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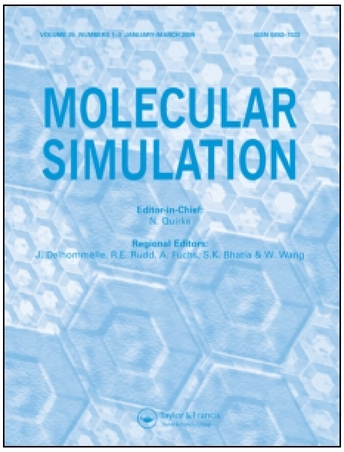

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REORIENTATIONAL CORRELATION FUNCTIONS, QUATERNIONS AND WIGNER ROTATION MATRICES

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The main results of this paper are tabulations of Wigner rotation matrix elements in terms of quaternion parameters and direction cosines. These will be useful for the calculation of orientational probability functions or reorientational correlation functions from simulations of molecular systems using programs based either on quaternions or constraints. We review the relationship between quaternions and the $L = \frac{1}{2}$ Wigner rotation matrix, give some useful properties of quaternions and Wigner rotation matrices and show how the Lth Wigner rotation matrix can be constructed from the quaternion parameters without first obtaining the Euler angles.

KEY WORDS: Wigner rotation matrix, quaternions, direction cosines, reorientational correlation functions.

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1. INTRODUCTION

In simulations of molecular liquids one often wishes to calculate reorientational correlation functions, C_k^L to compare with theories of reorientational motion and with experimental spectroscopic line shapes or NMR relaxation rates. It is not universally realised how easily these functions may be constructed either directly from quaternion parameters or from the atomic positions generated by a constraint algorithm. The purpose of this paper is to give these simple relationships and the main results are presented in tabular form. First we review different methods of describing the orientation of molecules in terms of Euler angles, quaternions, Cayley-Klein parameters and Wigner rotation matrices and exhibit the close relation between the four numbers forming a quaternion, the four Cayley-Klein parameters and the four elements of the $L = \frac{1}{2}$ Wigner rotation matrix [1]. The representation of the probability of orientation and the probability of reorientation in time t can be expanded in terms of complete set of Wigner rotation matrices and we show how these can be built up from quaternion parameters.

2. REPRESENTATION OF MOLECULAR ORIENTATION

In order to specify the orientation of a non-linear molecule relative to a given axis system (such as the "laboratory axes") three parameters are needed. The most familiar way to do this is to state three Euler angles (α, β, γ). Unfortunately there are different conventions in use for defining these angles. First, one may rotate either the molecule relative to a fixed axis system (active convention) or the system of coordinates relative to the molecule (passive convention). We shall use the active convention. Secondly the axis about which the second rotation is made can be taken to be the x

axis (Goldstein convention [2]) or the y axis (Whittaker convention [3]). We use the latter convention, as do Brink and Satchler [4], Rose [5], and Gray and Gubbins [6]; but it must be emphasised that Evans followed the convention of Goldstein when he introduced the idea of quaternion parameters to the molecular simulation community [7, 8] and Allen and Tildesley [9] give his expressions. Fortunately the two conventions are quite easily related: if the angles α_G, β_G, γ_G represent a rotation in the Goldstein convention and α_W, β_W, γ_W the same rotation in the Whittaker convention, then

$$\begin{aligned}\alpha_G &= \alpha_W + \pi/2\\ \beta_G &= \beta_W\\ \gamma_G &= \gamma_W - \pi/2.\end{aligned}$$

We shall use the greek symbols χ, ξ, η, ζ for the quaternion parameters generated by a program using the equation of motion of Evans [7] and Evans and Murad [8]. Pawley also uses quaternions to describe molecular orientation [9], but the parameters coming from his programs correspond directly to the four numbers (q_0, q_1, q_2, q_3) forming the quaternion describing the rotation.

We define Euler angles in the following way: suppose that initially a set of axes (X, Y, Z) in a molecule coincide with a set of laboratory axes (x, y, z). Rotate the molecule by α in a right handed sense about the Z axis (i.e. in the direction of the fingers if the right hand thumb is pointing along the Z direction); rotate the molecule by β about the current Y axis; finally rotate the molecule by γ about the current Z axis. The final position is described by the Euler angles (α, β, γ). The same result can be achieved by performing the rotations in the reverse order about the z, y and z axes in the laboratory system Euler's theorem states that any general displacement of a rigid body may be described by a translation of the centre of mass together with a single rotation about some axis through the centre of mass. We shall define the angle of this single rotation as ψ and the direction of the axis by the unit vector $\boldsymbol{\lambda}$, and use the notation $R(\psi\boldsymbol{\lambda})$ to describe this rotation. It is often necessary to transform between molecular and laboratory coordinate systems. For instance a function $f_M(\theta,\phi)$, expressed in terms of coordinates θ, ϕ that are measured with respect to a coordinate system fixed in the molecule, will be unchanged as the molecule rotates, because the coordinate system and the function both rotate together. However the description of the same function using laboratory coordinates will change as the molecule rotates. The function in laboratory coordinates can be written as

