Tetrahedral harmonics revisited

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Tetrahedral harmonics revisited

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Linear combinations of spherical harmonics are derived that are adapted to the molecular symmetry group $T_d(M)$ and its isomorphic point groups $T_d$ and $O$. The alternating group $T(M)$, consisting of even permutations, is the semi-direct product $V_4 @ C_3$, where $C_3 = \{E, (123), (132)\}$ is a cyclic group and $V_4 = \{E, (12)(34), (13)(24), (14)(23)\}$. Further $T_d(M) = T(M) @ \{E, (12)^\ast\}$. This structure of the group enables one to write down simple closed expressions for basis functions. Using the program Maple, tables up to and including $l = 10$ are generated.

1. Introduction

In the course of our work on the rovibrational spectra of methane–argon [1–3], the need arose to have explicit expressions for tetrahedral harmonics. Tetrahedral harmonics are linear combinations of spherical harmonic functions $Y_{lm}$ of the same order ($l$) and of different $m$ that carry irreducible representations (irreps) of the tetrahedral group $T_d$. In our argon–methane work we described the atom–molecule interaction in terms of spherical harmonic functions depending on the position vector of the argon atom. This vector was expressed in a body-fixed frame on methane. For such a floppy system as Ar–CH$_4$, the concept of a point group is of no use, and the molecular symmetry (MS) group $T_d(M)$ enters the theory in its stead. This group consists of the feasible [4] permutations and permutation-inversions of the hydrogens. Hence we will begin by addressing the question of how the methane permutation-inversions (PIs) act on the spherical harmonics. Next we will describe an easy way to construct tetrahedral harmonics in the context of the MS group $T_d(M)$. Because the groups $T_d$ and $T_d(M)$ are isomorphic, the present MS group derivation can be transcribed without any difficulty to the point group $T_d$, and we mention this later in the paper.

The construction of tetrahedral harmonics has a long history. Bethe considered them as long ago as 1929 in his seminal work on term splittings in crystals [5]. The first extensive tables of these functions were published in 1962 by Altmann and Bradley [6]. These tables are not in a very convenient form because neither the expansions nor the spherical harmonic basis functions are normalized. On the other hand, this enabled the authors to present the expansion coefficients as non-factorized integers. For the higher values of $l$ these integers become unwieldily large: up to 12 digits. Also, it seems that there are some errors in these tables [7]. In 1970 a fairly long and complicated paper [8] appeared that described in detail how the tetrahedral functions may be constructed. For his 1979 book Tang Au-Chin [7] reworked the Altmann–Bradley tables and presented the expansion coefficients in a more convenient (normalized and factorized) form. In their fairly recent book [9] Altmann and Herzig presented tables in a complex basis. The (complex) expansion coefficients were given in a 13 digit floating point format.

All these workers used the following well known group-theoretical formula for constructing the tetrahedral harmonics:

$$|l, m, G, \lambda, i\rangle = \frac{f_\lambda}{|G|} \sum_{g \in G} D^{(\lambda)}(g^{-1})_{ij} gY_{lm},$$

where $|G|$ is the order of the group ($|T_d| = 24$). The sum runs over all group elements and $\lambda$ labels an irrep of the group $G$. For $T_d$; $\lambda = A_1, E, F_1, F_2$. The quantity $f_\lambda$ is the dimension of $D^{(\lambda)}$ and $D^{(\lambda)}(g^{-1})_{ij}$ is an element of the actual matrix representation. The main purpose of this work is to point out that this formula is much more complicated than necessary: it requires explicit knowledge of all matrix elements $D^{(\lambda)}_{ij}$ and entails a sum over all group elements. We will prove instead the following simple formulae for the functions spanning the irreps of $T_d(M)$ ($m$ even, unnormalized functions; primitive functions of odd $m$ are not needed, as we will see below).

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Table 1. Euler angles (in deg) of permutations in the group Td(M).

