A Method to Calculate the g-Coefficients of the Molecular Pair Correlation Function from Molecular Dynamics Simulations

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A METHOD TO CALCULATE THE g-COEFFICIENTS OF THE MOLECULAR PAIR CORRELATION FUNCTION FROM MOLECULAR DYNAMICS SIMULATIONS

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It is known that the rotational equation of motion of rigid molecules in MD simulations can be solved in a singularity-free form if quaternions are used for the description of the rotational motion. We show that these quaternions are also suited for the calculation of the so-called 'g-coefficients', which are the expansion coefficients of the molecular pair correlation function (MPCF) in terms of Wigner functions. This is due to the fact that quaternions are themselves a representation of the rotation group and can be referred to an arbitrary coordinate frame in a particularly simple way. As an application for the quaternion formalism we calculate some g-coefficients of the MPCF of methylene chloride (CH_2Cl_2).

1 INTRODUCTION

The statistical theory of simple atomic liquids tells us that many thermodynamic quantities can be expressed in terms of the pair correlation function $g(\vec{R}_1, \vec{R}_2)$, $\vec{R}_1, \vec{R}_2$ being the positions of two atoms, if the intermolecular potential is assumed to be pairwise additive. Due to the homogenity and the isotropic symmetry of a liquid the pair correlation function is translationally and rotationally invariant i.e. it can be written as $g(R)$, where $R = |\vec{R}_1 - \vec{R}_2|$. There are two generalizations of the usual pair correlation function for the case of a molecular liquid: (a) the description of the liquid structure in terms of intermolecular *site pair correlation functions* $g_{\alpha\beta}(R)$ and (b) the description of the liquid structure in terms of the *molecular pair correlation function* (MPCF) $g(R, \Omega_1, \Omega_2, \Omega_{12})$ [1, 2, 3], generally depending on the center of mass (cms) separation distance $R = |\vec{R}_1 - \vec{R}_2|$, the orientations Ω_1, Ω_2 of two molecules and the

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orientation Ω_{12} of the unit vector along the axis $\vec{R}_2 - \vec{R}_1$. Corresponding to the case of atomic liquids the MPCF has to be translationally and rotationally invariant, which reduces the number of independent variables from 9 to 6. The two descriptions of the liquid structure mentioned above are not really equivalent, since quantities as the dielectric constant, which depend on the orientational correlation between the molecules, cannot be expressed rigorously by the site pair correlation functions.

Site pair correlation functions are often used to extract the structure of a molecular liquid from neutron diffraction experiments, because the differential cross section for the neutrons can be very easily expressed in terms of their Fourier-Bessel transforms. In that case the number of sites is equal to the number of non-equivalent atoms in one molecule yielding the following fundamental difference between the two descriptions of the liquid structure mentioned above: Expanding the MPCF in a series of orientation dependent basis functions, with coefficients (called 'g-coefficients') only depending on R, it is evident that the *infinte* set of g-coefficients mathematically cannot be equivalent to the *finite* set of $N(N + 1)/2$ site pair correlation functions, N being the number of non-equivalent atoms per molecule. Of course the question arises how many of the g-coefficients must be taken into account to give a *satisfactory* description of the liquid structure.

Questions like that could in principle be answered by direct calculation of the differential neutron cross sections from the local particle density [4] and by calculating it according to its representation in terms of g-coefficients as given by Blum, Narten and Zeidler [5, 6]. At the same time this would be a test for the potential used for the MD-simulation. Another interesting aspect that can be studied by a g-coefficient analysis is the character of intermolecular orientations in a liquid consisting of non-linear molecules: do the molecules of a special liquid behave similar as spherical molecules, linear molecules, or does the intramolecular structure of the molecule play an important role?

Quaternions introduced by the Irish mathematician W.R. Hamilton, have become quite popular in MD simulations, because the rotational equation of motion for rigid molecules can be solved in a singularity-free form, if the rotational motion is described in terms of quaternion parameters [7]. We show in this paper that they are also useful for the calculation of g-coefficients, since they can be easily referred to an arbitrary coordinate system. In section 2 we give a short review of the most important formulas and relations concerning the so-called rotational invariant and irreducible expansion of the MPCF and in section 3 we describe how to use quaternions for the calculation of g-coefficients. Finally we apply our algorithm to calculate some g-coefficients for methylene chloride $(CH_2 Cl_2)$ which is a molecule with C_{2v}-symmetry having a permanent dipole moment.

2 THE MOLECULAR PAIR CORRELATION FUNCTION

As already mentioned, the molecular pair correlation function for rigid molecules is a straightforward generalization of the usual pair correlation function for atomic liquids. In general, the position of a pair of *non linear* molecules is fixed by

1. the separation distance R_{ij} of the molecular centers of mass, $R_{ij} = |\vec{R}_i - \vec{R}_j|$, where $\vec{R}_i$, $\vec{R}_j$ denote the cms coordinates of molecule i resp. j,

2. the orientation Ω_{ij} of the unit vector along $\vec{R}_{ij} = \vec{R}_j - \vec{R}_i$, specified by the two angles Φ_{ij} (azimuthal angle) and Θ_{ij} (polar angle),

3. the orientation Ω_i of molecule i, specified by the three Euler angles $\alpha_i, \beta_i, \gamma_i$,

4. the orientation Ω_j of molecule j, specified by the three Euler angles $\alpha_j, \beta_j, \gamma_j$.

A possible way of representing the MPCF is to expand it in a series of orientation dependent basis functions $\Phi_{m_1,n_1,m_2,n_2,n_{12}}^{l_1,l_2,l_{12}} (\Omega_1, \Omega_2, \Omega_{12})$, each of them being simply the following product of Wigner functions:

$$\Phi_{m_1,n_1,m_2,n_2,n_{12}}^{l_1,l_2,l_{12}} (\Omega_1, \Omega_2, \Omega_{12}) = D_{m_1,n_1}^{l_1} (\Omega_1) D_{m_2,n_2}^{l_2}(\Omega_2) D_{0,n_{12}}^{l_{12}}(\Omega_{12}). \tag{1}$$

The expansion of the MPCF in terms of the basis functions, given in (1) reads (summation over all indices is understood):

$$g(R, \Omega_1, \Omega_2, \Omega_{12}) = \Sigma\, g_{m_1,n_1,m_2,n_2,n_{12}}^{l_1,l_2,l_{12}}(R) \cdot \Phi_{m_1,n_1,m_2,n_2,n_{12}}^{l_1,l_2,l_{12}} (\Omega_1, \Omega_2, \Omega_{12}) \tag{2}$$

