^*_{m,m'}{}^1(-\delta\gamma_\omega, -\delta\beta_\omega, -\delta\alpha_\omega) = \delta_{m',0}. \tag{40}$$

The completeness property of these functions gives the desired result if $-\delta\gamma_\omega = \phi_{\omega s}$, $-\delta\beta_\omega = \theta_{\omega s}$, and $-\delta\alpha_\omega$ can be arbitrary. Thus the normalized eigenfunctions of the rotational Liouville operator in configuration space are

$$g_m{}^j(\alpha, \beta) = \sum_r Y_{j,r}(\alpha, \beta) D_{r,m}{}^j(\phi_{\omega s}{}^0, \theta_{\omega s}{}^0, \psi), \tag{41}$$

where ψ is an arbitrary angle. The set of eigenfunctions $w_m{}^j(\Gamma)$ given by

$$w_m{}^j(\Gamma) = g_m{}^j(\alpha, \beta)\delta(\vec{L} - \vec{L}^0) \tag{42}$$

are orthogonal and complete, i.e.,

$$\int w^*_{m'}{}^{j'}(\Gamma) w_m{}^j(\Gamma) d\Gamma$$
$$= \delta_{j,j'}\delta_{m,m'}\delta(\vec{L}^0 - \vec{L}^{0\prime}) \tag{43}$$

and

$$\int \sum_{j=0}^{\infty} \sum_{m=-j}^{+j} w_m^{*j}(\Gamma_1) w_m^{j}(\Gamma_2) d\vec{\mathrm{L}}^0$$

$$= \delta(\alpha_1 - \alpha_2)\delta(\beta_1 - \beta_2)\delta(\vec{\mathrm{L}}_1 - \vec{\mathrm{L}}_2). \tag{44}$$

[Equations (43) and (44) are proved in Appendix A.] We can now write an explicit expression for the probability density for the linear molecule. It is

$$W(\Gamma, t) = \sum_{j=0}^{\infty} \sum_{m=-j}^{+j} c_m^{j} e^{-im\omega^0 t}$$

$$\times \sum_{r=-j}^{+j} [Y_{j,r}(\alpha,\beta) D_{r,m}^{j}(\phi_{\omega s}^{0}, \theta_{\omega s}^{0}, \psi)\delta(\vec{\mathrm{L}} - \vec{\mathrm{L}}^0)]. \tag{45}$$

The initial condition of the problem will enable one to determine the factors c_m explicitly and to eliminate the arbitrary angle ψ.

B. Symmetric-Top (and Spherical-Top) Molecule

Although the space-fixed components (L_X, L_Y, L_Z) of the angular momentum vector for a potential-free symmetric top are constant in time, the body-fixed components must satisfy the torque-free version of Euler's equations of motion, namely,

$$\frac{dL_x}{dt} = \left(\frac{1}{I_z} - \frac{1}{I}\right) L_y L_z,$$

$$\frac{dL_y}{dt} = -\left(\frac{1}{I_z} - \frac{1}{I}\right) L_z L_x, \quad \frac{dL_z}{dt} = 0. \tag{46}$$

Equation (46) gives the well-known result that the L_x and L_y components precess about the figure (body-fixed z) axis with frequency

$$\omega_p = \left(\frac{1}{I_z} - \frac{1}{I}\right) L_z,$$

whereas the L_z component is a constant of the motion.

In solving the Liouville equation for this case, it will prove convenient to transform into a body-fixed precessing frame. In this coordinate system not only does L_z remain constant, but the other two components, denoted by L_ξ and L_η, also become constants of the motion. If $R\ (\alpha, \beta, \gamma)$ denotes the Eulerian rotations which carry the space-fixed into the body-fixed frame, and $R\ (\alpha', \beta', \gamma')$ the same operations for carrying the space-fixed into the precessing frame, than a moment's reflection will show that in fact $\alpha' = \alpha$, $\beta' = \beta$, but $\gamma' = \gamma + \omega_p t$. (Furthermore the Eulerian momenta conjugate to both sets of angles are the same.) The rotation operator which transforms from the body-fixed (x, y, z) to the precessing (ξ, η, z) frame is given by

$$R = \exp[\omega_p t(\partial/\partial\gamma)]. \tag{47}$$

Then

$$\mathcal{L}' = R\mathcal{L}R^{-1}, \tag{48}$$

$$W' = RW, \tag{49}$$

and it can readily be shown that the Liouville equation in the precessing frame becomes

$$\frac{\partial W'}{\partial t} = -i\left(\mathcal{L}' - \omega_p \frac{1}{i}\frac{\partial}{\partial\gamma'}\right) W'. \tag{50}$$

After separating variables [recall Eqs. (12)–(14)], we obtain

$$(\mathcal{L}' - \omega_p l_z) w_n(\Gamma') = \Lambda_n w_n(\Gamma'), \tag{51}$$

where $l_z = -i(\partial/\partial\gamma')$, and Γ' denotes the phase-space variables in the precessing body frame. Since the components of the angular momentum are constants along these axes, one can write

$$w_{k,m}^{j}(\Gamma') = g_{k,m}^{j}(\alpha, \beta, \gamma')\delta(L_\xi - L_\xi^{0})$$

$$\times \delta(L_\eta - L_\eta^{0})\delta(L_z - L_z^{0}). \tag{52}$$

The function $g_{k,m}^{j}$ is an eigenfunction of the configurational part of the Liouville operator, and is a function only of the angles. An explicit form for it will be derived below. L_ξ^0, L_η^0, and L_z^0 are the precessing frame components of $\vec{\mathrm{L}}$ at time zero. [Observe that L_ξ, L_η, and L_z are related to the Eulerian momenta through Eq. (8) but with $\gamma'(= \gamma + \omega_p t)$ replacing γ.] If Eq. (52) is substituted into Eq. (51) and both sides are integrated over the momentum variables, it readily follows that

$$\frac{1}{i}\left[\left(\frac{\partial H}{\partial p_\alpha}\right)_0 \frac{\partial}{\partial\alpha} + \left(\frac{\partial H}{\partial p_\beta}\right)_0 \frac{\partial}{\partial\beta} + \left(\frac{\partial H}{\partial p_\gamma}\right)_0 \frac{\partial}{\partial\gamma'}\right.$$

$$\left. -\omega_p \frac{\partial}{\partial\gamma'}\right] g_{k,m}^{j}(\Omega') = \Lambda_{k,m}^{j} g_{k,m}^{j}(\Omega'), \tag{53}$$

where $\Omega' = \alpha, \beta, \gamma'$. The subscript zero indicates that the momenta are assigned their initial values. It can thus be seen (as in the case of the linear rotor) that the effect of the term $(\partial H/\partial\beta)(\partial/\partial p_\beta)$ in $\mathcal{L}'$, operating on the δ functions, yields zero after integrating over the momenta. If one changes from the Eulerian momenta to the precessing frame components and substitutes

$$\left(\frac{1}{I_z} - \frac{1}{I}\right) L_z^{0}$$

for ω_p, Eq. (53) becomes

$$\frac{1}{I}\left(L_\xi^{\,0} l_\xi + L_\eta^{\,0} l_\eta + L_z^{\,0} l_z\right) g_{k,m}^{\,j} = \Lambda_{k,m}^{\,j} g_{k,m}^{\,j}, \tag{54}$$