$$f_L(\theta,\phi) = \hat{R}f_M(\theta,\phi), \tag{1}$$

where θ and ϕ are now referred to the laboratory coordinates and $\hat{R}$ is the operator that describes the rotation of the molecule from a reference orientation. We may write $\hat{R}$ more explicitly as $\hat{R}(\alpha, \beta, \gamma)$ or $\hat{R}(\psi\ \boldsymbol{\lambda})$ to emphasize the dependence on the Euler angles or the angle and axis of rotation. If $\hat{J}_\lambda$ is the infinitesimal rotation operator for rotations about the axis $\boldsymbol{\lambda}$, then

$$\hat{R}(\psi\boldsymbol{\lambda}) = exp(-i\psi\hat{J}_\lambda) = \exp(-i\psi\hat{\boldsymbol{J}}\cdot\boldsymbol{\lambda}),$$

and, if we recall that $\hat{R}(\alpha, \beta, \gamma)$ is a sequence of rotations about the y and z axes, we see that

$$\hat{R}(\alpha, \beta, \gamma) = exp(-i\alpha\hat{J}_z)exp(-i\beta\hat{J}_y)exp(-i\gamma\hat{J}_z).$$

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In particular, if we rotate a spherical harmonic Y^L_k in this way, the rotated function (which is still Y^L_k in molecular axes) becomes in laboratory axes a linear combination of spherical harmonics with the same L:

$$
\begin{aligned}
\hat{R}|Y^L_k> &= \sum_m |Y^L_m\rangle\langle Y^L_m| \hat{R} | Y^L_k\rangle \\
&= \sum_m Y^L_m \, D^L_{mk}(\alpha, \beta, \gamma)
\end{aligned}
$$

so that

$$
Y^L_k \text{ (mol axes)} = \sum_m Y^L_m \text{ (lab axes) } D^L_{mk} \tag{2}
$$

The set of unitary $(2L + 1) \times (2L + 1)$ matrices $D^L(\alpha, \beta, \gamma)$ are known as the Wigner rotation matrices [4, 5]. The simplest of these is the 2×2 $D^{\frac{1}{2}}$ matrix

$$
\begin{array}{cc|cc}
 & \mathrm{k} = & \frac{1}{2} & -\frac{1}{2} \\
\mathrm{m} = & \frac{1}{2} & A & B \\
 & -\frac{1}{2} & -B^* & A^*
\end{array} \tag{4}
$$

where A and B are complex functions of α, β, γ which, as the matrix is unitary, satisfy

$$
AA^* + BB^* = 1. \tag{5}
$$

This matrix is the rotation matrix for spinors (spin $\frac{1}{2}$ particles). We shall show how all other Wigner rotation matrices may be constructed from the functions A and B.

The instantaneous orientation of a molecule could be specified by the current values of any of the Wigner rotation matrices, but this would contain redundant information as only three rather than $(2L + 1)^2$ parameters are needed. The most economical way to do it is to use the four parameters of the $L = \frac{1}{2}$ matrix together with condition (5). Another set of parameters used to describe the orientation of a rigid body are the four Cayley-Klein parameters [2, 3] $(\alpha, \beta, \gamma, \delta)$ which are identical to $(A^*, B^*, -B, A)$. The Cayley-Klein parameters α, β, γ are, of course, quite different from the Euler angles α, β, γ.

The connection between the $L = \frac{1}{2}$ Wigner matrix and the quaternion description of orientation can be found by expanding the matrix as

$$
\boldsymbol{D}^{\frac{1}{2}} = A_r\boldsymbol{I} - B_i\boldsymbol{i} - B_r\boldsymbol{j} - A_i\boldsymbol{k} \tag{6}
$$

where $\boldsymbol{I}$ is the 2×2 unit matrix, A_r and A_i are the real and imaginary parts of A respectively, and the 2×2 matrices $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ are

$$
\boldsymbol{i} = \begin{pmatrix} 0 & -\mathrm{i} \\ -\mathrm{i} & 0 \end{pmatrix} \quad \boldsymbol{j} = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \quad \boldsymbol{k} = \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} \tag{7}
$$

which satisfy the multiplication rules

$$
\boldsymbol{i}^2 = \boldsymbol{j}^2 = \boldsymbol{k}^2 = -\boldsymbol{I} \tag{8}
$$