<table>
<thead>
<tr>
<th>Permutation</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(12)(34)</td>
<td>0</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>(13)(24)</td>
<td>0</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>(14)(23)</td>
<td>0</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>(123)</td>
<td>270</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>(12)*</td>
<td>0</td>
<td>180</td>
<td>90</td>
</tr>
</tbody>
</table>

where $\vec{h}_i$ is a vector pointing from carbon to hydrogen $h_i$. These vectors span a space that is invariant under T(M). Thus for any $P \in T(M)$ we have

$$P(\vec{g}_x, \vec{g}_y, \vec{g}_z) = (\vec{g}_x, \vec{g}_y, \vec{g}_z)P.$$ (3)

The matrices $P^*$ can be derived readily by permuting the labels on the $h_i$. In doing so, it is found that the permutations in the group T(M) all give rise to proper orthogonal matrices. These can be factorized as $R_z(\alpha)R_y(\beta)R_z(\gamma)$, where $R_k(\omega)$ is the matrix representing a rotation around the coordinate axis $k$ over an angle $\omega$, see for instance, [10], p. 23, for the explicit definition of these matrices. In this manner one can derive the Euler angles given in table 1. The Euler angles of the elements in the coset Td(M)\T(M) can be found in a similar manner. These elements are of the form $PE^*$, where $P$ is a permutation of odd parity and $E^*$ is inversion with respect to the centre of mass (the carbon atom in equilibrium methane). Using $E^* \vec{h}_i = -\vec{h}_i$ we find

$$PE^*(\vec{g}_x, \vec{g}_y, \vec{g}_z) = (\vec{g}_x, \vec{g}_y, \vec{g}_z)$$

with Euler angles: $(0, \pi, \pi/2)$. The element $(12)^*$ is the only one that we will need from the coset. The 24 proper rotation matrices generated in this manner constitute the point group $O$, which by definition is the group of proper 3 x 3 matrices that leave an octahedron invariant. The octahedral group $O$ being isomorphic with $Td(M)$, we are considering in fact a faithful representation of $Td(M)$. The elements of this representation are the ‘equivalent rotations’ of Bunker and Jensen [11]. The fact that we are considering the group O rather than $T_d$ has a consequence for the labelling of the irreps. It is well known that tetrahedral harmonics are equal to octahedral harmonics, the only difference between the two kinds of harmonic being the irrep label. For odd $l$ the subscripts on the $A_{1,2}$ and $F_{1,2}$ irrep labels are interchanged between $O$ and $T_d$.\n
2. Action of $T_d(M)$ on spherical harmonics

We use equilibrium methane as a model for the group $T_d(M)$ and define the following body-fixed basis vectors (which form an Eckart frame):

$$\vec{g}_x = (\vec{h}_1 + \vec{h}_2 + \vec{h}_3 - 2\vec{h}_4)/2,$$
$$\vec{g}_y = (\vec{h}_1 + \vec{h}_2 - \vec{h}_3 + \vec{h}_4)/2,$$
$$\vec{g}_z = (\vec{h}_1 + \vec{h}_2 - \vec{h}_3 - \vec{h}_4)/2,$$

where $A_{lm}$ and $B_{lm}$ are real and normalized combinations of spherical harmonics. The permutations (123) and (132) are elements of the molecular symmetry group $T_d(M)$ and $E$ is the identity element of this group. Whether the function is $A_l$, or $A_l^2$ is determined by the value of $m$. Also the choice between $F_l$ and $F_l^2$ is dictated by $m$. The existence of such transparent relations is due to two facts. In the first place $T_d(M)$ has a simple structure: it can be written as a semi-direct product. Second, the functions $A_{lm}$ and $B_{lm}$ are for even $m$ eigenfunctions of $(12)'$ with eigenvalues $A(-1)^m/2$. We will consider the action of the permutations on the primitive functions and derive closed expressions. We present tables of tetrahedral harmonics up to and including $l = 10$. We include these tables because the book of Tan Au-Chin, published in 1979 in Beijing, is not generally available. Nowadays it is easy to generate such tables because of the existence of formula manipulation packages, such as Maple, that can handle radical numbers in an exact way. In addition, our work may be seen as a check of the older works. The basis for $A_{1,2}$ and $E$ is exactly the same as found in [7] (we found only one typographical error in [7]), but for $F_{1,2}$ we have a different convention for the basis of the matrix irrep.
Consider a vector \( \vec{R} = (\vec{g}_x, \vec{g}_y, \vec{g}_z) \mathbf{R} \), which is invariant under the operations in \( T_d(M) \). (This vector is, e.g. the position vector of an argon atom expressed in the body-fixed frame on methane). Defining \( \vec{R}' \) by
\[
\vec{R}' = P(\vec{g}_x, \vec{g}_y, \vec{g}_z) \mathbf{R}^t,
\]
we find from equation (3) that \( \mathbf{PR'} = \mathbf{R} \). Hence
\[
Y_{lm}(\vec{R}') = \sum_{m=-l}^{l} Y_{lm}(\mathbf{R}) D_{m'm}(\mathbf{P}),
\]
where \( Y_{lm} \) is a spherical harmonic function and the matrix \( D_{m'm}(\alpha, \beta, \gamma) \equiv e^{-im\alpha} d_{m'm}(\beta) e^{-im\gamma} \) depends on the three Euler angles corresponding to the permutation \( \mathbf{P} \).