where

$$l_\xi = \frac{1}{i}\left(-\frac{\cos\gamma'}{\sin\beta}\,\frac{\partial}{\partial\alpha} + \sin\gamma'\frac{\partial}{\partial\beta} + \cos\gamma'\cot\beta\frac{\partial}{\partial\gamma'}\right),$$

$$l_\eta = \frac{1}{i}\left(\frac{\sin\gamma'}{\sin\beta}\,\frac{\partial}{\partial\alpha} + \cos\gamma'\frac{\partial}{\partial\beta} - \sin\gamma'\cot\beta\frac{\partial}{\partial\gamma'}\right), \tag{55}$$

$$l_z = \frac{1}{i}\,\frac{\partial}{\partial\gamma'}.$$

These operators will be recognized in quantum mechanics as the body-fixed components (or, more precisely, the precessing frame components) of the angular momentum operator, apart from a factor of $\hbar$. In complete analogy with the case of the linear rotor, the operator on the left-hand side of Eq. (54) is the configurational Liouville operator and will be denoted by $\mathcal{L}_{\Omega'}$. The superscripts 0 will be dropped whenever no ambiguity arises.

The advantage of working in the precessing frame now becomes apparent. The time dependence due to the precession of L_x and L_y is eliminated, and the partial differential equation in six variables can be reduced to a more tractable equation in the three angular variables. If we perform an analysis for the spherical-top molecule paralleling Eqs. (50)–(54) above, the eigenfunctions turn out to be

$$w_{k,m}^{\,j}(\Gamma)_{\text{sph}} = g_{k,m}^{\,j}(\alpha,\beta,\gamma)\delta(L_x - L_x^{\,0}) \times \delta(L_y - L_y^{\,0})\delta(L_z - L_z^{\,0}). \tag{56}$$

This is because all three body-fixed components L_x, L_y, and L_z are constants, ω_p being zero. The configurational Liouville operator can be written as

$$\mathcal{L}_{\Omega(\text{sph})} = \vec{\omega}\cdot\vec{l}, \tag{57}$$

since the angular velocity and angular momentum vectors are parallel.

Returning to Eq. (54) and continuing with the analysis for the symmetric-top molecule, one can write the configurational Liouville operator as

$$\mathcal{L}_{\Omega'} = \frac{1}{I}\sum_{\mu=-1,0,+1} (-1)^\mu L_\mu l_{-\mu}, \tag{58}$$

where

$$L_{\pm 1} = \mp 2^{-1/2}(L_\xi \pm iL_\eta) = \mp 2^{-1/2} L \sin\theta_L \exp(\pm i\phi_L), \tag{59}$$

$$L_0 = L_z = L\cos\theta_L,$$

with θ_L, ϕ_L defined as the polar and azimuthal angles of the angular momentum vector in the precessing body frame. Furthermore we have

$$l_{\pm 1} = \mp 2^{-1/2}(l_\xi \pm il_\eta), \quad l_0 = l_z. \tag{60}$$

The eigenvalue equation can also be written as

$$\left(\frac{L}{I}\sum_{m=-1}^{+1} D_{m,0}^{\,1}(\phi_L,\theta_L) l_m\right) g_{k,m}^{\,j} = \Lambda_{k,m}^{\,j} g_{k,m}^{\,j}. \tag{61}$$

Equation (61) can readily be solved if we perform a diagonalizing transformation of the operator $\mathcal{L}_{\Omega'}$ in a manner entirely similar to the case of the linear rotor [recall Eqs. (33)–(41)]. The result is that

$$\mathcal{L}_{\Omega''} = R(\delta\Omega_L)\mathcal{L}_{\Omega'}R^{-1}(\delta\Omega_L) \tag{62}$$

$$= (L/I)l_0(\Omega'') \tag{63}$$

where $\Omega'' = \alpha''$, β'', γ'' are the angular variables in the transformed operator, and $\delta\Omega_L = \delta\alpha_L$, $\delta\beta_L$, $\delta\gamma_L$ are the angles of the transformation. Thus

$$l_0(\Omega'')D_{k,m}^{\,j}(\Omega'') = -mD_{k,m}^{\,j}(\Omega''). \tag{64}$$

If one continues to apply the arguments used in the linear molecule problem to this case, it can be shown that $\delta\alpha_L$ is arbitrary whereas $\delta\beta_L = -\theta_L$, $\delta\gamma_L = -\phi_L$. The eigenvalues and eigenfunctions of Eq. (61) are thus

$$\Lambda_{k,m}^{\,j} = -mL^0/I, \tag{65}$$

$$g_{k,m}^{\,j}(\Omega') = \left(\frac{2j+1}{8\pi^2}\right)\sum_{r=-j}^{+j} D_{k,r}^{\,j}(\alpha,\beta,\gamma') \times D_{r,m}^{\,j}(\phi_L^{\,0},\theta_L^{\,0},\psi). \tag{66}$$

Note that the quantity L^0/I is the rate of precession of the figure axis about the direction of $\vec{L}$ as viewed by a space-fixed observer, and is not ωp (cf. Landau and Lifshitz[3]).

Reverting again momentarily to the spherical top case, it is immediately seen that the solutions for this case can be written as

$$\Lambda_{k,m}^{\,j} = -m\omega^0, \tag{67}$$

$$g_{k,m}^{\,j}(\alpha,\beta,\gamma) = \left(\frac{2j+1}{8\pi^2}\right)\sum_r D_{k,r}^{\,j}(\alpha,\beta,\gamma) \times D_{r,m}^{\,j}(\phi_{\omega b}^{\,0},\theta_{\omega b}^{\,0},\psi), \tag{68}$$

where $\theta_{\omega b}^{\,0}$ and $\phi_{\omega b}^{\,0}$ are the polar and azimuthal angles of the angular velocity vector relative to the body-fixed frame. The superscripts zero on the momentum variables, which were omitted earlier, are being indicated in the final results, Eqs. (65)-(68).

In Appendix A, it is proved that the set of functions $\{w_{k,m}{}^{j}(\Gamma')\}$, explicitly obtained upon combining Eq. (66) with Eq. (52), are orthogonal and complete in phase space. That is,

$$\int w^{*}_{k',m'}{}^{j'}(\Gamma')\,w_{k,m}{}^{j}(\Gamma')\,d\alpha\,\sin\beta\,d\beta\,d\gamma'\,dL_{\xi}\,dL_{\eta}\,dL_{z}$$

$$=\delta_{j,j'}\delta_{k,k'}\delta_{m,m'}\delta(L_{\xi}{}^{0}-L_{\xi}{}^{0\prime})\delta(L_{\eta}{}^{0}-L_{\eta}{}^{0\prime})\delta(L_{z}{}^{0}-L_{z}{}^{0\prime}) \tag{69}$$

and

$$\int\sum_{j=0}^{\infty}\sum_{k,m=-j}^{+j} w^{*}_{k,m}{}^{j}(\Gamma_1')\,w_{k,m}{}^{j}(\Gamma_2')\,dL_{\xi}{}^{0}\,dL_{\eta}{}^{0}\,dL_{z}{}^{0}$$

$$=\delta(\alpha_1-\alpha_2)\delta(\beta_1-\beta_2)\delta(\gamma_1'-\gamma_2')\delta(L_{\xi 1}-L_{\xi 2})\delta(L_{\eta 1}-L_{\eta 2})\delta(L_{z1}-L_{z2}), \tag{70}$$