This representation of the MPCF is called the *reducible representation*. Taking into account that a simple molecular liquid is *isotropic* it makes more sense to expand the MPCF in a set of angular dependent basis functions which are invariant under rotations. Such a set of basis functions can be found by constructing the standard eigenfunctions of the total angular momentum $\vec{L} = \vec{L}_1 + \vec{L}_2 + \vec{L}_{12}$ with total angular momentum $L = 0$. An eigenfunction corresponding to $L = 0$ transforms like a scalar, i.e. invariant, under rotations. Noting that the Wigner functions are themselves eigenfunctions of the angular momentum operator in the position representation (expressed in terms of Euler angles) [8], one can construct the desired basis functions in the following way [8]:

$$\Phi_{m_1,m_2}^{l_1,l_2,l_{12}} (\Omega_1, \Omega_2, \omega_{12}) = \sum_{n_1,n_2,n_{12}} \begin{pmatrix} l_1\, l_2\, l_{12} \\ n_1 n_2 n_{12} \end{pmatrix} D_{m_1,n_1}^{l_1}(\Omega_1) D_{m_2,n_2}^{l_2}(\Omega_2) D_{0,n_{12}}^{l_{12}}(\Omega_{12}). \tag{3}$$

The symbols $\begin{pmatrix} l_1\, l_2\, l_{12} \\ n_1 n_2 n_{12} \end{pmatrix}$ are the *Wigner 3${}_j$-symbols* [8, 9]. The expansion of the MPCF in the basis functions given in (3) is known as *rotational invariant representation* [3]:

$$g(R, \Omega_1, \Omega_2, \Omega_{12}) = \Sigma\, g_{m_1,m_2}^{l_1,l_2,l_{12}}(R) \cdot \Phi_{m_1,m_2}^{l_1,l_2,l_{12}} (\Omega_1, \Omega_2, \Omega_{12}) \tag{4}$$

Since $g(R, \Omega_1, \Omega_2, \Omega_{12})$ is invariant under rotations one can choose a coordinate frame in which $\vec{R}_{12}$ is parallel to the z-axis, i.e. $\Omega_{12} = (0, 0)$. As a consequence one has $D_{0,n_{12}}^{l_{12}}(\Omega_{12}) = D_{0,n_{12}}^{l_{12}}(0, 0) = \delta_{0,n_{12}}$. Taking into account that the sum of the lower indices in the 3_j-symbol must be zero, one obtains the *irreducible representation* of the MPCF:

$$g(R, \Omega_1', \Omega_2') = \Sigma\, g_{m_1,m_2;n_1}^{l_1,l_2}(R) \cdot D_{m_1,n_1}^{l_1}(\Omega_1') D_{m_2,-n_1}^{l_2}(\Omega_2'), \tag{5}$$

where

$$g_{m_1,m_2;n_1}^{l_1,l_2}(R) = \sum_{l_{12}=|l_1-l_2|}^{l_{12}=l_1+l_2} \begin{pmatrix} l_1 & l_2 & l_{12} \\ n_1 & -n_1 & 0 \end{pmatrix} g_{m_1,m_2}^{l_1,l_2,l_{12}}(R). \tag{6}$$

The primes indicate that the orientations refer to a coordinate frame in which $\vec{R}_{12}$ is parallel to the z-axis. We drop in the following this labelling for reasons of convenience in case that no confusion can happen.

The inversion of (6) can be obtained by using the orthogonality relation [9]

$$\sum_{\alpha,\beta} (2c + 1) \begin{pmatrix} abc \\ \alpha\beta\gamma \end{pmatrix} \begin{pmatrix} abc' \\ \alpha\beta\gamma' \end{pmatrix} = \delta_{c,c'}\delta_{\gamma,\gamma'}. \tag{7}$$

With $a = l_1$, $\alpha = n_1$, $b = l_2$, $\beta = -n_1$, $c = l_{12}$, $\gamma = 0$, and the condition $\alpha + \beta + \gamma = 0$ one has:

$$g_{m_1,m_2}^{l_1,l_2,l_{12}}(R) = (2l_{12} + 1) \sum_{n_1} \begin{pmatrix} l_1 & l_2 & l_{12} \\ n_1 & -n_1 & 0 \end{pmatrix} g_{m_1,m_2,n_1}^{l_1,l_2}(R). \tag{8}$$

The upper and lower limit for the summation over n_1 is $min(l_1, l_2)$ and $-min(l_1, l_2)$.

3 CALCULATION OF g-COEFFICIENTS FROM MD SIMULATIONS

3.1 Basic Strategy

Equation (5) is the starting point for the calculation of g-coefficients from MD simulations. From the orthogonality relation of the Wigner functions [8]

$$\int_0^{2\pi} \int_0^\pi \int_0^{2\pi} d\gamma d\beta d\alpha \sin\beta \, D_{m_1,n_1}^{*l_1}(\alpha, \beta, \gamma) D_{m_2,n_2}^{l_2}(\alpha, \beta, \gamma) \tag{9}$$

$$= \frac{8\pi^2}{2_{j_1} + 1} \cdot \delta_{j_1,j_2} \delta_{m_1,m_2} \delta_{n_1,n_2},$$

one obtains immediately

$$g_{m_1,m_2,n_1}^{l_1,l_2}(R) = \frac{(2l_1 + 1)(2l_2 + 1)}{64\pi^4}$$

$$\times \iint d\Omega_1 d\Omega_2 g(R, \Omega_1, \Omega_2) D_{m_1,n_1}^{*l_1}(\Omega_1) D_{m_2,-n_1}^{*l_2}(\Omega_2). \tag{10}$$

In particular the $g_{0,0;0}^{0,0}$-coefficient is identical with the pair correlation function for the cms positions of the molecules.

Writing down the MPCF as a straightforward generalization of the atomic case one obtains:

$$g(R, \Omega_1, \Omega_2) = \frac{N}{\varrho_1\varrho_2} \left\langle \sum_{i\neq j} \delta(\vec{R} - \vec{R}_{ij})\delta(\Omega_1 - \Omega_i)\delta(\Omega_2 - \Omega_j) \right\rangle, \tag{11}$$

$$= \frac{V^2}{N} \cdot \frac{64\pi^4}{4\pi R^2} \left\langle \sum_{i\neq j} \delta(R - R_{ij})\delta(\Omega_1 - \Omega_i)\delta(\Omega_2 - \Omega_j) \right\rangle.$$

with $\varrho_1 = \varrho_2 = N/V \cdot 1/(8\pi^2)$. Inserting this expression into (10) yields

$$g_{m_1,m_2;n_1}^{l_1,l_2}(R) = (2l_1 + 1)(2l_2 + 1) \frac{V^2}{N} \frac{1}{4\pi R^2} \tag{12}$$

$$\times \left\langle \sum_{i\neq j} \delta(R - R_{ij}) D_{m_1,n_1}^{*l_1}(\Omega_1) D_{m_2,-n_1}^{*l_2}(\Omega_j) \right\rangle.$$

We remember that Ω_i and Ω_j must be referred to a coordinate system in which $\vec{R}_{ij}$ is parallel to $\vec{e}_z$! Equation (12) shows that the g-coefficients for the irreducible representation of the MPCF are calculated basically with the same strategy as for usual

pair correlation functions. The only difference is that instead of incrementing the histogram channels by one for each pair of molecules they are now incremented by a product of Wigner functions, depending on the orientation of the molecules.