3. Adaptation to the group \( V_4 \)

It is convenient to work with spherical harmonic functions that have Racah's phase, i.e. \( Y_{lm}^* = (-1)^{l+m} Y_{l,-m} \). In equation (1) and (2) we defined the real-valued functions \( A_{lm} \) and \( B_{lm} \).

The group \( T(M) \) is the semi-direct product \( V_4 \otimes C_3 \), where \( C_3 \) is the cyclic subgroup generated by \( (123) \) and where Klein's 'Vierergruppe'
\[
V_4 \equiv \{ E, (12)(34), (13)(24), (14)(23) \}
\]
is an invariant subgroup of \( T(M) \). Since \( V_4 = \{ E, (12)(34) \} \otimes \{ E, (13)(24) \} \), adaptation of \( Y_{lm} \) to \( V_4 \) is done by the projectors
\[
[E \pm (12)(34)] [E \pm (13)(24)].
\]
Using for integer \( m \):
\[
d_{m'm}(\pi) = \delta_{m,-m'} (-1)^{l+m},
\]
we find from equation (4), from the explicit formula for the \( D \) matrix, and from the Euler angles in table 1, that
\[
(12)(34)Y_{lm} = (-1)^{m} Y_{l,-m},
\]
\[
(13)(24)Y_{lm} = (-1)^{l+m} Y_{l,-m},
\]
\[
(14)(23)Y_{lm} = (-1)^{l} Y_{l,-m}.
\]
The \( V_4 \) functions are
\[
|l, m, V_4, A_1\rangle = A_{lm}(1 + (-1)^m),
\]
\[
|l, m, V_4, B_1\rangle = A_{lm}(1 - (-1)^m),
\]
\[
|l, m, V_4, B_2\rangle = B_{lm}(1 + (-1)^m),
\]
\[
|l, m, V_4, B_3\rangle = B_{lm}(1 - (-1)^m).
\]
Note that the first and third functions vanish if \( m \) is odd, whereas the second and fourth vanish if \( m \) is even. Complete sets of basis functions can be obtained from the primitive functions \( |l, m, V_4, A_1\rangle \) and \( |l, m, V_4, B_2\rangle \) only, so that \( m \) can be taken to be even. The fact that the sets obtained from even-\( m \) primitive functions are complete follows from inspection of the multiplicity table for the subduction of \( SO(3) \) to \( O \), as for instance given by Hougen [12]. This multiplicity table can be derived readily from the irreducible characters of \( SO(3) \) and \( O \).

4. A functions of \( T(M) \)

Induction to the group \( T(M) \) is achieved by the usual projectors of the cyclic group \( C_3 \):
\[
|l, m, T, A_1\rangle = [E + (123) + (132)]|l, m, V_4, A_1\rangle,
\]
\[
|l, m, T, A_2\rangle = [E + w_3(123) + w_3^2(132)]|l, m, V_4, A_1\rangle,
\]
\[
|l, m, T, A_3\rangle = [E + w_3(123) + w_3^2(132)]|l, m, V_4, A_1\rangle,
\]
where \( w_3 = \exp(i2\pi/3) \). By definition these functions span 1-dimensional irreps of \( C_3 \). Because \( V_4 \) is an invariant subgroup we have \( g^{-1} h g = h' \), so that \( h g = g h' \) for \( h, h' \in V_4 \) and \( g \in C_3 \) and hence the functions are \( A_1 \) under \( V_4 \). The three functions span 1-dimensional irreps of \( T(M) \).