If we incorporate Eqs. (56), (65), and (66) into the expression for the probability density function (in the precessing frame), we obtain

$$W'=\sum_{j=0}^{\infty}\sum_{k,m=-j}^{+j} c_{k,m}{}^{j}\,e^{imL^{0}t/I}\left(\frac{2j+1}{8\pi^{2}}\right)\sum_{r} D_{k,r}{}^{j}(\alpha,\beta,\gamma')$$

$$\times D_{r,m}{}^{j}(\phi_{L}{}^{0},\theta_{L}{}^{0},\psi)\delta(L_{\xi}-L_{\xi}{}^{0})\delta(L_{\eta}-L_{\eta}{}^{0})\delta(L_{z}-L_{z}{}^{0}). \tag{71}$$

Recall that the sextet of Eulerian variables, Γ', refers to the coordinates (Ω') which carry the space-fixed axes (X, Y, Z) into the precessing frame (ξ, η, z) together with their conjugate momenta. This in fact alters only the third Eulerian angle γ. The analog of Eq. (71) for the spherical-top molecule will not be explicitly given, but can be readily obtained if Eqs. (56), (67), and (68) are combined with Eq. (12).

We note here the resemblance between the solutions obtained for the rotational problem and those discussed by Prigogine,[4] (Chap. 1 and Appendix II), for a freely translating particle. In each case the appropriate momentum is conserved and has a continuous spectrum of eigenvalues. However, the rotational coordinate eigenvalues are discrete rather than continuous as in the case of translation in a box of infinite volume. This difference is evidently associated with the fact that configuration space has a finite volume $(8\pi^2)$ for the Eulerian angles, but can become infinite for Cartesian variables.

III. CORRELATION FUNCTIONS

A. Linear Molecule

We are now in a position to obtain an explicit expression for the propagator $W^{c}(\Gamma, t; \Gamma^{0})$. Inasmuch as the equation of motion for this function is the Liouville equation, the general solution given in Eq. (45) is applicable to $W^{c}(\Gamma, t; \Gamma^{0})$ as well as to $W(\Gamma, t)$. Indeed the two distribution functions differ only in the constants $c_{m}{}^{j}$. In the case of the propagator, these constants are determined by requiring that Eq. (17) be valid; however, the completeness property of the eigenfunctions allows us to write

$$W^{c}(\Gamma,0;\Gamma^{0})=\int\sum_{j=0}^{\infty}\sum_{m} w^{*}_{m}{}^{j}(\Gamma^{0})\,w_{m}{}^{j}(\Gamma)\,d\vec{\mathrm{L}}^{0\prime}, \tag{72}$$

where the angular momentum $\vec{\mathrm{L}}^{0\prime}$ is the common argument in the δ functions belonging to both $w^{*}_{m}{}^{j}(\Gamma^{0})$ and $w_{m}{}^{j}(\Gamma)$. Upon substitution of Eqs. (41) and (42) into Eq. (72), comparison with Eq. (45) gives

$$c_{m}{}^{j}=\sum_{r'} Y^{*}_{j,r'}(\alpha^{0},\beta^{0})\exp(ir'\phi_{\omega s}{}^{0})\,d_{r',m}{}^{j}(\theta_{\omega s}{}^{0}) \tag{73}$$

and

$$W^{c}(\Gamma,t;\Gamma^{0})=\sum_{j=0}^{\infty}\sum_{m,r,r'}\exp(im\omega^{0}t)\exp(ir'\phi_{\omega s}{}^{0})\exp(-ir\phi_{\omega s}{}^{0})$$

$$\times Y_{j,r}(\alpha,\beta)Y^{*}_{j,r'}(\alpha^0,\beta^0)d_{r,m}{}^{j}(\theta_{\omega s}{}^0)d_{r',m}{}^{j}(\theta_{\omega s}{}^0)\delta(\vec{L}-\vec{L}^0). \tag{74}$$

Of course, $\Omega_{\omega s}=\Omega_{Ls}$ and similarly for the orientations of the angular velocity and momentum vectors in the body-fixed frame.

We can now calculate angular correlation functions for the freely rotating linear molecule. In particular we will consider $\langle D_{0,0}{}^{l}(\delta\Omega(t))\rangle$. Of course, any vector of interest must lie along the internuclear axis in this case, so we are actually calculating correlations of molecular orientation. According to Eqs. (21) and (22) we first calculate a conditional average which is dependent upon the initial angular momentum and then average over an initial distribution which is just the angular Maxwell-Boltzmann function for an equilibrium ensemble:

$$W(\vec{L}^0)=(2\pi IkT)^{-1}\exp\{-[(L_x{}^0)^2+(L_y{}^0)^2]/2IkT\}\delta(L_z{}^0), \tag{75}$$

where these angular momenta are fixed in the body frame, and the δ function is included to handle the integration over the third component which is along the internuclear axis and is always zero for linear molecules. (It is interesting to note that this is a natural result of taking the limit $I_z\rightarrow 0$ in the Maxwell-Boltzmann distribution for $\vec{L}$ for a symmetric top.)

In order to calculate a conditional average using Eq. (74) it is necessary to convert angular momentum from laboratory axes to body fixed in order to utilize Eq.(75) in the average over initial variables. The shift from the space-fixed to body-fixed frame can be done at time zero to give

$$\exp(-ir\phi_{\omega s}{}^0)d_{r,m}{}^{j}(\theta_{\omega s}{}^0)=\textstyle\sum_{r''}\exp(-ir\alpha^0)d_{r,r''}{}^{j}(\beta^0)\exp(-ir''\phi_{\omega b}{}^0)d_{r'',m}{}^{j}(\theta_{\omega b}{}^0), \tag{76}$$

where $\phi_{\omega b}{}^0$, $\theta_{\omega b}{}^0$ are the azimuthal and polar angles of the angular velocity vector relative to the body-fixed axes at time zero. Furthermore one has

$$\exp(-ir\alpha^0)d_{r,r''}{}^{j}(\beta^0)=\textstyle\sum_k\exp(-ir\alpha)d_{r,k}{}^{j}(\beta)\exp(ir''\delta\alpha)d_{r'',k}{}^{j}(\delta\beta), \tag{77}$$

where $\delta\alpha$, $\delta\beta(=\delta\Omega)$ are the changes in α,β during time t. Incorporating Eqs. (76) and (77) into Eq. (74) and performing several summations (by using the closure property of the $D_{k,m}{}^{j}$), we finally obtain

$$\begin{aligned} W^{c}(\delta\Omega,\vec{L},t;\vec{L}^0)=\sum_{j}\sum_{m,r}\frac{2j+1}{4\pi}\exp(im\omega^0t)\exp(im\phi_{\omega b}{}^0)d_{0,m}{}^{j}(\theta_{\omega b}{}^0)\\ \times\exp(-ir\phi_{\omega b}{}^0)d_{r,m}{}^{j}(\theta_{\omega b}{}^0)\exp(ir\delta\alpha)d_{r,0}{}^{j}(\delta\beta)\delta(\vec{L}-\vec{L}^0). \end{aligned} \tag{78}$$

Note that this conditional distribution depends only upon the momenta and the change in orientation and is independent of initial orientation as it should be.