3.2 Spatial Rotations and Quaternions

Now we come to the connection between quaternions and rotations in space. The quaternions are so-called 'hypercomplex numbers' with one basis element 1, representing the '1', and three 'imaginary' basis elements I, J, and K. An arbitrary quaternion is written as

$$Q = q_0 \cdot 1 + q_1 \cdot I + q_2 \cdot J + q_3 \cdot K, \tag{13}$$

where q_0, q_1, q_2, q_3 are real numbers. The basis elements obey the following algebra:

$$
\begin{array}{c|cccc}
 & 1 & I & J & K \\
\hline
1 & 1 & I & J & K \\
I & I & -1 & K & -J \\
J & J & -K & -1 & I \\
K & K & J & -I & -1 \\
\end{array}
\tag{14}
$$

From this multiplication table it is obvious that quaternion multiplication is not commutative. One possible matrix representation of the basis elements is given as follows:

$$
1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad
I = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}
$$

$$
J = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \quad
K = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}
\tag{15}
$$

Therefore the matrix representation of an arbitrary quaternion is according to (13):

$$
Q = \begin{pmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{pmatrix}
\tag{16}
$$

One can define the *complex conjugate* of a quaternion analogous to the complex conjugate of a usual complex number:

$$Q^{(cc)} \doteq q_0 \cdot 1 - q_1 \cdot I - q_2 \cdot J - q_3 \cdot K. \tag{17}$$

From (15) it follows immediately that the matrix representation of the complex conjugate quaternion is given by the transposed matrix. It is natural to define the 'length' $\|Q\|$ of a quaternion by

$$\|Q\| \doteq \sqrt{q_0^2 + q_1^2 + q_2^2 + q_3^2}, \tag{18}$$

because the relation

$$Q^t Q = (q_0^2 + q_1^2 + q_2^2 + q_3^2)\cdot 1 \tag{19}$$

holds. From (19) it can be seen immediately that a quaternion of length one is represented by an *orthogonal* matrix.

Defining (a) $Q(\vec{n}, \Phi)$ by

$$\left.\begin{aligned}
q_0(\vec{n}, \Phi) &= \cos(\Phi/2) \\
q_1(\vec{n}, \Phi) &= \sin(\Phi/2)n_x, \\
q_2(\vec{n}, \Phi) &= \sin(\Phi/2)n_y, \\
q_3(\vec{n}, \Phi) &= \sin(\Phi/2)n_z,
\end{aligned}\right\} \tag{20}$$

and (b)

$$A = \alpha_x \cdot I + a_y \cdot J + \alpha_z \cdot K, \tag{21}$$

we have the following relation for $A' = Q^t A Q$:

$$A' = Q^t A Q = \alpha'_x \cdot 1 + a'_y \cdot J + \alpha'_z \cdot K, \tag{22}$$

$$\vec{a}' = D^t(\vec{n}, \Phi)\vec{a}. \tag{23}$$

The components $\vec{a}'$ transform exactly as the components of a vector $\vec{a}$ under a rotation of the coordinate system, described by a rotation matrix $D(\vec{n}, \Phi)$, given in terms of the unit vector $\vec{n}$ along the rotation axis and the rotation angle Φ (see Appendix A). Therefore equations (22, 23) express a relation between quaternions and rotation matrices: Each rotation matrix $D(\vec{n}, \Phi)$ can be mapped on a unique quaternion $Q(\vec{n}, \Phi)$. It should be noted that the reverse is not true, since we have $D(\vec{n}, 2\pi) = 1_{(3)}$ and $Q(\vec{n}, 2\pi) = -1_{(4)}$ ($1_{(3)}$ and $1_{(4)}$ denote the unit matrix in 3 and 4 dimensions) As a consequence $Q(\vec{n}, 2\pi) = -1_{(4)}$ and $Q(\vec{n}, 4\pi) = 1_{(4)}$ are mapped both on $1_{(3)}$: We have an *homomorphism* between quaternions and spatial rotation matrices and not an *isomorphism*. We remark that equations (22, 23) are known from spin 1/2-algebra in quantum mechanics. Indeed, the basis elements I, J, and K are *real* representations of $-i\sigma_x$, $-i\sigma_y$, $-i\sigma_z$. σ_x, σ_y, σ_z being the *Pauli spin matrices*. Therefore quaternions of length one can be considered as a real representation of the group $SU(2)$ (Special Unitary transformations in 2 dimensions). The rotation matrices $D(\vec{n}, \Phi)$ represent the group $SO(3)$ (Special Orthogonal transformations in 3 dimensions). 'Special' means that the determinant of the matrices, representing the respective group, is equal to one.

We can now easily derive the relation between quaternion parameters and Euler angles. With help of this relation the Wigner functions in the expansion of the MPCF can be expressed by quaternion parameters, which will turn out to be very useful for the numerical calculation of the g-coefficients. Writing the Euler rotation matrix as

$$D(\alpha, \beta, \gamma) = D(\vec{e}_z, \alpha)D(\vec{e}_y, \beta)D(\vec{e}_z, \gamma). \tag{24}$$

(see Appendix B), and using equation (20) we have consequently

$$Q(\alpha, \beta, \gamma) = Q(\vec{e}_z, \alpha)Q(\vec{e}_y, \beta)Q(\vec{e}_z, \gamma). \tag{25}$$

This yields the desired relation between quaternion parameters and Euler angles:

$$q_0(\alpha, \beta, \gamma) = \cos\left(\frac{\beta}{2}\right)\cos\left(\frac{\gamma + \alpha}{2}\right),$$

$$q_1(\alpha, \beta, \gamma) = \sin\left(\frac{\beta}{2}\right)\sin\left(\frac{\gamma - \alpha}{2}\right),$$

$$q_2(\alpha, \beta, \gamma) = \sin\left(\frac{\beta}{2}\right)\cos\left(\frac{\gamma - \alpha}{2}\right),$$

$$q_3(\alpha, \beta, \gamma) = \cos\left(\frac{\beta}{2}\right)\sin\left(\frac{\gamma + \alpha}{2}\right).$$

$$(26)$$

The rotation matrix, $D(\alpha, \beta, \gamma)$, expressed in terms of quaternion parameters, denoted by the shorthand Q, reads:

$$D(Q) = \begin{pmatrix} 1 - 2(q_2^2 + q_3^2) & 2(-q_0 q_3 + q_1 q_2) & 2(q_0 q_2 + q_1 q_3) \\ 2(q_0 q_3 + q_1 q_2) & 1 - 2(q_1^2 + q_3^2) & 2(-q_0 q_1 + q_2 q_3) \\ 2(-q_0 q_2 + q_1 q_3) & 2(q_0 q_1 + q_2 q_3) & 1 - 2(q_1^2 + q_2^2) \end{pmatrix} \quad (27)$$

We now show how Wigner functions can be expressed in terms of quaternion parameters. The Wigner functions $D_{m,n}^j(\alpha, \beta, \gamma)$ can be written in the following form [8]:

$$D_{m,n}^j(\alpha, \beta, \gamma) = e^{im\alpha} d_{m,n}^j(\beta) e^{in\gamma}. \quad (28)$$