$\boldsymbol{ij} = -\boldsymbol{ji} = \boldsymbol{k}$ for cyclic permutations of $\boldsymbol{i}, \boldsymbol{j}$ and $\boldsymbol{k}$. These matrices are related to the Pauli spin matrices by

$$
\boldsymbol{i} = -i\boldsymbol{\sigma}_x, \quad \boldsymbol{j} = -i\boldsymbol{\sigma}_y, \quad \boldsymbol{k} = -i\boldsymbol{\sigma}_z. \tag{9}
$$

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It is evident from (9) that we have to distinguish carefully between i, which is a number whose square is -1, and $\boldsymbol{i}$, which is a matrix whose square is $-\boldsymbol{I}$. The notation is used to emphasize the close analogy between the two quantities, but confusion can easily arise. A set of four coefficients of $\boldsymbol{I}, \boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ is known as a quaternion — a quadruple of numbers obeying the multiplication law one obtains from the above matrices. Often the coefficient of $\boldsymbol{I}$ is known as the scalar part of the quaternion, which we shall denote by a subscript 0, while the coefficients of $\boldsymbol{i}, \boldsymbol{j}$ and $\boldsymbol{k}$ are known as the vector part here denoted by either a vector (in bold type) or by subscripts 1, 2 and 3. Some authors (e.g. Pawley [10]) use the subscript 4 for the scalar part. The use of the four Euler-Rodrigues parameters q_0 — q_3 [11] to represent the orientation of a rigid body is identical to specifying these coefficients, that is $(q_0, \boldsymbol{q})$ is a normalised quaternion. The rule for multiplication of quaternions can be derived by using the fact that the quaternion representation is just another way of writing the $\boldsymbol{D}^{\frac{1}{2}}$ matrix. Since we combine successive rotations by multiplying their $\boldsymbol{D}$ matrices together after ordering them with earlier rotations to the right of later rotations, it follows that the result of a rotation $(q_0, \boldsymbol{q})$ followed by a rotation $(Q_0, \boldsymbol{Q})$ can be written

$$\begin{aligned}(Q_0,\boldsymbol{Q}) \times (q_0,\boldsymbol{q}) &= (Q_0\boldsymbol{I} + Q_1\boldsymbol{i} + Q_2\boldsymbol{j} + Q_3\boldsymbol{k})(q_0\boldsymbol{I} + q_1\boldsymbol{i} + q_2\boldsymbol{j} + q_3\boldsymbol{k}) \\ &= (Q_0q - \boldsymbol{Q}\cdot\boldsymbol{q}, Q_0\boldsymbol{q} + q_0\boldsymbol{Q} + \boldsymbol{Q} \wedge \boldsymbol{q}) \qquad (10)\end{aligned}$$

It is evident that multiplication is not commutative unless the vector parts are parallel. Notice that the identity is represented by the quaternion $(1, \boldsymbol{0})$ and the inverse of $(q_0, \boldsymbol{q})$ is $(q_0, -\boldsymbol{q})$.

Thus the parameters A and B can be thought of as defining the D matrices or the Cayley-Klein parameters, or as defining the Euler-Rodrigues parameters of the quaternion. These are three equivalent ways of describing the rotation that takes the molecule from an orientation aligned with the laboratory frame to its actual orientation. One important advantage of using A and B rather than Euler angles is that the equations of motion of a rigid body then have no singularities.

The quaternion also represents the rotation in a particularly clear way in terms of the direction of the rotation axis $\boldsymbol{\lambda}$ and the angle of rotation ψ. Consider the rotation operator $\hat{R}$ which describes this rotation

$$\hat{R} = \exp[-i\psi\boldsymbol{\lambda}\cdot\hat{\boldsymbol{J}}]. \qquad (11)$$

where $\hat{\boldsymbol{J}}$ is the infinitesimal rotation operator and $\boldsymbol{\lambda}$ is a unit vector in the direction of the rotation axis. Within the $S = \frac{1}{2}$ manifold, $\hat{\boldsymbol{J}}$ is the spin operator $\hat{\boldsymbol{S}}$, that is half the Pauli operator $\hat{\boldsymbol{\sigma}}$, giving

$$\hat{R} = \exp[-i\psi\boldsymbol{\lambda}\cdot\hat{\boldsymbol{\sigma}}/2].$$

Expanding the exponential as a power series and using the fact that

$$\sigma_i\sigma_j + \sigma_j\sigma_i = 2\delta_{ij}$$

so that $(\boldsymbol{\lambda}\cdot\boldsymbol{\sigma})^2 = |\lambda|^2 = 1$, yields

$$\boldsymbol{D}^{\frac{1}{2}}(\psi\lambda) = \cos(\psi/2)\,\boldsymbol{I} - i\sin(\psi/2)\sum \boldsymbol{\lambda}_j\cdot\boldsymbol{\sigma}_j \qquad (12)$$