Carrying out the prescription of Eq. (21), we obtain

$$\langle D_{0,0}{}^{l}(\delta\Omega)\rangle_{\vec{L}^0}=\sum_{m=-l}^{+l}\exp(im\omega^0t)\{d_{0,m}{}^{l}(\theta_{\omega b}{}^0)\}^2. \tag{79}$$

This result can be further simplified if we recollect that the body-fixed angular momentum is always perpendicular to the internuclear axis of a linear molecule so that $\theta_{\omega b}{}^0=\frac{1}{2}\pi$. Thus Eq. (79) can be shown to become

$$\langle D_{0,0}{}^{l}(\delta\Omega)\rangle_{\vec{L}^0}=P_l(\cos\omega^0t), \tag{80}$$

where P_l is the lth Legendre polynomial.

The average over initial angular velocities can be performed if one writes the Maxwell-Boltzmann distribution of Eq. (75) as

$$Wd^3\omega^0=(2\pi)^{-1}\exp(-\omega^{*2}/2)\omega^*d\omega^*d\phi_{\omega b}{}^0, \quad \text{where}\quad \omega^*=(I/kT)^{1/2}\omega^0. \tag{81}$$

When Eqs. (80) and (81) are combined, it is seen that[5]

$$\langle D_{0,0}{}^{l}(\delta\Omega)\rangle=\int_0^\infty\exp(-\omega^{*2}/2)P_l(\cos\omega^*t^*)\omega^*d\omega^*, \tag{82}$$

where the reduced time variable is $t^*=(kT/I)^{1/2}t$. Using the explicit representation for the Legendre polynomial P_l given by Eq. (17) of Bateman[6] (p. 180 in Vol. 2) and performing some algebraic manipulations, Eq. (82) can be integrated in closed form, the result being

$$\langle D_{0,0}{}^{l}(\delta\Omega)\rangle = \frac{1}{2^{2l}} \sum_{m=0}^{l} \begin{bmatrix} 2m \\ m \end{bmatrix} \begin{bmatrix} 2l-2m \\ l-m \end{bmatrix} \{1-(l-2m)^2 t^{*2} \exp[-\tfrac{1}{2}(l-2m)^2 t^{*2}] M(\tfrac{1}{2},\tfrac{3}{2};\tfrac{1}{2}(l-2m)^2 t^{*2})\}. \tag{83}$$

The function $M(a,b;x)$ is Kummer's confluent hypergeometric function defined by Eq. (23) of Bateman[6] (p. 266 in Vol. 1). This expression for the correlation function of the free linear rotor can be shown to be equivalent to the one obtained by Agrawal and Yip.[7]

B. Symmetric-Top (and Spherical-Top) Molecule

Using the results of Sec. II we can obtain explicit expressions for the propagators $W^c(\Gamma', t; \Gamma'^0)$ associated with spherical- and symmetric-top molecules. The completeness property of the eigenfunctions $w_{k,m}{}^{j}(\Gamma')$ permits us to write an extended version of Eq. (72):

$$W^c(\Gamma', 0; \Gamma'^0) = \int \sum_{j=0}^{\infty} \sum_{k,m} w^{*}_{k,m}{}^{j}(\alpha^0, \beta^0, \gamma^{0\prime}, L_\xi{}^0, L_\eta{}^0, L_z{}^0) w_{k,m}{}^{j}(\alpha, \beta, \gamma', L_\xi, L_\eta, L_z) dL_\xi{}^{0\prime} dL_\eta{}^{0\prime} dL_z{}^{0\prime}. \tag{84}$$

Pursuing the same line of argument as in the linear molecule case, but using Eqs. (52) and (66) for the eigenfunctions rather than Eqs. (41) and (42), we find

$$c_{k,m}{}^{j} = [(2j+1)/8\pi^2]^{\frac{1}{2}} \sum_r D^{*}_{k,r}{}^{j}(\Omega^0) \exp(ir\phi_L{}^0) d_{r,m}{}^{j}(\theta_L{}^0), \tag{85}$$

where, as earlier, the angles $\phi_L{}^0$, $\theta_L{}^0$ denote the orientation of $\vec{L}$ in the precessing frame. When Eq. (85) is substituted into the general expression for the propagator, the result can be written as

$$W^c(\Gamma', t; \Gamma'^0) = \sum_{j=0}^{\infty} \sum_{k,m} \sum_{r,r'} \frac{2j+1}{8\pi^2} \exp(imL^0 t/I) \exp[i(r\phi_L{}^0 - r'\phi_L)]$$

$$\times D^{*}_{k,r}{}^{j}(\Omega'^0) D_{k,r'}{}^{j}(\Omega') d_{r,m}{}^{j}(\theta_L{}^0) d_{r',m}{}^{j}(\theta_L{}^0) \delta(L_\xi - L_\xi{}^0) \delta(L_\eta - L_\eta{}^0) \delta(L_z - L_z{}^0). \tag{86}$$

This expression can be shortened somewhat by employing the changes in Eulerian angles, $\delta\Omega$, instead of Ω. A slightly generalized version of Eq. (77) will give

$$\sum_k D^{*}_{k,r}{}^{j}(\Omega^0) D_{k,r'}{}^{j}(\Omega'(t)) = D_{r,r'}{}^{j}(\delta\Omega') = D_{r,r'}{}^{j}(\delta\Omega) \exp(ir'\omega_p t). \tag{87}$$

The equality on the right appears when we switch from the precessing frame to the molecule-fixed frame. Observe that the precessing frame is taken to be coincident with the body-fixed frame at $t = 0$.

In calculating angular correlation functions for a symmetric-top molecule, we must treat the case where the vector of interest is not coincident with the symmetry axis of the molecule, but has (constant) azimuthal and polar angles Φ, Θ in the body-fixed frame. Denoting the orientation of this vector at time t in the laboratory axes by $\Omega_v(t)$, one has

$$D_{r,0}{}^{j}(\Omega_v(t)) = \sum_{r'} D_{r,r'}{}^{j}(\Omega(t)) D_{r',0}{}^{j}(\Phi, \Theta), \tag{88}$$

where $\Omega(t)$ denotes, as usual, the orientation of the principal axes of the molecule. Suppose now we wish to evaluate the correlation function $\langle D_{0,0}{}^{l}\rangle$ with argument $\delta\Omega_v$, the change in orientation of the vector of interest in time t. One has

$$D_{0,0}{}^{l}(\delta\Omega_v) = \sum_k D^{*}_{k,0}{}^{l}(\Omega_v(0)) D_{k,0}{}^{l}(\Omega_v(t)) = \sum_{k,r,r'} D^{*}_{k,r}{}^{l}(\Omega^0) D^{*}_{r,0}{}^{l}(\Phi, \Theta) D_{k,r'}{}^{l}(\Omega(t)) D^{*}_{r',0}{}^{l}(\Phi, \Theta). \tag{90}$$