The functions $d_{m,n}^j(\beta)$ are given by [16]

$$d_{m,n}^j(\beta) = \sum_t (-)^{t+n-m} \frac{[(j + m)!(j - m)!(j + n)!(j - n)!]^{1/2}}{(j + m - t)!(j - n - t)!t!(t + n - m)!} \quad (29)$$

$$\times \cos(\beta/2)^{2j+m-n-2t} \sin(\beta/2)^{2t+n-m}.$$

To express the Wigner functions in terms of quaternion parameters we follow ROSE [10] and introduce the complex parameters a and b,

$$a = q_0 + iq_3, \quad b = q_2 + iq_1, \quad (30)$$

where the quaternion parameters are given by equation (26). With those definitions, using the shorthand $Q = (q_0, q_1, q_2, q_3)$, the following expression is obtained:

$$D_{m,n}^j(Q) = \sum_t (-)^{t+n-m} \frac{[(j + m)!(j - m)!(j + n)!(j - n)!]^{1/2}}{(j + m - t)!(j - n - t)!t!(t + n - m)!} \quad (31)$$

$$\times a^{j-m-t}(a^*)^{j-n-t} b^{t+n-m}(b^*)^t.$$

This can be verified by straightforward insertion of the definitions for a and b, given in (30).

3.3 An Algorithm for the Calculation of g-Coefficients

As shown in 3.1, the main point in calculating g-coefficients for the irreducible representation of the MPCF from MD simulations is to evaluate a product of Wigner functions depending on the orientation of two molecules i and j. The orientation of the molecules must be referred to a coordinate system in which the joining vector of

the two molecular centers $\vec{R}_{ij}$ is parallel to the z-axis. This can be accomplished in three steps:

0. Start with the orientation parameters Ω_i, Ω_j of the two molecules and the joining vector $\vec{R}_{ij}$ in the space fixed frame.

1. Find the orientation parameters Ω_{ij} of the joining vector $\vec{R}_{ij}$ in the space fixed frame.

2. Perform an orthogonal coordinate transformation in which the z-axis of the new coordinate system coincides with the joining vector $\vec{R}_{ij}$ ($i - j$-system) and calculate the orientation parameters Ω_i', Ω_j' which refer to that *new* coordinate system.

3. Calculate the Wigner functions in terms of the *new* orientation parameters Ω_i' resp. Ω_j'.

The central idea of this paper is to use quaternion parameters for the numerical calculation of g-coefficients, because

● in many MD programs quaternions can be directly accessed since they are used for the solution of the rotational equation of motion,

● quaternions can be easily referred to rotated coordinate systems, since a rotation of the coordinate system can be mapped on a simple quaternion multiplication,

● Wigner functions can be expressed conveniently in terms of quaternion parameters (see equation (31)).

Following the steps for the calculation of the Wigner functions in the $i - j$-system, as listed above, we have first to find the quaternion parameters for the orthogonal transformation that rotates $\vec{e}_z$ on $\vec{n}_{ij}$, which is the unit vector along $\vec{R}_{ij}$. From figure 1 it can be seen that *one possible way* to perform such a rotation is to rotate about a rotation axis $\vec{n}_Q$. given by

$$\vec{n}_Q = \begin{cases} \dfrac{\vec{n}_{ij} + \vec{e}_z}{|\vec{n}_{ij} + \vec{e}_z|}, & \text{if } \vec{n}_{ij} \neq -\vec{e}_z, \\ \vec{n}_y & \text{if } \vec{n}_{ij} = -\vec{e}_z. \end{cases} \tag{32}$$

and a rotation angle $\Phi = \pi$. From (20) the components of the corresponding quaternion Q_{ij} are given by:

$$q_{ij,0} = 0 \tag{33}$$

$$q_{ij,1} = n_{Q,x} \tag{34}$$

$$q_{ij,2} = n_{Q,y} \tag{35}$$

$$q_{ij,3} = n_{Q,z}. \tag{36}$$

Now we have to calculate the quaternions Q_i', Q_j', in the rotated coordinate system. For that purpose we start with two molecular fixed frames being identical with the space fixed frame and build up the orientation of molecule i and j by two succesive rotations: A first rotation that rotates the molecular fixed z-axis on $\vec{n}_{ij}$, and a second rotation that rotates the molecule to its final position.

$$D(\Omega_i) = D(\Omega_i')D(\Omega_{ij}), \tag{37}$$
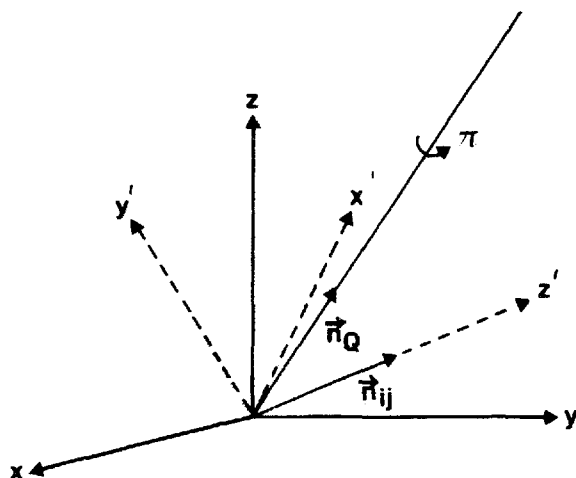
Figure 1 Rotation into the $i - j$ system.

$$D(\Omega_j) = D(\Omega'_j)D(\Omega_{ij})$$ (38)

As a consequence we have

$$Q'_i = Q_iQ'_{ij},$$ (39)

$$Q'_j = Q_jQ'_{ij}.$$ (40)

Having found the quaternion parameters Q'_i and Q'_j, the Wigner functions $D^{l_1}_{m_1,n_1}(Q_i)$ resp. $D^{l_2}_{m_2,-n_1}(Q_j)$ in equation (12) can be evaluated according to equation 31.