In order to obtain a closed expression for these functions, we use Euler angles of \( (123) \) given in table 1 and recall that \( m \) is even:
\[
(123) A_{lm} = \frac{1}{2} \sqrt{2 - \delta_{m0}} \sum_{m'=-1}^{1} Y_{lm'} \times [\xi_{m'm} w_4^{-3m'} + (-1)^{l+m'} \xi_{m'-m} w_4^{3m'}],
\]
where \( w_4^{3m'} = \exp(\pm i\pi/2) m = \exp(\pm i3\pi/2) = (-1)^{m/2} \) Further
\[
\xi_{m'm} = d_{m'm}(\pi/2). \quad (5)
\]
Noting that \( \xi_{m'}(-m') = (-1)^{l+m'} \xi_{m'm} \), we find
\[
(123) A_{lm} = (-1)^{m/2} (2 - \delta_{m0})^{1/2} \sum_{m' > 0} A_{lm'} \xi_{m'm}.
\]
Likewise,
\[
(132) A_{lm} = (2 - \delta_{m0})^{1/2} \sum_{m' > 0} (2 - \delta_{m'0})^{1/2} (-1)^{m'/2} A_{lm'} \xi_{m'm}.
\]
In total (dropping the overall factor, \( m \) even):
$$|l, m, T, A_l\rangle = A_{lm} + (2 - \delta_{mb})^{1/2} \times \sum_{m' \geq 0 \text{ even}} (2 - \delta_{m'b})^{1/2} A_{lm'} \xi_{m'm}^{l'}$$

$$\times [(-1)^{m/2} + (-1)^{m'/2}]$$

It is readily derived from Varshalovich et al. [13], equation (5), §4.3, that

$$\xi_{m'm}^{l'} = \frac{(-1)^{m-m'}}{4^{l/2}} \sqrt{(l + m'!)(l - m'!)}$$

$$\times \sum_k (-1)^k \left( \begin{array}{c} l + m' \\ k \\ k \end{array} \right) \left( \begin{array}{c} l - m' \\ k + m' - m \end{array} \right),$$

where $\xi_{m'm}^{l'}$ is defined by equation (5). Using this expression we generated the $A$ functions in table 2 up to and including $l = 10$.

It is now easy to obtain the $A_2$ and $A_3$ functions of the group $T(M)$. These functions contain the complex factors $w_3$ and $w_4$, and are seen to be connected by complex conjugation. Hence, it is convenient to consider $|l, m, T, A_2\rangle \pm |l, m, T, A_3\rangle$, because these functions are real or purely imaginary, although in the group $T(M)$ there is no good reason to consider these combinations of different irreps of $T(M)$. In the group $T_d(M)$, however, the functions $|l, m, T, A_2\rangle$ and $|l, m, T, A_3\rangle$ span together the 2-dimensional irrep $E$. This is seen as follows. First,

$$(12)^* [E + w_3(123) + w_4^2(132)]$$

$$= [E + w_3(132) + w_4^2(123)](12)^*.$$

From the Euler angles in table 1 it readily follows for even $m$ that

Table 2. Normalized $A_{1,2}$ functions of the groups $T_d$ and $O$. The group $O$ is equal to the faithful representation of $T_d(M)$ considered in this work.

<table>
<thead>
<tr>
<th>$O$</th>
<th>$T_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_{0,0}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_{32}$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>$\frac{1}{6}\sqrt{3.7}A_{40} + \frac{1}{2}\sqrt{3.5}A_{44}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$\frac{1}{4}\sqrt{2}A_{60} - \frac{1}{2}\sqrt{2.7}A_{64}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$\frac{1}{4}\sqrt{11}A_{62} - \frac{1}{2}\sqrt{5}A_{66}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$\frac{1}{8}\sqrt{2.3.3.13}A_{42} + \frac{1}{8}\sqrt{2.3.11}A_{66}$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>$\frac{1}{4}\sqrt{3.5}A_{48} + \frac{1}{8}\sqrt{3.7}A_{44} + \frac{1}{12}\sqrt{3.5.13}A_{88}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$\frac{1}{4}\sqrt{3.13}A_{84} - \frac{1}{8}\sqrt{2.3.7}A_{98}$</td>
</tr>
</tbody>
</table>