With the aid of Eq. (87) this becomes

$$D_{0,0}{}^{l}(\delta\Omega_v) = \sum_{r,r'} D_{r,r'}{}^{l}(\delta\Omega) D_{r,0}{}^{l}(\Phi, \Theta) D^{*}_{r',0}{}^{l}(\Phi, \Theta) \exp(ir'\omega_p t). \tag{91}$$

In contrast to the linear molecule case, Eq. (86) for the symmetric-top propagator will give conditional averages directly in terms of the body-fixed angular momenta, which appear in the Maxwell-Boltzmann distributions for these rotors. In fact, Eqs. (86) and (91) can be combined, and integrations over $\vec{L}$ and $\delta\Omega$ performed to give

$$\langle D_{0,0}{}^{l}(\delta\Omega_v)\rangle_{\vec{L}^0} = \sum_{m,m',m''} \exp(imL^0t/I)\exp(im''\omega_p t)\exp[i(m'-m)\phi_L{}^0]$$

$$\times d_{m'm}{}^{l}(\theta_L{}^0)\,d_{m'',m}{}^{l}(\theta_L{}^0)\exp[i(m'-m'')\Phi]\,d_{m',0}{}^{l}(\Theta)\,d_{m'',0}{}^{l}(\Theta)\,. \tag{92}$$

In order to complete this calculation, the initial distribution of angular momentum is required. In an equilibrium ensemble this can be written as

$$W(\vec{L}^0) = \frac{1}{(2\pi kT)^{3/2} I (I_z)^{1/2}} \exp\left\{-\frac{1}{2kT}\left[\frac{(L^0)^2}{I} + \left(\frac{1}{I_z} - \frac{1}{I}\right)(L^0)^2 x^2\right]\right\} \quad , \tag{93}$$

where $x = \cos\theta_L{}^0$. In Eq. (92) the average over $\phi_L{}^0$ is trivial, and gives (after dropping the superscript 0)

$$\langle D_{0,0}{}^{l}(\delta\Omega_v)\rangle = [(b+1)/2\pi]^{\frac{1}{2}} \sum_{m,m'} d_{m',0}{}^{l}(\Theta)\,d_{m'0}{}^{l}(\Theta)$$

$$\times \int_{-1}^{+1}\int_0^{\infty} \exp[-\tfrac{1}{2}(1+bx^2)(L^*)^2]\,\exp[i(m+m'bx)L^*t^*]\,d_{m',m}{}^{l}(x)\,d_{m',m}{}^{l}(x)(L^*)^2\,dL^*\,dx\,, \tag{94}$$

where $\quad L^* = L^0/(IkT)^{1/2}, \quad t^* = (kT/I)^{1/2}t, \quad b = I/I_z - 1\,.$ (95)

It is possible to analytically integrate this equation with respect to the L^* variable. The integrated expressions are given in Appendix B for the cases $l = 1$ and 2. The integrations over x from -1 to $+1$ must then be carried out on the computer. In this work, calculations were performed for several values of the parameter b and the reduced time t^*.

The parameter b is defined in the range $-\frac{1}{2} \leqslant b < \infty$ (and is the negative of the parameter c employed by Agrawal and Yip[7]). The limit $b = -\frac{1}{2}$ is obtained when $I_z = 2I$ implying that the molecule has the shape of a flat disk; we obtain the other limit $b \to \infty$ when the symmetric top approaches the linear rotor ($I_z = 0$). If this latter limit $b \to \infty$ (or, equivalently $I_z \to 0$) is taken in the expression for the correlation function given by Eq. (94), the linear-rotor result is obtained, i.e., Eq. (82), if this limit is taken before any integrations over L^* or x are performed (otherwise the expression takes on an indefinite form). As a separate consideration, it must also be remembered that $m' = 0$ in Eq. (94), since $\Theta = 0$ in a linear rotor.

When $b = 0$, the equations of Appendix B reduce to the expressions obtained by Steele[8] who derived correlation functions for a spherical molecule by first directly integrating the equations of motion for the angular velocity β, and then averaging $\cos\beta$ and $(\frac{3}{2}\cos^2\beta - \frac{1}{2})$ over the initial distribution. As expected these correlation functions become independent of the polar angle Θ because of spherical symmetry.

IV. DISCUSSION

The conditional distribution functions derived here for a classical ensemble of freely rotating molecules can be used in a variety of problems.[9,10] Although the assumption of free rotation is not strictly correct in any physical system, one can use this model to describe not only the behavior of molecules in gases at low densities, but also in some liquids. When the full Liouville operator is written out, it is apparent that the potential energy terms omitted here involve the torques on the molecules of the system. If the angle dependence of the intermolecular interactions is small so that torques are small, and if molecular moments of inertia are large, rotational motion can be described as "inertial" even in dense fluids[8,11]; in this case, the angular momenta undergo small fluctuations about their initial values as the time variable evolves, and a free rotation treatment is a good approximation to the actual situation, at least for time intervals that are not too long.

Many kinds of experimental data have been expressed in terms of angular correlation functions. Nuclear and electronic spin relaxation times in liquids[12] were among the earliest to be treated in this way, and it is well known[13] that dipole-dipole interactions of pairs of spins on the same molecule and quadrupole-electric field gradient couplings give rise to relaxations expressible in terms of angular correlation functions of rank 2; that is, the problem involves expressions of the form of Eq. (94) with $l=2$. The inertial (or free rotational) model has previously been applied to this problem only for spherical top molecules,[14,15] and the results obtained here for the symmetric top can be used in a significant generalization of this approach. Since these relaxation times are often inversely proportional to the integral of the correlation function over all times, it is necessary to somehow treat the loss of correlation occurring at long times. (Among other difficulties, angular correlation functions for free rotors generally approach a constant, nonzero value as $t \to \infty$; unless correlation is somehow destroyed, the integrals of such functions are clearly infinite.) Such difficulties can be overcome merely by approximating the function as a Gaussian in time.[8] The evaluation of the constant in the Gaussian is straightforward; if one has a function $f(t)$ normalized to unity at $t=0$, which is represented by $\exp(-at^2/2)$, the constant a is given by

$$a = (d^2f/dt^2)_{t=0} . \tag{96}$$

In fact, the Gaussian approximations to the angular correlation functions for a symmetric top are particularly convenient. In the cases of $l=1,2$, Eqs. (B.2)–(B.6) and (B.8)–(B.20) are differentiated twice with respect to time. When the time variable is set equal to zero in the results, the integrations over x can be analytically performed to give the desired constants. With the aid of Eqs. (B.1) and (B.7), one eventually finds

$$\langle\cos\delta\beta_v(t)\rangle$$

$$= \sin^2\Theta \exp(-At^{*2}) + \cos^2\Theta \exp(-t^{*2}) , \tag{97}$$

$$\text{where } A = (2+3b+b^2)/2(1+b) \tag{98}$$

and

$$\langle \tfrac{3}{2}\cos^2\delta\beta_v(t) - \tfrac{1}{2}\rangle = \tfrac{3}{4}\sin^4\Theta \exp(-Bt^{*2})$$

$$+ 3\cos^2\Theta \sin^2\Theta \exp(-Ct^{*2})$$

$$+ \tfrac{1}{4}(3\cos^2\Theta - 1)^2 \exp(-3t^{*2}) , \tag{99}$$

$$\text{where } B = (3+5b+2b^2)/(1+b) , \tag{100}$$

$$C = (6+7b+b^2)/2(1+b) . \tag{101}$$

The behavior in time of $\langle D_{0,0}{}^1(\delta\Omega_v)\rangle$ is shown graphically in Fig. 1 for the following situation: $b=-0.365$ and $\Theta = 68°$. Curve 1 is the numerical result based on Eqs. (B.1)–(B.6); curve 2 is the Gaussian approximation based on Eqs. (97) and (98); and curve 3 is the result of Agrawal and Yip.[7] For long times ($t^* \to \infty$) curve 1 approaches the time-independent constant $\cos^2\Theta[(b+1)^{1/2}/2]Z_5$ [(cf. Eqs. (B.1) and (B.6)] which equals 0.056.