4. AN EXAMPLE

Here we apply the algorithm for the calculation of g-coefficients outlined above to methylene chloride (CH_2Cl_2). The molecules of methylene chloride have the geometry shown in figure 2. The characteristic bond lengths and angles are given in (41) according to [11].

$$\left.\begin{array}{rcl} r_{C-Cl} & = & 1.767 \pm 0.002\text{Å,} \\ r_{C-H} & = & 1.085 \pm 0.002\text{Å,} \\ \angle_{H-C-H} & = & 112.1 \pm 0.2°, \\ \angle_{Cl-C-Cl} & = & 112.2 \pm 0.1°. \end{array}\right\}$$ (41)

Methylene chloride has a permanent dipole moment of $1.6\,D$ in the gas phase [12]. The dipole vector directs along the b-axis in figure 2. Due to the C_{2v}-symmetry of the CH_2Cl_2 molecule the $g^{l_1,l_2}_{m_1,m_2;n_1}$-coefficients vanish unless m_1 and m_2 are *even* numbers [5], if the z-axis is chosen to be the symmetry axis of the molecule. We show in figure 3 the non-vanishing $g^{l,l}_{m_1,m_2;0}$-coefficients for $l = 0, 1, 2$. The MD simulation was carried
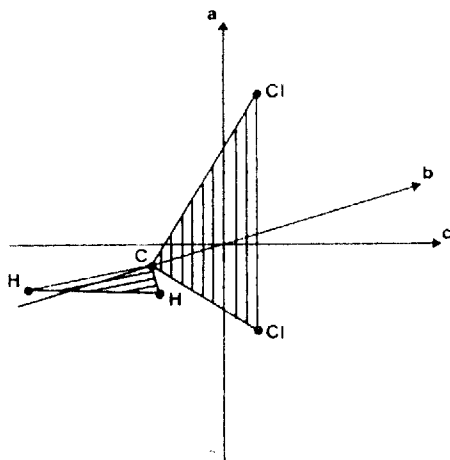
Figure 2 Geometry of a CH_2Cl_2 molecule. The axis a, b, c are principal axis of inertia.

out with the program MDMPOL [13]. In MDMPOL a quaternion leapfrog algorithm [7, 13] is used for the solution of the rotational equation of motion. To be consistent with our definitions of the quaternion parameters and Euler angles we modified in MDMPOL the formula for the rotation matrix in terms of quaternion parameters (see equation (27)) and the formula for the relation between the space fixed coordinates of the angular velcity and the time derivatives of the quaternion parameters (see equation (66), app. C) [17].

It can be seen from figure 3 that the intramolecular structure of the CH_2Cl_2 molecule plays an important role for orientational correlations. For example the $g_{2,-2,0}^{2,2}$-coefficient has the same order of magnitude as the $g_{0,0,0}^{2,2}$-coefficent, whereas for linear molecules all $g_{m_1,m_2,m_1}^{l_1,l_2}$ – coefficients vanish unless m_1 and m_2 are equal to zero. A graphical description of the mutual orientation of the molecules can be obtained from the g-coefficients by introducing into equation (12) the Wigner functions as explicit expressions, containing the Euler angles. Taking $g_{0,0,0}^{1,1}$ (r) as an example, the large peak above 4 Å can thus be interpreted as resulting from preferred parallel orientations, whereas the negative region below 4 Å indicates, that very close cms approach of two molecules can only be achieved by more antiparallel orientations. More detailed discussions of g-coefficients along such lines can be found for example in references [6] and [15].

Finally a remark has to be made with respect to the precision of the g-coefficients calculated from MD simulations. To obtain the statistical accuracy of normal atom pair correlation functions one has to use much more MD configurations for the calculation of g-coefficients: The configurational space which has to be 'scanned' while running through the MD configurations and filling up the g-histogram is given by all possible cms separation distances and all possible values of the five independent Euler angles describing the orientation of the molecules, whereas in the case of the atom pair correlation functions only the one dimensional space of the atom separation distance has to be sampled. For our calculations we generally used 16000 MD configurations of 108 CH_2Cl_2-molecules having a time distance of 20 fs (4 MD time steps). An exception was made for the $g_{0,0,0}^{0,0}$-coefficient, which is identical with the cms pair correlation function: According to the above considerations it was sufficient to
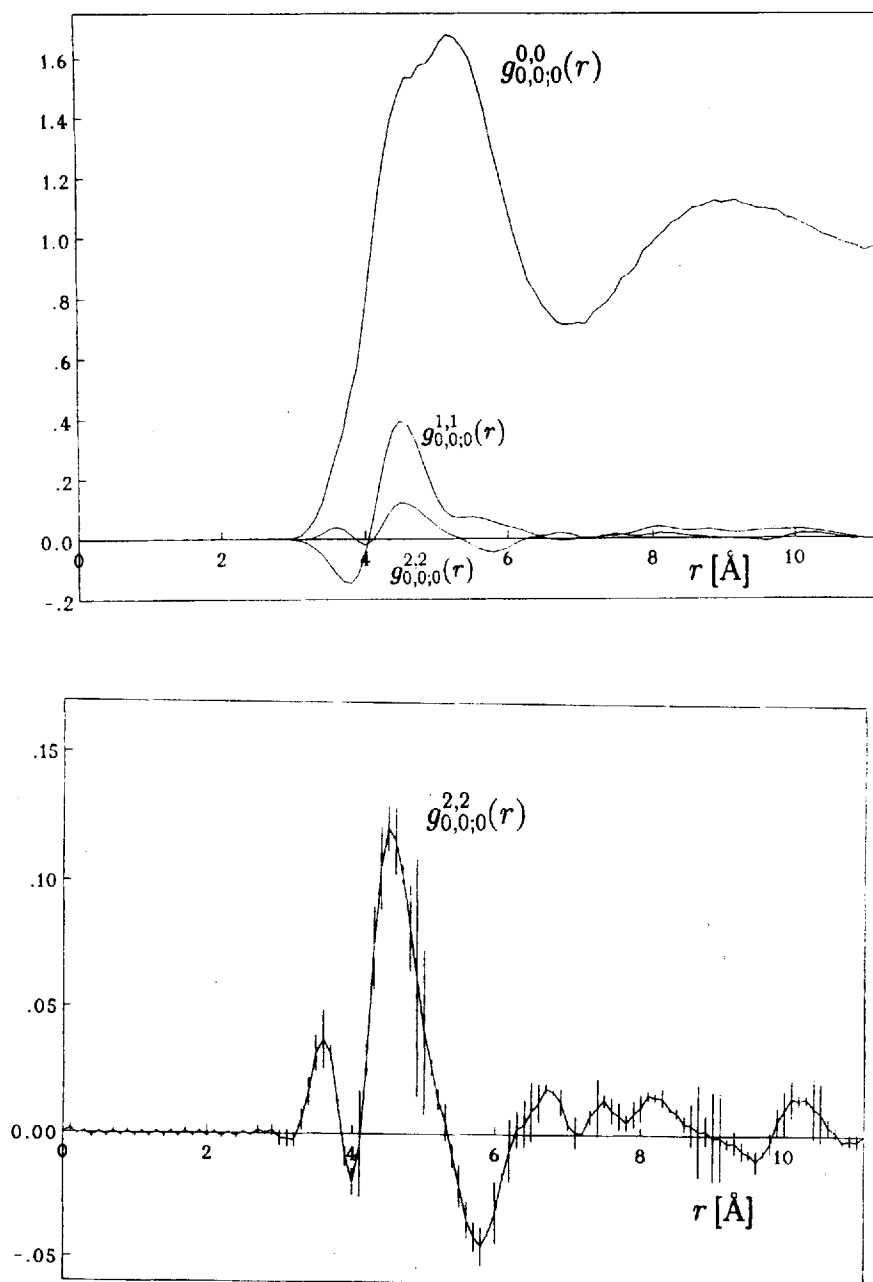
Figure 3 Some g-coefficients of CH_2Cl_2.