This shows that the scalar part of the quaternion gives the cosine of half the angle of rotation and the vector part is in the direction of the axis of rotation. In fact, we can use equation (9) to write

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$$\hat{R} = I\cos(\psi/2) + (i\lambda_1 + j\lambda_2 + k\lambda_3)\sin(\psi/2)$$

or

$$q_0 = \cos(\psi/2), \quad \boldsymbol{q} = \boldsymbol{\lambda}\sin(\psi/2)$$

Using this together with the definitions of the rotations associated with the Euler angles we find that, in terms of Euler angles,

$$\begin{aligned} A &= \cos(\beta/2)\exp[-i(\alpha+\gamma)/2] \\ B &= -\sin(\beta/2)\exp[-i(\alpha-\gamma)/2] \end{aligned} \tag{13}$$

or

$$\begin{aligned} q_0 &= \cos(\beta/2)\cos((\alpha+\gamma)/2) \\ q_1 &= \sin(\beta/2)\sin((\gamma-\alpha)/2) \\ q_2 &= \sin(\beta/2)\cos((\gamma-\alpha)/2) \\ q_3 &= \cos(\beta/2)\sin((\alpha+\gamma)/2) \end{aligned} \tag{14}$$

in agreement with the $D^{\frac{1}{2}}$ matrix in Brink and Satchler. The quaternion parameters produced by Evans' equations of motion (χ, ξ, η, ζ) and the Euler-Rodrigues parameters are related to A and B by

$$\begin{aligned} A &= \chi - i\zeta = q_0 - iq_3 \\ B &= \xi - i\eta = -q_2 - iq_1 \end{aligned} \tag{15}$$

The Euler angle definitions of these parameters follows the Whittaker convention used in this paper, and differ from those given by Evans [7] who used the alternative convention of Goldstein [2].

In a constraints program one obtains atomic positions. Although one can construct A and B from these, it is usually easier to work in terms of direction cosines. One might think that specifying the three direction cosines X_x, Y_y and Z_z would provide the three independent parameters needed to specify the orientation of the body. In fact these quantities do not specify a unique orientation, as rotations of $+\psi$ or $-\psi$ about an axis λ give identical values of these three direction cosines. However knowledge of these parameters is sufficient to determine the probability distribution of rotations if the probability of a forward and a reverse rotation are known to be equal for symmetry reasons.

3. SOME USEFUL PROPERTIES OF QUATERNIONS AND WIGNER ROTATION MATRICES

In this section we review some properties of these quantities which are useful to the molecular dynamicist, including the combining of rotations, the equation of motion of quaternions and Wigner matrices, and the way in which Wigner rotation matrices can be used to describe the probability of molecular reorientation.

First we note that a rotation and its inverse are easily related. If the specified rotation is by ψ about $\boldsymbol{\lambda}$, then the inverse rotation is obviously a rotation of $-\psi$ about the same axis. In terms of quaternions, we have seen that (q_0, $\mathbf{q}$) and (q_0, $-\boldsymbol{q}$) are inverses. In terms of Wigner rotation matrices: if

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$$Y^{L}_{k}(\text{mol axes}) = \sum_{m} Y^{L}_{m}\,(\text{lab axes})\; D^{L}_{mk}\,(\Omega) \tag{16}$$

then the inverse rotation is

$$Y^{L}_{m}\,(\text{lab axes}) = \sum_{k} Y^{L}_{k}\,(\text{mol axes}) D^{L}_{km}\,(\Omega^{-1}) \tag{17}$$

with $D^{L}_{km}\,(\Omega^{-1}) = \{D^{L}_{mk}\,(\Omega)\}^{*}$ because the Wigner matrices are unitary, and

$$D^{L}_{mk}\,(\Omega) = (-1)^{m-k} D^{L}_{-m-k}\,(\Omega)$$

Successive rotations, for example of Ω_1 followed by Ω_2 are given by matrix multiplication of the Wigner matrices,

$$D^{L}_{mk}\,(\Omega_f) = \sum_{n} D^{L}_{mn}\,(\Omega_2)\; D^{L}_{nk}\,(\Omega_1) \tag{18}$$

or by multiplying the quaternions using the rule in equation (10), remembering in both cases that the order is important.