Figure 1 shows that there is a considerable discrepancy between the correlation function as calculated in this work and that obtained by Agrawal and Yip.[7] In our notation, their result can be written as

$$\langle D_{0,0}{}^1(\delta\Omega_v(t^*))\rangle = \cos^2\Theta g(t^*)$$

$$+ \tfrac{1}{2}\sin^2\Theta \exp[(b/2)t^{*2}][1+g(t^*)] , \tag{102}$$

where $g(t^*)$ is the correlation function for a linear molecule. Their derivation consists in an evaluation of the classical limit of the exact quantum-mechanical correlation function. In doing so, these authors correctly treated the expressions in the limit of large values of the quantum number J, but unfortunately only considered small values of the projection quantum number K. Although this procedure may be allowable for an almost linear molecule, it is clearly in error as the molecule approaches spherical-top behavior, since all values of K between $+J$ and $-J$ are equally probable in this case. Among other defects, Eq. (102) predicts that the correlation function for a spherical top ($b=0$) is still dependent upon the angle Θ; however, the orientation of the principal axes (and thus Θ) is arbitrary for the spherical top.

More curves illustrating the behavior of $\langle\cos\delta\Omega_v(t^*)\rangle$ with time are shown in Fig. 2. Curve 1 is the computer result based on Eqs.

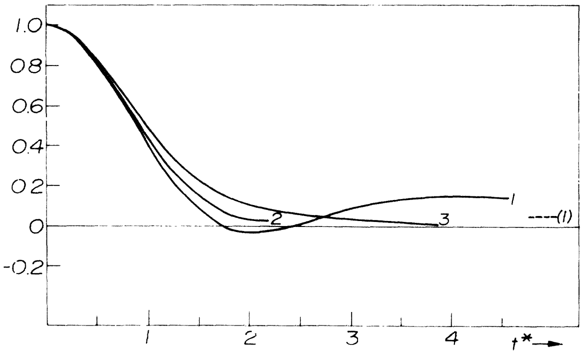

FIG. 1. Rotational correlation function $\langle D_{0,0}{}^1\rangle$ for a symmetric molecule corresponding to $b=-0.365$ and $\Theta=68°$. Curve 1 is the numerical result obtained using Eqs. (B.1)–(B.6). Curve 2 is the Gaussian approximation based on Eqs. (97) and (98). Curve 3 is the result of Agrawal and Yip. The dashed line is the asymptotic value (0.056) approached by curve 1 as $t^* \to \infty$.

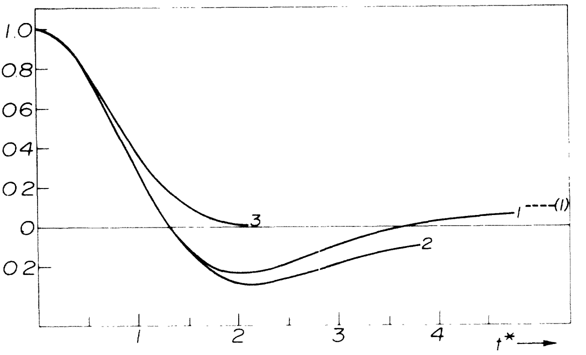

FIG. 2. Rotational correlation function $\langle D_{0,0}^{1}\rangle$. Curve 1 is the numerical result for a symmetric molecule corresponding to $b = 10$ and $\Theta = 0$ using Eqs. (B.1)–(B.6). The dashed line is the asymptotic value (0.096) approached by curve 1 as $t^* \rightarrow \infty$. Curve 2 is the time correlation function for a linear molecule. Curve 3 is the Gaussian approximation to curve 1 using Eqs. (97) and (98).

(B.1)–(B.6) with $\Theta = 0$ and $b = 10$. This value of the parameter b indicates that the molecule is almost linear (in fact, that $I = 11I_z$). The asymptotic value approached by curve 1 as $t \rightarrow \infty$ is equal to 0.096 and indicated by the dashed line in the figure. Curve 2 is the classical correlation function for the linear rotor, which was seen to agree with the results of Agrawal and Yip[7] and Sears.[16] These curves both show a pronounced dip below zero; this dip disappears as the molecule becomes more spherical (see Fig. 1) and presumably is to be associated with the rapid precessional velocities found in nearly linear molecules. Curve 3 is the Gaussian approximation to curve 1, and shows two important differences from the exact curves: It does not dip below zero, and it vanishes at long times. Certainly the effects of collisions which are omitted here will cause the correlation functions for real systems to vanish as $t^* \rightarrow \infty$, but there is no reason to suppose that the dip in curve 1 is physically unreal. Thus it appears that the Gaussian approximation will not always reproduce the features of interest, especially for correlation functions of linear or nearly linear molecules.

The time behavior of $\langle \frac{3}{2}\cos^2\delta\beta_v - \frac{1}{2}\rangle$ is illustrated in Fig. 3. Curve 1 is the numerical result based on Eqs. (B.7)–(B.20) for the parameters $b = -0.365$, $\Theta = 68°$; curve 2 is the corresponding Gaussian approximation using Eqs. (99)–(101) and curve 3 is the numerical result for $b = 10$, $\Theta = 0$. The Gaussian approximation to curve 3 closely follows the numerical result for $t^* \lesssim 1$, and so was omitted from the figure. The numerical results of curves 1 and 3 are based on Eqs. (B.7)–(B.20). The time-independent constant approached by each for long times is $\frac{1}{4}(3\cos^2\Theta - 1)Y_{13}$ [cf. Eq. (B.20)] which equals 0.018 for curve 1 and 0.186 for curve 3.