The functions of $T(M)$ can be derived from the functions of $T_d(M)$ as follows:

$$(12)^* A_{lm} = (-1)^{m/2} A_{lm},$$

so that

$$(12)^* (|l, m, T, A_2\rangle, |l, m, T, A_3\rangle) = (|l, m, T, A_2\rangle, |l, m, T, A_3\rangle)$$

$$\times (-1)^{m/2} \left( \begin{array}{c} 0 \\ 1 \\ 1 \end{array} \right).$$

It can be proved that the only matrix commuting with this matrix and the diagonal matrices representing $A_2 \oplus A_3$ of $T(M)$ is a scalar times the $2 \times 2$ unit matrix. Hence, by Schur’s lemma this representation is irreducible under $T_d(M)$. Now, using that $w_3 + w_4^2 = -1$ and $-i(w_3 - w_4^2) = 3$, we have for even $m$ the two partners spanning the $E = A_2 \oplus A_3$ rep of $T(M)$:

$$|l, m, T_d, E, 1\rangle = [2E - [(123) + 132]] A_{lm}$$

$$\propto 2A_{lm} - (2 - \delta_{mb})^{1/2} \times \sum_{m' \geq 0 \text{ even}} (2 - \delta_{m'b})^{1/2} A_{lm'} \xi_{m'm}^{l'}$$

$$\times [(-1)^{m/2} + (-1)^{m'/2}],$$

$$|l, m, T_d, E, 2\rangle = [(123) - (132)] A_{lm}$$

$$\propto (2 - \delta_{mb})^{1/2} \times \sum_{m' \geq 0 \text{ even}} (2 - \delta_{m'b})^{1/2} A_{lm'} \xi_{m'm}^{l'}$$

$$\times [(-1)^{m/2} - (-1)^{m'/2}].$$

See table 3 for the normalized functions up to and including $l = 10$ that span the $E$ rep. For $l = 8$ the $E$ rep occurs twice. Although not really necessary, we orthogonalized the second basis (obtained by projecting $A_{44}$) onto the first basis (obtained by projecting $A_{42}$). In the case of $l = 10$ we also explicitly orthogonalized the second $E$ space onto the first.

5. $F$-Functions of $T(M)$

Turning to the $F$ irrep of $T(M)$, we observe first that different equivalent matrix irreps can constructed. As we will see below, it will be convenient to depart from the function $|l, m, V_4, B_2\rangle = B_{lm} (1 + (-1)^m)$ in the step from $T(M)$ to $T_d(M)$, since this is an eigenfunction of (12)* for even $m$: 

$$(12)^* B_{lm} = (-1)^{m/2} B_{lm}.$$ 

One basis could be

$$[E + (123) + (132)] |l, m, V_4, B_2\rangle,$$

$$[E + w_3(123) + w_4^2(132)] |l, m, V_4, B_2\rangle,$$

$$[E + w_3(132) + w_4^2(123)] |l, m, V_4, B_2\rangle.$$

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which offers a complex diagonal representation of \( C_3 \).
The other is the obvious linear combination:

\[
\begin{align*}
|l, m, T, F, 1\rangle &= |l, mV_4, B_2\rangle, \\
|l, m, T, F, 2\rangle &= (123)|l, m, V_4, B_2\rangle, \\
|l, m, T, F, 3\rangle &= (132)|l, m, V_4, B_2\rangle,
\end{align*}
\]

which offers a representation to \( C_3 \) consisting of real \( 3 \times 3 \) permutation matrices. Because the second basis is easier to construct we will consider it further.