Applying this to the $\mathbf{D}^{\frac{1}{2}}$ matrix gives:

$$\begin{aligned} A &= A_2A_1 - B_2B_1^{*} \\ B &= A_2B_1 + B_2A_1^{*}. \end{aligned} \tag{19}$$

One often needs to construct the change in orientation in time t, that is the rotation that takes a molecule from an orientation described by parameters A_1, B_1 at time $t = 0$ to A_2, B_2 at time t. If this rotation is denoted by $\delta\Omega$, we need to use

$$\boldsymbol{D}^{L}\,(\Omega_2) = \boldsymbol{D}^{L}\,(\delta\Omega)\;\boldsymbol{D}^{L}\,(\Omega_1) \tag{20}$$

which gives

$$\boldsymbol{D}^{L}\,(\delta\Omega) = \boldsymbol{D}^{L}\,(\Omega_2)\;\boldsymbol{D}^{L}\,(\Omega_1^{-1}). \tag{21}$$

and

$$\begin{aligned} A_\delta &= A_2A_1^{*} + B_2B_1^{*} \\ B_\delta &= -A_2B_1 + B_2A_1 \end{aligned} \tag{22}$$

where A_δ and B_δ are the parameters for the change in orientation.

The equation of motion of A and B can be determined readily from the rule for successive rotations If a molecule has an instantaneous angular velocity ω, then it rotates by $\omega\delta t$ about the direction of $\boldsymbol{\omega}$ in time δt, so that (using equation 11)

$$\boldsymbol{D}^{L}\,(\Omega(t + \delta t)) = exp\,(-i\delta t\boldsymbol{\omega}\cdot\hat{\boldsymbol{J}})\;\boldsymbol{D}^{L}\,(\Omega(t)),$$

giving the rate of change of the Wigner rotation matrices, D^{L}, to be

$$d/dt\;\mathbf{D}^{L} = -\,i\boldsymbol{\omega}\cdot\hat{\boldsymbol{J}}\;\boldsymbol{D}^{L} \tag{23}$$

and for the particular case of $L = \frac{1}{2}$, where $\hat{J}_\alpha = \frac{1}{2}\hat{\sigma}_\alpha$,

$$d/dt\begin{pmatrix} A & B \\ -B^{*} & A^{*} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} -i\omega_z & -i\omega_x + \omega_y \\ -i\omega_x - \omega_y & -i\omega_z \end{pmatrix}\begin{pmatrix} A & B \\ -B^{*} & A^{*} \end{pmatrix} \tag{24}$$

In this equation the components of the angular velocity vector are specified in the

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laboratory frame, where the equations of motion are those obtained by cyclic permutations of x, y and z in

$$I_{xx}\dot{\omega}_x + I_{xy}\dot{\omega}_y + I_{xz}\dot{\omega}_z = T_x \tag{25}$$

where $\boldsymbol{T}$ is the torque acting on the molecule and $\boldsymbol{I}$ is the moment of inertia tensor in laboratory axes. Unless the molecule is a spherical top so that its moment of inertia tensor is isotropic, the equations of motion are more readily solved using a molecule fixed axis system which coincides with the principal axes of the inertia tensor. In this axis system the equations of motion become cyclic permutations of X, Y, and Z in

$$I_{XX}\dot{\omega}_X = T_X + (I_{YY} - I_{ZZ})\omega_Y\omega_Z. \tag{26}$$

Using equations (16) and (17) for the relation of spherical harmonics in the laboratory and molecular frames one can show that the rotation operator in the molecule fixed frame is represented by a matrix which multiplies the **D** matrix from the right so that

$$d/dt\begin{pmatrix} A & B \\ -B^* & A^* \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} A & B \\ -B^* & A^* \end{pmatrix}\begin{pmatrix} -i\omega_Z & -i\omega_X + \omega_Y \\ -i\omega_X - \omega_Y & -i\omega_Z \end{pmatrix} \tag{27}$$

This reversed order of multiplication is another facet of the rule that a sequence of rotations about axes fixed in space is equivalent to the same sequence of rotations taken in the reverse order about axes fixed in the molecule.

The other property of Wigner rotation matrix elements that is useful to simulators is the fact that they form a complete (infinite) set of orthogonal functions in Ω space. Any property of orientation can be expanded in terms of these functions, which in this context can be called Wigner functions. This is particularly useful for two properties, the distribution of orientation in an anisotropic environment [12] and the probability of reorientation by $\delta\Omega$ in time t in either an isotropic or an anisotropic environment.

Taking the first case we can write the probability distribution function as

$$P(\Omega) = \sum p^{L}_{mk} D^{L}_{mk}(\Omega)\,(2L + 1) \tag{28}$$

where the normalisation factor of $(2L + 1)$ is included to ensure that the p coefficients are equal to the ensemble averages of the corresponding Wigner matrix elements:

$$p^{L}_{mk} = \langle D^{L*}_{mk} \rangle \tag{29}$$

Obviously $p(\Omega)$ must be unaffected by symmetry operations of either the molecule or the environment. The molecular symmetry operations may be expressed as rotations in the molecular frame and the symmetry operations of the environment as operations in the laboratory frame. Applying this type of argument one can find which coefficients are zero and which are related to each other. This type of expansion has been used extensively in studies of orientationally disordered crystals [12, 13, 14]. In the case of linear molecules in an environment with cubic symmetry the independent non-zero terms in the expansion are known as cubic (or kubic) harmonics [12].