In addition to the magnetic relaxation times, which are dependent upon correlation functions with $l = 2$, neutron scattering cross sections can be expressed in terms of a sum of correlation functions over all values of l. Since this application is discussed in detail by Agrawal and Yip,[7] we will not consider it further here. Another rather important application of this formalism is in the evaluation of rotational band envelopes in infrared[17–19] and Raman[17,20] spectroscopy. For example, shapes of vibrational infrared lines for symmetric tops are given by Fourier transforms of correlation functions with $l = 1$, and with Θ denoting the angle between the vibrational transition moment vector and the principal axis of the molecule. Similarly, depolarized Raman band shapes are observed by inelastic light scattering,[21,22] and are the Fourier transforms of correlations of the anisotropic part of the molecular polarizability tensor (angular functions with $l = 2$). Alternately, one can inversely transform experimentally measured bands to obtain correlation functions. Comparison of such functions with calculations such as those presented here for the free rotor can then be used (and are presently being used) to obtain information about the time dependence and magnitudes of the intermolecular torques on the molecules of the system.[23,24]

Finally, it might be noted that Prigogine and co-workers[4] have developed a quite rigorous approach to the nonequilibrium statistical mechanics of monatomic systems which is based on the application of perturbation theory to the eigenvalues and eigenfunctions of the classical Liou-

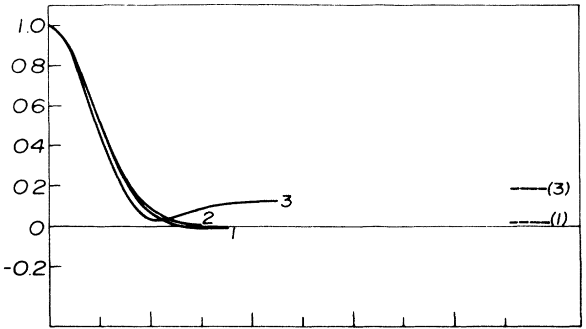

FIG. 3. Rotational correlation function $\langle D_{0,0}^{2}\rangle$. Curve 1 is the numerical result for a symmetric molecule corresponding to $b = -0.365$ and $\Theta = 68°$, obtained using Eqs. (B.7)–(B.20). Curve 2 is the Gaussian approximation to curve 1 based on Eqs. (99)–(101). Curve 3 is the numerical result for a symmetric molecule corresponding to $b = 10$ and $\Theta = 0$. Curves 1 and 3 approach the asymptotic values (0.018) and (0.186), respectively, for long times.

ville operator for free particles. If one were to attempt to extend this approach to more complex molecules with rotational degrees of freedom, it is evident that the corresponding eigenfunctions for the potential-free rotational Liouville operator will be needed as basis functions. The results derived here can thus be viewed as the first step in such a treatment, at least for linear and symmetric-top molecules.

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APPENDIX A

In this appendix we will prove the properties of orthogonality and completeness first for the set of functions $w_m{}^j(\Gamma)$ belonging to the linear rotor, and then for the corresponding set $w_{k,m}{}^j(\Gamma)$ of the symmetric-top molecule.

Reverting to Eq. (43) and denoting the left-hand side as F_1, we can write

$$F_1 = \int \sum_{r,r'} Y^*_{j',r'}(\Omega) D^{*\,j'}_{r',m'}(\phi_{\omega s}{}^0, \theta_{\omega s}{}^0, \psi) Y_{j,r}(\Omega) D_{r,m}{}^j(\phi_{\omega s}{}^0, \theta_{\omega s}{}^0, \psi) \delta(\vec{\mathrm{L}} - \vec{\mathrm{L}}^0) \delta(\vec{\mathrm{L}} - \vec{\mathrm{L}}^{0\prime}) d\Omega\, dL_X\, dL_Y\, dL_Z \,. \tag{A1}$$

Of course, the space-fixed polar and azimuthal angles of the $\vec{\omega}$ and $\vec{\mathrm{L}}$ vectors are identical. Orthogonality of the spherical harmonics yields

$$\int Y^*_{j',r'}(\Omega) Y_{j,r}(\Omega) d\Omega = \delta_{r,r'} \delta_{j,j'} \,. \tag{A2}$$

We then obtain, in turn, that

$$\sum_r D^{*\,j}_{r,m'}(\phi_{\omega s}{}^0, \theta_{\omega s}{}^0, \psi) D_{r,m}{}^j(\phi_{\omega s}{}^0, \theta_{\omega s}{}^0, \psi) = \delta_{m,m'} \tag{A3}$$

and $\int \delta(\vec{\mathrm{L}} - \vec{\mathrm{L}}^0) \delta(\vec{\mathrm{L}} - \vec{\mathrm{L}}^{0\prime}) d\vec{\mathrm{L}} = \delta(\vec{\mathrm{L}}^0 - \vec{\mathrm{L}}^{0\prime})$. (A4)

Incorporating Eqs. (A. 2), (A. 3), and (A. 4) into Eq. (A. 1) we finally obtain

$$F_1 = \delta_{j,j'} \delta_{m,m'} \delta(\vec{\mathrm{L}}^0 - \vec{\mathrm{L}}^{0\prime}) \,. \tag{A5}$$

Revert now to Eq. (44) and denote the left-hand side by F_2. We then have that

$$F_2 = \int \sum_{j=0}^{\infty} \sum_{m,r,r'=-j}^{+j} Y^*_{j,r'}(\Omega_1) D^{*\,j}_{r',m}(\Omega_{\omega s1}, \psi) Y_{j,r}(\Omega_2) D_{r,m}{}^j(\Omega_{\omega s2}, \psi) \delta(\vec{\mathrm{L}}_1 - \vec{\mathrm{L}}^0) \delta(\vec{\mathrm{L}}_2 - \vec{\mathrm{L}}^0) \sin\beta_1 dL^0 \,. \tag{A6}$$

If we first integrate over the momentum variables, the angular arguments $\Omega_{\omega s1}$ and $\Omega_{\omega s2}$ become equal, which permits us to write

$$\sum_{m=-j}^{+j} D^{*\,j}_{r',m}(\Omega_{\omega s1}, \psi) D_{r,m}{}^j(\Omega_{\omega s1}, \psi) = \delta_{r',r} \,. \tag{A7}$$

Furthermore using the completeness relation

$$\sum_{j=0}^{\infty} \sum_{r=-j}^{+j} Y^*_{j,r}(\Omega_1) Y_{j,r}(\Omega_2) = \delta(\alpha_1 - \alpha_2) \delta(\cos\beta_1 - \cos\beta_2) \,, \tag{A8}$$

we can write that

$$F_2 = \delta(\alpha_1 - \alpha_2) \delta(\beta_1 - \beta_2) \delta(\vec{\mathrm{L}}_1 - \vec{\mathrm{L}}_2) \tag{A9}$$

or $F_2 = \delta(\alpha_1 - \alpha_2) \delta(\beta_1 - \beta_2) \delta(p_{\alpha 1} - p_{\alpha 2}) \delta(p_{\beta 1} - p_{\beta 2}) \{\delta(p_{\gamma 1})\}$. (A10)

There remains to be proved the orthogonality and completeness properties for the eigenfunctions $w_{k,m}{}^{j}(\Gamma)$ of the symmetric-top molecule as given by Eqs. (69) and (70). The procedure followed is similar to that given by Eqs. (A. 1)–(A. 10) for the linear rotor, and so will not be repeated in depth. It is sufficient to point out that in place of Eqs. (A. 2) and (A. 8), we use, respectively,

$$\int D^{*}_{k',r'}{}^{j'}(\alpha,\beta,\gamma')D_{k,r}{}^{j}(\alpha,\beta,\gamma')\,d\alpha\,\sin\beta d\beta d\gamma' = \delta_{j,j'}\delta_{k,k'}\delta_{r,r'}(8\pi^2)/(2j+1) \tag{A11}$$

and

$$\sum_{j=0}^{\infty}\ \sum_{k,m=-j}^{+j} \frac{2j+1}{8\pi^2} D^{*}_{k,m}{}^{j}(\alpha_1,\beta_1,\gamma_1')D_{k,m}{}^{j}(\alpha_2,\beta_2,\gamma_2') = \delta(\alpha_1-\alpha_2)\delta(\cos\beta_1-\cos\beta_2)\delta(\gamma_1'-\gamma_2')\,. \tag{A12}$$

Furthermore since the functions $w_{k,m}{}^{j}(\Gamma')$ for the symmetric-top molecule can be specialized to include the case of the spherical top, proofs for this case need not be given.