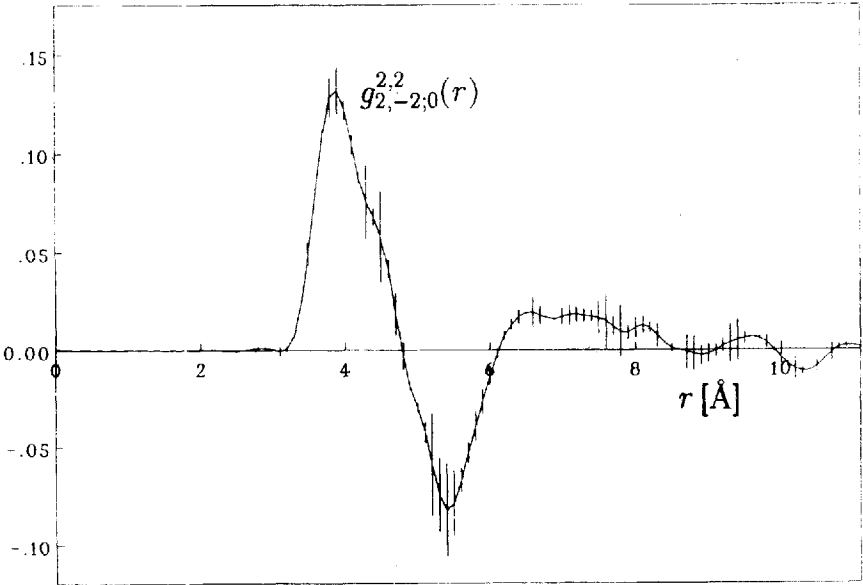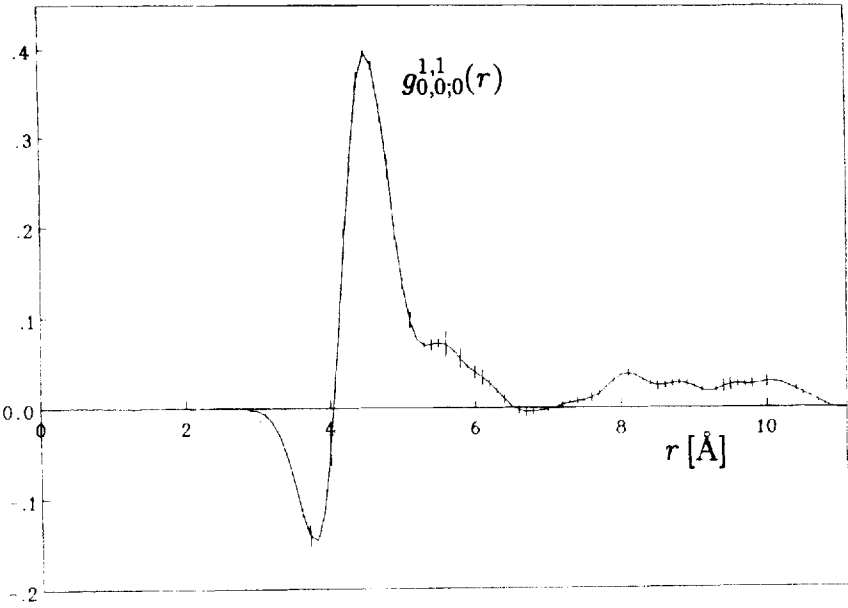**Figure 3** *(continued.)*

$$g_{2,0;0}^{2,2}(r) = g_{-2,0;0}^{2,2}(r)$$

$$r \, [\text{Å}]$$

$$g_{2,2;0}^{2,2}(r) = g_{-2,-2;0}^{2,2}(r)$$
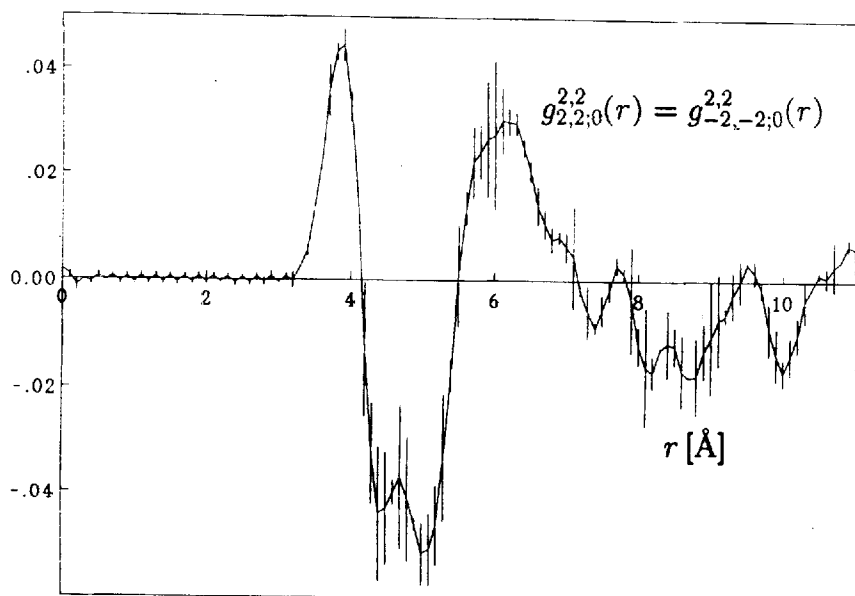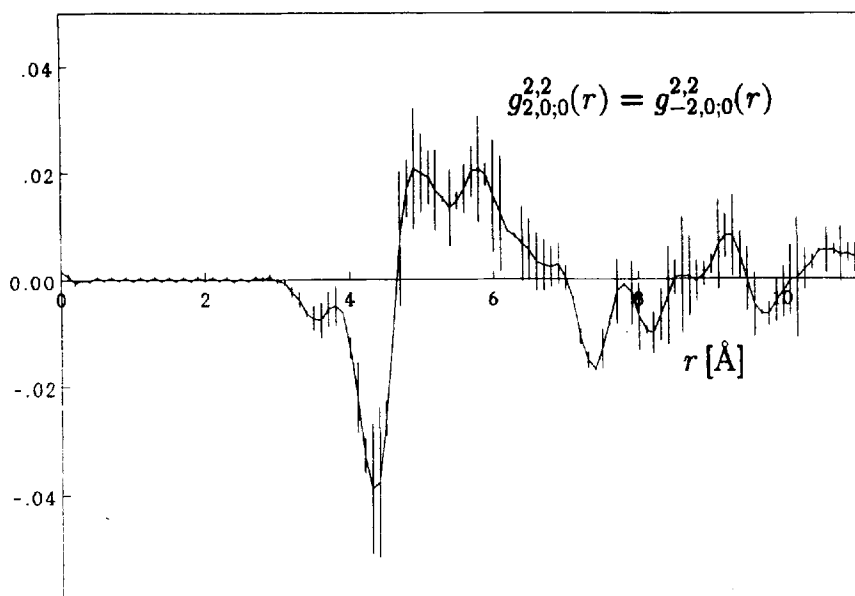
$$r \, [\text{Å}]$$

Figure 3   (*continued.*)

calculate this g-coefficient from 500 MD configuations to obtain a comparable statistical accuracy. For 16000 MD configurations we need about one CPU hour on a CRAY XM-P with our program GCOEFF, which is vectorized in the most time consuming parts. The size of the 'error bars' in fig. 3 indicates the difference between the 'raw data' of the g-coefficients and the corresponding smoothed curves. The smoothing was done by empirical spectral filtering: We suppressed the higher frequencies in the spectra of the g-coefficients in such a way that the resulting error bars had the same order of magnitude as the estimated statistical error. To estimate the statistical error we calculated some g-coefficients which should be zero due to the molecular symmetry and looked at their average deviations from zero.