It is again straightforward to prove that the only matrix commuting with the matrix representation of \( T(M) \) spanned by these functions is a scalar times the \( 3 \times 3 \) unit matrix, so that this \( F \) representation of \( T(M) \) is irreducible. Taking \( m \) even, we consider

\[
\frac{1}{2i} (Y_{lm'} + Y_{l,-m'}(-1)^{l-m}) = \frac{1}{2i} (Y_{lm'} - Y_{l,-m'}(-1)^{l-m})
\]

for odd \( m' \) and even \( m \). Thus,

\[
(123)B_{lm} = (-1)^{m'/2} \sqrt{2 - \delta_{m0}} \sum_{m' > 0} e_i^{l} \xi_{m'm} B_{lm'}.
\]

The last partner in the \( F \) irrep is \( \frac{1}{2} (132)|l, m, V_4, B_2\rangle \).
Then along the same lines we find (even \( m \)):

\[
(132)B_{lm} = \sqrt{2 - \delta_{m0}} \sum_{m' > 0} (-1)^{m'/2} e_i^{l} \xi_{m'm} A_{lm'}.
\]

where we used

\[
Y_{lm'} + Y_{l,-m'}(-1)^{l-m}w_4^m = Y_{lm'} + Y_{l,-m'}(-1)^{l-m} = 2(2 - \delta_{m0})^{-1/2} A_{lm'}
\]

and

\[
\frac{1}{2i} (Y_{lm'} + Y_{l,-m'}(-1)^{l-m}) = \frac{1}{2i} (Y_{lm'} - Y_{l,-m'}(-1)^{l-m})
\]

for odd \( m' \) and even \( m \). Thus,
Table 4. Normalized partners in the $F_{1,2}$ irrep of the groups $T_d$ and $O$. The group $O$ is equal to the faithful representation of $T_d(M)$ considered in this work.