APPENDIX B

Restricting ourselves here to the special cases $l=1,2$, the result of carrying out the L^* integration for $l=1$ in Eq. (94) can be written as

$$\langle\cos\delta\beta_v(t^*)\rangle = \sin^2\Theta(b+1)^{1/2}\tfrac{1}{8}(Z_1+Z_2+Z_3)+\cos^2\Theta(b+1)^{1/2}\tfrac{1}{2}(Z_4+Z_5)\,, \tag{B1}$$

where

$$Z_1 = \int_{-1}^{+1}(1+x)^2U^{-5/2}[U-(1+bx)^2t^{*2}]\exp[-t^{*2}(1+bx)^2/2U]\,dx\,, \tag{B2}$$

$$Z_2 = 2\int_{-1}^{+1}(1-x^2)U^{-5/2}[U-b^2x^2t^{*2}]\exp[-b^2x^2t^{*2}/2U]\,dx\,, \tag{B3}$$

$$Z_3 = \int_{-1}^{+1}(1-x)^2U^{-5/2}[U-(1-bx)^2t^{*2}]\exp[-t^{*2}(1-bx)^2/2U]\,dx\,, \tag{B4}$$

$$Z_4 = \int_{-1}^{+1}(1-x^2)U^{-5/2}[U-t^{*2}]\exp[-t^{*2}/2U]\,dx\,, \tag{B5}$$

$$\begin{aligned} Z_5 &= -2/b(1+b)^{1/2}+(2/b^{3/2})\ln[(1+b)^{1/2}+b^{1/2}]\,, &&\text{if } b>0\,,\\ &= 2/a(1-a)^{1/2}-(2/a^{3/2})\sin^{-1}a^{1/2}\,, &&\text{if } b<0\,, \end{aligned} \tag{B6}$$

and where $a=|b|$, $U=1+bx^2$. For the case when $l=2$, the correlation function becomes

$$\begin{aligned}\langle\tfrac{3}{2}\cos^2\delta\beta_v(t^*)-\tfrac{1}{2}\rangle &= \sin^4\Theta(1+b)^{1/2}\tfrac{3}{8}(Y_1+Y_2+Y_3+Y_4+Y_5)\\ &\quad+\cos^2\Theta\,\sin^2\Theta\,(1+b)^{1/2}\tfrac{3}{2}(Y_6+Y_7+Y_8+Y_9+Y_{10})+(3\cos^2\Theta-1)^2(1+b)^{1/2}\tfrac{1}{4}(Y_{11}+Y_{12}+Y_{13})\,,\end{aligned} \tag{B7}$$

where

$$Y_1 = \int_{-1}^{+1}[(1+x)/2]^4U^{-5/2}[U-4(1+bx)^2t^{*2}]\exp[-4(1+bx)^2t^{*2}/2U]\,dx\,, \tag{B8}$$

$$Y_2 = \int_{-1}^{+1}\tfrac{1}{4}(1-x^2)(1+x)^2U^{-5/2}[U-(1+2bx)^2t^{*2}]\exp[-(1+2bx)^2t^{*2}/2U]\,dx\,, \tag{B9}$$

$$Y_3 = \int_{-1}^{+1}(1-x^2)^2(\tfrac{3}{8})U^{-5/2}(U-4b^2x^2t^{*2})\exp(-4b^2x^2t^{*2}/2U)\,dx\,, \tag{B10}$$

$$Y_4 = \int_{-1}^{+1}\tfrac{1}{4}(1-x^2)(1-x)^2U^{-5/2}[U-(1-2bx)^2t^{*2}]\exp[-(1-2bx)^2t^{*2}/2U]\,dx\,, \tag{B11}$$

$$Y_5 = \int_{-1}^{+1}[(1-x/2)]^4U^{-5/2}[U-4(1-bx)^2t^{*2}]\exp[-4(1-bx)^2t^{*2}/2U]\,dx\,, \tag{B12}$$

$$Y_6 = \int_{-1}^{+1}\tfrac{1}{4}(1-x^2)(1+x)^2U^{-5/2}[U-(2+bx)^2t^{*2}]\exp[-(2+bx)^2t^{*2}/2U]\,dx\,, \tag{B13}$$

$$Y_7 = \int_{-1}^{+1}\tfrac{1}{4}(1-x-2x^2)^2U^{-5/2}[U-(1+bx)^2t^{*2}]\exp[-(1+bx)^2t^{*2}/2U]\,dx\,, \tag{B14}$$

$$Y_8 = \int_{-1}^{+1}\tfrac{3}{2}x^2(1-x^2)U^{-5/2}(U-b^2x^2t^{*2})\exp(-b^2x^2t^{*2}/2U)\,dx\,, \tag{B15}$$

$$Y_9 = \int_{-1}^{+1}\tfrac{1}{4}(1+x-2x^2)^2U^{-5/2}[U-(1-bx)^2t^{*2}]\exp[-(1-bx)^2t^{*2}/2U]\,dx\,, \tag{B16}$$

$$Y_{10} = \int_{-1}^{+1} \tfrac{1}{4}(1 - x^2)(1 - x)^2 U^{-5/2}[U - (2 - bx)^2 t^{*2}] \exp[- 2 - bx)^2 t^{*2}/2U]\, dx\,, \tag{B17}$$

$$Y_{11} = \int_{-1}^{+1} \tfrac{3}{8}(1 - x^2)^2 U^{-5/2} (U - 4t^{*2}) \exp(- 4t^{*2}/2U)\, dx\,, \tag{B18}$$

$$Y_{12} = \int_{-1}^{+1} \tfrac{3}{2}(1 - x^2)x^2\, U^{-5/2} (U - t^{*2}) \exp(- t^{*2}/2U)\, dx\,, \tag{B19}$$

$$\begin{aligned} Y_{13} &= \frac{(2b^2 + 21b + 27)}{8b^2(1 + b)^{1/2}} - \frac{(6.75 + 3b)}{2b^2(b)^{1/2}} \ln[(1 + b)^{1/2} + b^{1/2}]\,, \quad \text{if } b > 0 \\ &= \frac{(2a^2 - 21a + 27)}{8a^2(1 - a)^{1/2}} + \frac{1.5}{a^2(a)^{1/2}} (a - 2.25) \sin^{-1} a^{1/2}\,, \quad \text{if } b < 0\,. \end{aligned} \tag{B20}$$

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