The description of the average time dependence of reorientation can be treated in the same way. In an anisotropic environment (plastic crystal or liquid crystal) the probability of reorientation depends on the initial orientation, but in an isotropic liquid all initial orientations are equivalent so one may write

$$P(\delta\Omega, t) = \sum C^{L}_{mk}(t)\, D^{L}_{mk}(\delta\Omega)\,(2L + 1) \tag{30}$$

for the probability that the molecule has rotated by a total of $\delta\omega$ in time t. The coefficients C^{L}_{mk} are examples of time correlation functions and can be computed in a simulation from

$$C^{L}_{mk}(t) = \langle D^{L*}_{mk}(\delta\Omega) \rangle. \tag{31}$$

These time correlation functions are important because they are directly related to spectroscopic measurements. For example Infra-Red line shapes are determined by the $L = 1$ correlation functions and Raman line shapes and N.M.R. relaxation by the $L = 2$ functions. The diagonal correlation functions, C^{L}_{kk}, are equal to one at time $t = 0$, while the off diagonal functions are initially equal to zero. In symmetric top and spherical top molecules the symmetry restricts the off-diagonal correlation functions to remain equal to zero, and the diagonal correlation functions are often referred to with a single subscript, e.g. C^{L}_{k} for C^{L}_{kk}. Anisotropy of reorientation of a symmetric top (spinning and tumbling motion [15]) is shown by differences between orientational correlation functions with the same L, but different values of k. In an asymmetric top, such as H_2O, any difference in motion about the X and Y axes will show up as a non-zero off-diagonal correlation function (for example C^{L}_{1-1} and C^{L}_{20}). There may also be other relations between correlation functions and some requirements that certain cross correlation functions are zero; these depend on the symmetry of the particular molecule concerned. Further discussion and examples are given in refs [16, 17].

4. COMPUTATION OF ORIENTATIONAL CORRELATION FUNCTIONS

Any Wigner rotation matrix element can be built up from the $L = \frac{1}{2}$ elements, and general formulae are given in text books on angular momentum theory [4, 5]. However, as an eigenfunction of angular momentum with $l = m = L$ can be constructed from 2 L spin $= 1/2$ functions by

$$|L,L\rangle = \alpha_1\alpha_2\alpha_3 \ . \ . \ . \ \alpha_{2L},$$

the top left element of the Wigner rotation matrix in the customary arrangement (which labels the rows and columns in the order $L, L-1, \ . \ . \ . \ . \ , -L$) is given by

$$D^{L}_{LL} = A^{2L}, \tag{32}$$

and the rest of the matrix can be constructed using two operators $\hat{\mathscr{R}}$ and $\hat{\mathscr{B}}$ which operate to generate the matrix elements on the right and beneath respectively. These operators are related to the infinitesimal rotation operators in the molecular and laboratory systems by $\hat{\mathscr{R}} = \hat{J}^{\mathrm{mol}}_{+}$ and $\hat{\mathscr{B}} = \hat{J}^{\mathrm{lab}}$ respectively so that

$$\hat{\mathscr{R}}\, D^{L}_{mk} = (L(L+1) - k(k-1))^{\frac{1}{2}}\, D^{L}_{m\,k-1} \tag{33}$$

$$\hat{\mathscr{B}}\, D^{L}_{mk} = (L(L+1) - m(m-1))^{\frac{1}{2}}\, D^{L}_{m-1\,k}$$

The effect of $\hat{\mathscr{R}}$ and $\hat{\mathscr{B}}$ on A, A^*, B and B^* can be read off from equation (4) by moving to the right or downwards in the $D^{\frac{1}{2}}$ matrix. For example $\hat{\mathscr{R}}\, A = B$ and $\hat{\mathscr{R}}\, B = 0$. As these operators are differential operators they obey the usual rule for differentiation of products so that, for example, we have

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Table 2 Rotation matrix elements D^L_{mk} for $L = 1$, 2 and 3 in terms of A, B, and Z. Note that $D^L_{-m-k} = (-1)^{m-k}(D^L_{mk})^*$. A and B are defined by equations 22 and 15.