APPENDIX

A. The General Form of a Rotation Matrix

We derive now the basic formula for a rotation matrix $D(\vec{n}, \Phi)$ in terms of the unit vector $\vec{n}$ along the rotation axis and the rotation angle Φ. $D(\vec{n}, \Phi)$ is defined to be the rotation matrix which rotates the x-, y-, z-axis of a given coordinate system into the x'-, y'-, z'-axis of a new coordinate system. Using the definition of the *infintesimal generators* of rotations about the x-, y-, z-axis, $L_i \doteq -\sqrt{-1}\ \dfrac{d}{d\phi_i}\ D(\vec{e}_i, \Phi_i)\Big|_{\Phi_i=0}$ (i (i

stands for x, y, z), explicitly written as

$$L_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}, \qquad L_y = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \qquad L_z = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (42)$$

the rotation matrix $D(\vec{n}, \Phi)$ can be written in the following form:

$$D(\vec{n}, \Phi) = e^{i\Phi \vec{n}\cdot\vec{L}} = (\cos \Phi)1 + (1 - \cos \Phi)\vec{n} \otimes \vec{n} + i(\sin \Phi)\vec{n}\cdot\vec{L}. \quad (43)$$

The symbol '$\otimes$' denotes the dyadic product. This form for $D(\vec{n}, \Phi)$ can be easily obtained by expanding $e^{i\Phi \vec{n}\cdot\vec{L}}$ in a power series and using the fact that $(\vec{n}\cdot\vec{L})^2 = 1 - \vec{n} \otimes \vec{n}$ is a projector on the plane perpendicular to the rotation axis. From (43) and (42) it follows immediately that $D(\vec{n}, \Phi)$ is an orthogonal matrix, having the property

$$D^{-1}(\vec{n}, \Phi) = D^t(\vec{n}, \Phi) = D(-\vec{n}, \Phi) = D(\vec{n}, -\Phi). \quad (44)$$

Due to the identity $(i\vec{n}\cdot\vec{L})\vec{a} = \vec{n}\wedge\vec{a}$, $\vec{a}$ being an arbitrary vector, it is immediately clear that $D(\vec{n}, \Phi)\vec{n} = \vec{n}$, i.e. $\vec{n}$ is the unit vector along the rotation axis. Writing $D(\vec{n}, \Phi)$ in an explicit matrix form one obtaines from (43)

$$D(\vec{n}, \Phi) = \quad (45)$$

$$\begin{pmatrix} n_x^2 + \cos\Phi(1 - n_x^2) & n_x n_y(1 - \cos \Phi) - n_z \sin \Phi & n_x n_z(1 - \cos \Phi) + n_y \sin \Phi \\ n_y n_x(1 - \cos \Phi) + n_z \sin \Phi & n_y^2 + \cos \Phi(1 - n_y^2) & n_y n_z(1 - \cos \Phi) - n_x \sin \Phi \\ n_z n_x(1 - \cos \Phi) - n_y \sin \Phi & n_z n_y(1 - \cos \Phi) + n_x \sin \Phi & n_z^2 + \cos \Phi(1 - n_z^2) \end{pmatrix}$$

In the cases of $\vec{n} = \vec{e}_x$, $\vec{n} = \vec{e}_y$, $\vec{n} = \vec{e}_z$, $D(\vec{n}, \Phi)$ reduces to the familiar rotation matrices describing rotations about the x-, y-, z-axis.

B. *The Rotation Matrix in Terms of Euler Angles*

The form of a rotation matrix in terms of Euler angles can be found with (43) according to the definition of the Euler angles [8]:

1. Rotation about the z-axis with angle α,
2. Rotation about the y'-axis ('line of nodes') with angle β,
3. Rotation about the z''-axis ('figure axis') with angle γ, from which we have for corresponding rotation matrix $D(\alpha, \beta, \gamma)$:

$$D(\alpha, \beta, \gamma) = D(\vec{e}_{z''}, \gamma)D(\vec{e}_{y'}, \beta)D(\vec{e}_z, \alpha), \tag{46}$$

where

$$\vec{e}_{y'} = D(\vec{e}_z, \alpha)\vec{e}_y, \tag{47}$$

$$\vec{e}_{z''} = D(\vec{e}_{y'}, \beta)\vec{e}_{z'} = D(\vec{e}_{y'}, \beta)\vec{e}_z. \tag{48}$$

It should be remarked that, instead of performing successive rotations about the z-, y'-, z''-axis with angles α, β, γ the same rotation is obtained by succesive rotations about the *space fixed* z-, y-, z-axis with angles γ, β, α:

$$D(\alpha, \beta, \gamma) = D(\vec{e}_z, \alpha)D(\vec{e}_y, \beta)D(\vec{e}_z, \gamma). \tag{49}$$

The explicit form for $D(\alpha, \beta, \gamma)$ reads

$$D(\alpha, \beta, \gamma) = \tag{50}$$

$$\begin{pmatrix} \cos\gamma\cos\beta\cos\alpha - \sin\gamma\sin\alpha & -\cos\gamma\sin\alpha - \cos\beta\cos\alpha\sin\gamma & \cos\alpha\sin\beta \\ \cos\gamma\cos\beta\sin\alpha + \cos\alpha\sin\gamma & \cos\gamma\cos\alpha - \cos\beta\sin\gamma\sin\alpha & \sin\beta\sin\alpha \\ -\cos\gamma\sin\beta & \sin\gamma\sin\beta & \cos\beta \end{pmatrix}$$

The inverse matrix of $D(\alpha, \beta, \gamma)$ is obtained by using eqs. (44), and (49):

$$D^{-1}(\alpha, \beta, \gamma) = D'(\alpha, \beta, \gamma) = D(-\gamma, -\beta, -\alpha). \tag{51}$$

C. *Angular Velocity*

In the following we list the relations between the time derivatives of the Euler angles and quaternion parameters as defined above and the components of the angular velocity in the space fixed and body fixed coordinate system. All formulas were generated with the algebraic programming system REDUCE [14]. We used the relation between the body fixed components of the angular velocity and the time ·derivatives of the quaternion parameters together with (27) to modify the quaternion leap-frog algorithm implemented in MDMPOL [13] with respect to the calculation of Wigner functions according to eqs. (26) and (31). All other relations are listed for reasons of completeness.