<table>
<thead>
<tr>
<th>$O$</th>
<th>$T_d$</th>
<th>$O$</th>
<th>$T_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td>$B_{10}$</td>
<td>$T_2$</td>
<td>$B_{22}$</td>
</tr>
<tr>
<td></td>
<td>$-B_{11}$</td>
<td></td>
<td>$2^{-6}[15\sqrt{6}B_{71} - 19\sqrt{2}B_{73} + 22B_{75} + \sqrt{2.7.11.13}B_{77}]$</td>
</tr>
<tr>
<td></td>
<td>$-B_{21}$</td>
<td></td>
<td>$2^{-6}[-15\sqrt{6}A_{71} - 19\sqrt{2}A_{73} - 22A_{75}$</td>
</tr>
<tr>
<td></td>
<td>$A_{21}$</td>
<td></td>
<td>$+\sqrt{2.7.11.13}A_{77}]$</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$B_{30}$</td>
<td>$T_2$</td>
<td>$B_{74}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[\sqrt{6}B_{31} - \sqrt{10}B_{33}]$</td>
<td></td>
<td>$2^{-2}[3\sqrt{33}B_{71} + \sqrt{11}B_{73} - 25B_{75} - \sqrt{2.7.13}B_{77}]$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[6A_{31} + \sqrt{10}A_{33}]$</td>
<td></td>
<td>$2^{-2}[3\sqrt{33}A_{71} - \sqrt{11}A_{73} - 25A_{75} + \sqrt{2.7.11.3}T_{77}]$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>$T_1$</td>
<td>$B_{32}$</td>
<td>$T_2$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[\sqrt{10}B_{31} + \sqrt{6}B_{33}]$</td>
<td></td>
<td>$2^{-6}[6.11.13B_{71} + 3\sqrt{2.11.13}B_{73} + 5\sqrt{26}B_{75}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[-\sqrt{10}A_{31} + \sqrt{6}A_{33}]$</td>
<td></td>
<td>$+\sqrt{14}B_{77}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[-\sqrt{2}A_{41} - \sqrt{14}A_{43}]$</td>
<td></td>
<td>$2^{-6}[-6.11.13A_{71} + 3\sqrt{2.11.13}A_{73} - 5\sqrt{26}A_{75}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[\sqrt{14}A_{41} + \sqrt{2}A_{43}]$</td>
<td></td>
<td>$+\sqrt{14}A_{77}]$</td>
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<tr>
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<td>$T_1$</td>
<td>$B_{54}$</td>
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<td>$2^{-2}[\sqrt{14}B_{41} + \sqrt{2}B_{43}]$</td>
<td></td>
<td>$2^{-6}[\sqrt{2.35}B_{81} - 3\sqrt{2.33}B_{83} + \sqrt{2.5.11.13}B_{85}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-2}\sqrt{14}A_{41} - \sqrt{2}A_{43}]$</td>
<td></td>
<td>$-\sqrt{2.7.11.13}A_{87}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-6}[-2.35A_{81} - 3\sqrt{2.33}A_{83} - \sqrt{2.5.11.13}A_{85}$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$2^{-2}[\sqrt{14}A_{41} - \sqrt{2}A_{43}]$</td>
<td></td>
<td>$-\sqrt{2.7.11.13}A_{87}]$</td>
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<td>$T_1$</td>
<td>$B_{80}$</td>
<td>$T_2$</td>
</tr>
<tr>
<td></td>
<td>$2^{-4}[-2\sqrt{15}B_{51} + \sqrt{70}B_{53} - 3\sqrt{14}B_{55}]$</td>
<td></td>
<td>$2^{-5}[\sqrt{7.11}B_{81} - 5\sqrt{15}B_{83} + 3\sqrt{13}B_{85} + \sqrt{5.7.13}B_{87}]$</td>
</tr>
<tr>
<td></td>
<td>$2^{-4}[-2\sqrt{15}A_{51} + \sqrt{70}A_{53} - 3\sqrt{14}A_{55}]$</td>
<td></td>
<td>$2^{-5}[\sqrt{7.11}A_{81} + 5\sqrt{15}A_{83} + 3\sqrt{13}A_{85} - \sqrt{5.7.13}A_{87}]$</td>
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<td>$T_1$</td>
<td>$B_{52}$</td>
<td>$T_2$</td>
</tr>
<tr>
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<td>$2^{-3}[-2\sqrt{15}B_{51} + \sqrt{6}B_{53} + \sqrt{30}B_{55}]$</td>
<td></td>
<td>$2^{-6}[6.11.13B_{81} - \sqrt{10.7.13}B_{83} - 7\sqrt{42}B_{85}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-3}[2\sqrt{15}A_{51} + \sqrt{6}A_{53} - \sqrt{30}A_{55}]$</td>
<td></td>
<td>$-3\sqrt{30}A_{87}]$</td>
</tr>
<tr>
<td></td>
<td>$2^{-4}[-2\sqrt{21}B_{51} - 9\sqrt{2}B_{53} - \sqrt{10}B_{55}]$</td>
<td></td>
<td>$2^{-6}[-6.11.13A_{81} - \sqrt{10.7.13}A_{83} + 7\sqrt{42}A_{85}$</td>
</tr>
<tr>
<td></td>
<td>$2^{-4}[-2\sqrt{21}A_{51} + 9\sqrt{2}A_{53} - \sqrt{10}A_{55}]$</td>
<td></td>
<td>$-3\sqrt{30}A_{87}]$</td>
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<td>$T_1$</td>
<td>$B_{62}$</td>
<td>$T_2$</td>
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<tr>
<td></td>
<td>$2^{-5}[-2\sqrt{10}B_{61} + 18B_{63} - 2\sqrt{11.15}B_{65}]$</td>
<td></td>
<td>$2^{-5}[\sqrt{5.11.13}B_{81} + \sqrt{3.7.13}B_{83} + \sqrt{35}B_{85} + B_{87}$</td>
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<td>$2^{-5}[2\sqrt{10}A_{61} + 18A_{63} - 2\sqrt{11.15}A_{65}]$</td>
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<td>$2^{-5}[\sqrt{5.11.13}A_{81} - \sqrt{3.7.13}A_{83} + \sqrt{35}A_{85} - A_{87}]$</td>
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<td>$T_1$</td>
<td>$B_{64}$</td>
<td>$T_1$</td>
</tr>
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<td></td>
<td>$2^{-8}[-21\sqrt{20}B_{91} + 2\sqrt{5.6.7.11}B_{93} - 6\sqrt{22.13}B_{95}$</td>
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<td>$2^{-3}[-2\sqrt{3}A_{61} - \sqrt{30}A_{63} + \sqrt{22}A_{65}]$</td>
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<td>$+3\sqrt{10.11.13}A_{97} - \sqrt{2.7.11.13}B_{99}]$</td>
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<tr>
<td></td>
<td>$2^{-8}[-21\sqrt{20}A_{91} - 2\sqrt{5.6.7.11}A_{93} - 6\sqrt{22.13}A_{95}$</td>
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<tr>
<td></td>
<td>$-3\sqrt{10.11.13}A_{97} - \sqrt{2.7.11.13}A_{99}]$</td>
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<td></td>
</tr>
<tr>
<td>$T_2$</td>
<td>$T_2$</td>
<td>$B_{92}$</td>
<td>$T_2$</td>
</tr>
<tr>
<td></td>
<td>$2^{-7}[-14\sqrt{22}B_{91} + 12\sqrt{21}B_{93} - 4\sqrt{65}B_{95}$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$2^{-7}[14\sqrt{22}A_{91} + 12\sqrt{21}A_{93} + 4\sqrt{65}A_{95}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-2\sqrt{7}A_{97} - 6\sqrt{13.17}A_{99}]$</td>
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</table>