$L = 1$

m	k	-1	0	1
1		A^2	$\sqrt{2}AB$	B^2
0		$-\sqrt{2}AB^*$	Z	$\sqrt{2}A^*B$
-1		B^{*2}	$-\sqrt{2}A^*B^*$	A^{*2}

$L = 2$

m	k	2	1	0
2		A^4	$2A^3B$	$\sqrt{6}A^2B^2$
1		$-2A^3B^*$	$A^2(2Z-1)$	$\sqrt{6}ABZ$
0		$\sqrt{6}A^2B^{*2}$	$-\sqrt{6}AB^*Z$	$\frac{1}{2}(3Z^2-1)$
-1		$-2AB^{*3}$	$B^{*2}(2Z+1)$	$-\sqrt{6}A^*B^*Z$
-2		B^{*4}	$-2A^*B^{*3}$	$\sqrt{6}A^{*2}B^{*2}$

$L = 3$

m	k	3	2	1	0
3		A^6	$\sqrt{6}BA^5$	$\sqrt{15}B^2A^4$	$2\sqrt{5}B^3A^3$
2		$-\sqrt{6}A^5B^*$	$A^4(3Z-2)$	$\frac{1}{2}\sqrt{10}BA^3(3Z-1)$	$\sqrt{30}B^2A^2Z$
1		$\sqrt{15}A^4B^{*2}$	$-\frac{1}{2}\sqrt{10}A^3B^*(1-3Z)$	$\frac{1}{4}A^2(15Z^2-10Z-1)$	$\frac{1}{2}\sqrt{3}AB(5Z^2-1)$
0		$-2\sqrt{5}A^3B^{*3}$	$\sqrt{30}A^2B^{*2}Z$	$\frac{1}{2}\sqrt{3}AB^*(1-5Z^2)$	$\frac{1}{2}(5Z^3-3Z)$
-1		$\sqrt{15}A^2B^{*4}$	$-\frac{1}{2}\sqrt{10}AB^{*3}(1+3Z)$	$\frac{1}{4}B^{*2}(15Z^2+10Z-1)$	$-\frac{1}{2}\sqrt{3}A^*B^*(5Z^2-1)$
-2		$-\sqrt{6}AB^{*5}$	$B^{*4}(3Z+2)$	$-\frac{1}{2}\sqrt{10}A^*B^{*3}(3Z+1)$	$\sqrt{30}B^{*2}A^{*2}Z$
-3		B^{*6}	$-\sqrt{6}A^*B^{*5}$	$\sqrt{15}B^{*4}A^{*2}$	$-2\sqrt{5}B^{*3}A^{*3}$

$$\begin{aligned}\hat{\mathscr{R}}\, D^2_{22} &= \sqrt{2}\, D^2_{21} \\ &= \hat{\mathscr{R}}\, A^4 = 4\, A^3 B\end{aligned} \tag{34}$$

so that $D^2_{21} = 2\sqrt{2}\, A^3 B$.

Table 1 gives diagonal elements up to L = 4 and table 2 gives the complete matrices for $L = 1$, 2 and 3 in terms of the functions A and B. These have been computed both by hand and by using a short REDUCE program. In using these tables one must first compute the values of A and B for the rotation that takes the molecule from its $t = 0$ orientation to its orientation at time t by combining the rotations as described in the previous section (equation 22).

If one is using a constraints program it is usually easier to work with direction cosines. Table 3 gives expressions for direction cosines in terms of A and B, from which one finds

$$\begin{aligned}A^2 &= \tfrac{1}{2}(X_x + \mathrm{i}Y_x - \mathrm{i}X_y + Y_y) \\ B^2 &= \tfrac{1}{2}(-X_x + \mathrm{i}Y_x + \mathrm{i}X_y + Y_y) \\ AA^* &= \tfrac{1}{2}(1 + Z_z) \\ BB^* &= \tfrac{1}{2}(1 - Z_z) \\ AB &= -\tfrac{1}{2}(Z_x - \mathrm{i}Z_y) \\ AB^* &= \tfrac{1}{2}(X_z + \mathrm{i}Y_z)\end{aligned} \tag{35}$$

It is unnecessary, however, to determine all the direction cosines if one only wants to construct the averages of the diagonal elements D^L_{kk}. These can be written in terms of just three direction cosines, X_x, Y_y, and Z_z, as the averages involve only the real parts of the even powers of A. For example, using equation 35, we find

$$A^2 + A^{*2} = X_x + Y_y$$

$$(A^2 + A^{*2})^2 = A^4 + 2A^2A^{*2} + A^{*4} = (X_x + Y_y)^2$$

so that

$$A^4 + A^{*4} = (X_x + Y_y)^2 - \tfrac{1}{2}(1 + Z_z)^2$$

Table 1 Values of diagonal rotation matrix elements D^L_{kk} in terms of A and Z. A is defined by equations 22 and 15; $Z = AA^* - BB^* = \chi^2 + \zeta^2 - \xi^2 - \eta^2 = q_0^2 - q_1^2 - q_2^2 + q_3^2$.