Starting from the orthogonality relation for a general rotation matrix depending on the time t,

$$D'D = DD' = 1, \tag{52}$$

we have by differentiating with respect to t:

$$\frac{d}{dt}(D'D) \;=\; D'\dot{D} + \dot{D}'D \;=\; D'\dot{D} + (D'\dot{D})' \;=\; 0 \tag{53}$$

$$\frac{d}{dt}(DD') \;=\; D\dot{D}' + \dot{D}D' \;=\; (\dot{D}D')' + \dot{D}D' \;=\; 0 \tag{54}$$

We see that $D'\dot{D}$ and $\dot{D}D'$ are both *antisymmetric* matrices:

$$\Omega_a \;\doteq\; D'\dot{D} \;=\; -\Omega_a', \tag{55}$$

$$\Omega_b \;\doteq\; \dot{D}D' \;=\; -\Omega_b'. \tag{56}$$

To get some insight in the physical meaning of Ω_a and Ω_b we define D to be the transformation matrix wich rotates the space fixed coordinate system into the body fixed coordinate system. Using that the components of a vector x and the basis vectors themselves transform *contragrediently*, we have (a prime denotes the body fixed frame):

$$\vec{x} \;=\; D\vec{x}', \quad \vec{x}' \;=\; D'\vec{x}. \tag{57}$$

Differentiating $\vec{x}$ and $\vec{x}'$ with respect to t and using (55) and (56) yields:

$$\dot{\vec{x}} \;=\; D(\dot{\vec{x}}' + \Omega_a\vec{x}'). \tag{58}$$

$$\dot{\vec{x}}' \;=\; D'(\dot{\vec{x}} - \Omega_b\vec{x}). \tag{59}$$

From this equations we have the following interpretation of Ω_a and Ω_b:

$$\Omega_a\vec{x}' \;=\; \vec{\omega}' \wedge \vec{x}', \; \Omega_b\vec{x} \;=\; \vec{\omega} \wedge \vec{x}, \tag{60}$$

where $\vec{\omega}$ and $\vec{\omega}'$ denote the components of the angular velocity in the space fixed resp. body fixed frame. Written in components, Ω_a and Ω_b read:

$$\Omega_a \;=\; \begin{pmatrix} 0 & -\omega_z' & \omega_y' \\ \omega_z' & 0 & -\omega_x' \\ -\omega_y' & \omega_x' & 0 \end{pmatrix}, \qquad \Omega_b \;=\; \begin{pmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{pmatrix}. \tag{61}$$

From (55), (56), and (61) the relation between the components of angular velocity and the time derivatives of the Euler angles resp. quaternion parameters can be calculated by an algebraic programming system like REDUCE. We have the following expressions for the relation between the components of the angular velocity and the time derivatives of the Euler angles:

$$\begin{pmatrix} \omega_x' \\ \omega_y' \\ \omega_z' \end{pmatrix} = \begin{pmatrix} -\cos\gamma\,\sin\beta & \sin\gamma & 0 \\ \sin\gamma\,\sin\beta & \cos\gamma & 0 \\ \cos\beta & 0 & 1 \end{pmatrix} \begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix}, \tag{62}$$

$$\begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = \begin{pmatrix} 0 & -\sin\alpha & \cos\alpha\,\sin\beta \\ 0 & \cos\alpha & \sin\alpha\,\sin\beta \\ 1 & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix}. \tag{63}$$

Inversion of (62) and (63) yields:

$$
\begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix} = \begin{pmatrix} -\dfrac{\cos\gamma}{\sin\beta} & \dfrac{\sin\gamma}{\sin\beta} & 0 \\ \sin\gamma & \cos\gamma & 0 \\ \cot\beta\,\cos\gamma & -\cot\beta\,\sin\gamma & 1 \end{pmatrix} \begin{pmatrix} \omega'_x \\ \omega'_y \\ \omega'_z \end{pmatrix},
\tag{64}
$$

$$
\begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix} = \begin{pmatrix} -\cot\beta\,\cos\alpha & -\cot\beta\,\sin\alpha & 1 \\ -\sin\alpha & \cos\alpha & 0 \\ \dfrac{\cos\alpha}{\sin\beta} & \dfrac{\sin\alpha}{\sin\beta} & 0 \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}
\tag{65}
$$

For the relation between the components of the angular velocity and the time derivatives of the quaternion parameters one has:

$$
\begin{pmatrix} 0 \\ \omega'_x \\ \omega'_y \\ \omega'_z \end{pmatrix} = 2\cdot \begin{pmatrix} q_0 & q_1 & q_2 & q_3 \\ -q_1 & q_0 & q_3 & -q_2 \\ -q_2 & -q_3 & q_0 & q_1 \\ -q_3 & q_2 & -q_1 & q_0 \end{pmatrix} \begin{pmatrix} \dot{q}_0 \\ \dot{q}_1 \\ \dot{q}_2 \\ \dot{q}_3 \end{pmatrix},
\tag{66}
$$

$$
\begin{pmatrix} 0 \\ \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = 2\cdot \begin{pmatrix} q_0 & q_1 & q_2 & q_3 \\ -q_1 & q_0 & -q_3 & q_2 \\ -q_2 & q_3 & q_0 & -q_1 \\ -q_3 & -q_2 & q_1 & q_0 \end{pmatrix} \begin{pmatrix} \dot{q}_0 \\ \dot{q}_1 \\ \dot{q}_2 \\ \dot{q}_3 \end{pmatrix}
\tag{67}
$$

Inversion of (66) and (67) yields:

$$
\begin{pmatrix} \dot{q}_0 \\ \dot{q}_1 \\ \dot{q}_2 \\ \dot{q}_3 \end{pmatrix} = \tfrac{1}{2}\cdot \begin{pmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{pmatrix} \begin{pmatrix} 0 \\ \omega'_x \\ \omega'_y \\ \omega'_z \end{pmatrix},
\tag{68}
$$

$$
\begin{pmatrix} \dot{q}_0 \\ \dot{q}_1 \\ \dot{q}_2 \\ \dot{q}_3 \end{pmatrix} = \tfrac{1}{2}\cdot \begin{pmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & q_3 & -q_2 \\ q_2 & -q_3 & q_0 & q_1 \\ q_3 & q_2 & -q_1 & q_0 \end{pmatrix} \begin{pmatrix} 0 \\ \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}
\tag{69}
$$

We remark that the zero component of the angular velocity in eqs. (66) and (67) is just the derivation of the identity $q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1$ with respect to time.

Acknowledgement

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[16] This form, except for a factor $(-1)^{n-m}$, is given in Brink and Satchler [9]. The Wigner functions in Brink and Satchler and related to those in Edmonds [8] by $D^j_{m,n}(\alpha, \beta, \gamma) = D^j_{m,n}(-\alpha, -\beta, -\gamma)$.

[17] In MDMPOL the so-called 'x-convention' for the definition of the Euler angles is used, i.e. the rotation axis for the second rotation with angle β is the x'-axis, whereas we use the 'y-convention', where the rotation axis for the second rotation is the y'-axis.