k	$L = 1$	$L = 2$	$L = 3$	$L = 4$
4				A^8
3			A^6	$A^6\,(4Z - 3)$
2		A^4	$A^4\,(3Z - 2)$	$A^4\,(7Z^2 - 7Z + 1)$
1	A^2	$A^2\,(2Z - 1)$	$\frac{1}{4}A^2\,(15Z^2 - 10Z - 1)$	$\frac{1}{4}A^2\,(28Z^3 - 21Z^2 - 6Z + 3)$
0	Z	$\frac{1}{2}\,(3Z^2 - 1)$	$\frac{1}{2}\,(5Z^3 - 3Z)$	$1/8(35Z^4 - 30Z^2 + 3)$

Table 3 Direction cosines in terms of the parameters A and B.

$$\begin{bmatrix} X_x & Y_x & Z_x \\ X_y & Y_y & Z_y \\ X_z & Y_z & Z_z \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(A^2 - B^2 + A^{*2} - B^{*2}) & -\frac{1}{2}i(A^2 + B^2 - A^{*2} - B^{*2}) & -AB + A^*B^* \\ \frac{1}{2}i(A^2 - B^2 + A^{*2} - B^{*2}) & \frac{1}{2}(A^2 + B^2 + A^{*2} - B^{*2}) & -i(AB - A^*B^*) \\ AB^* + A^*B & -i(AB^* - A^*B) & (AA^* - BB^*) \end{bmatrix}$$

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and, as the average of an even power of A must be real this is sufficient to determine all the diagonal Wigner matrix elements. Table 4 gives the formulae needed to compute these functions.

Table 4 Formulae needed to calculate averages of $\mathbf{D}^{L}_{kk}$ from the direction cosines between the molecular axes at times $t = 0$ and t. X, Y, Z are the direction cosines between the two x, two y and two z axes respectively. This table is to be used in conjunction with table 1.

n	$\langle A^n f(Z) \rangle$
2	$\frac{1}{2}\langle (X + Y) f(Z) \rangle$
4	$\frac{1}{2}\langle (X + Y)^2 f(Z) \rangle - \frac{1}{4}\langle (Z + 1)^2 f(Z) \rangle$
6	$\frac{1}{2}\langle (X + Y)^3 f(Z) \rangle - 3/8 \langle (X + Y)(Z + 1)^2 f(Z) \rangle$

References

[1] S.L. Altmann, Rotations, Quaternions and Double Groups, Oxford, 1986.

[2] H. Goldstein, Classical Mechanics, Addison Wesley, 1959.

[3] E.T. Whittaker, Analytical Dynamics, Cambridge, 1904.

[4] D.M. Brink and G.R. Satchler, Angular Momentum, 2nd Ed. Clarendon Press, Oxford, 1968.

[5] M.E. Rose, Elementary Theory of Angular Momentum, John Wiley, New York, 1957.

[6] C.G. Gray and K.E. Gubbins, Theory ofs Molecular Fluids, vol. 1, Oxford, 1984.

[7] D.J. Evans, "On the representation of orientation space", *Molec. Phys.*, **34**, 317 (1977).

[8] D.J. Evans and S. Murad, "Singularity free algorithm for molecular dynamics simulation of rigid polyatomics", *Molec. Phys.*, **34**, 327 (1977).

[9] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids, Oxford, 1987.

[10] G.S. Pawley, "Molecular dynamics simulation of the plastic phase; a model for SF_6", *Molec. Phys.*, **43**, 1321 (1981).

[11] L.C. Biedenharn and J.D. Louck, Angular Momentum in Quantum Physics: Theory and Application, Addison Wesley, 1981.

[12] A. Hüller and J.W. Kane, "Electrostatic model for the rotational potential in amonium halides", *J. Chem. Phys.*, **61**, 3599 (1974).

[13] A. Hüller and D.M. Kroll, "Rotational Tunneling in Solids", *J. Chem. Phys.*, **63**, 4495 (1975).

[14] M. Ferrario, M.L. Klein, R.M. Lynden-Bell and I.R. McDonald, "A molecular dynamics study of the rotator phase of t butyl bromide", *J. Chem. Soc. Farad. II*, **83**, 2097 (1987).

[15] R.M. Lynden-Bell, "Are models necessary to describe molecular reorientation of symmetrical molecules", *Chem. Phys. Letts.*, **70**, 477 (1980).

[16] H. Versmold, "On the symmetries of molecular reorientation processes in liquids", *Molec. Phys.*, **33**, 1051 (1977).

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