continued
Tetrahedral harmonics

Table 4. Continued.

<table>
<thead>
<tr>
<th>( T_1 )</th>
<th>( T_2 )</th>
<th>( B_{94} )</th>
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</thead>
<tbody>
<tr>
<td>( 2^{-7}[-2\sqrt{7.11.13}B_{94} + 2\sqrt{6.13}B_{93} + 6\sqrt{70}B_{95} )</td>
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<td></td>
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<tr>
<td>(-23\sqrt{14}B_{97} - 3\sqrt{14.17}B_{99} )</td>
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<td></td>
</tr>
<tr>
<td>( 2^{-7}[-2\sqrt{7.11.13}A_{91} - 2\sqrt{6.13}A_{93} + 6\sqrt{70}A_{95} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+23\sqrt{14}A_{97} - 3\sqrt{14.17}A_{99} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( T_1 )</th>
<th>( T_2 )</th>
<th>( B_{96} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2^{-6}[-2\sqrt{6.11.13}B_{96} - 2\sqrt{7.13}B_{93} + 10\sqrt{15}B_{95} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+21\sqrt{3}B_{97} + 3\sqrt{3.17}B_{99} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2^{-6}[\sqrt{6.11.13}A_{91} - 2\sqrt{7.13}A_{93} - 10\sqrt{15}A_{95} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+21\sqrt{3}A_{97} - 3\sqrt{3.17}A_{99} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( w_4^{3m'} = \exp(-i3m'\pi/2) = (-1)^{|m'|/2}i. \)

The constants \( \xi_{m'm} \) are defined by equation (5). See table 4 for normalized \( F \) functions up to and including \( l = 10 \). Note that from \( l = 3 \) onwards the \( F \) irrep occurs with multiplicity larger than one. The different \( F \) spaces are automatically orthogonal, because the functions \( B_{91}, B_{92}, \ldots \) are orthogonal. The fact that then also the total spaces are orthogonal follows from the group theoretical theorem that, given two bases \( r \) and \( q \), the overlap \( \langle r | q \rangle \) is the same for all \( i \).

6. The group \( T_d(M) \)

We finally turn to the group \( T_d(M) \) and consider \( (12)^* \), see equations (6) and (9). The \( A_1 \) functions of \( T(M) \) (see equation (6)) have even \( m \). Using \( (12)^*[E + (123) + (132)] = [E + (123) + (132)][(12)^* \)

and \( (12)^*A_{lm} = (-1)^{|m'/2}A_{lm} \), we find that the \( A_1 \) functions are eigenfunctions of \( (12)^* \) with eigenvalue \( (-1)^{|m'|/2} \). Hence these functions are automatically adapted to \( T_d(M) \); they are \( A_1 \) if \( (-1)^{|m'|/2} = 1 \) and \( A_2 \) otherwise. By a very similar argument the first \( E \) function (equation (7)) obtains the phase \( (-1)^{|m'|/2} \), whereas the second (equation (8)) obtains the phase \( -(-1)^{|m'|/2} \) upon acting with \( (12)^* \). These two functions carry the 2-dimensional \( E \) irrep of \( T_d(M) \).

Consider equation (10) for the behaviour of the \( F \) functions under \( (12)^* \). Recall that \( |l, m, V_4, B_2 \rangle = 2B_{lm} (m \text{ even}); \) then since \( (12)^*[E + (123) = (132)](12)^* \), the space spanned by the \( F \) functions is invariant under \( (12)^* \), so that the \( F \) functions are automatically adapted to \( T_d(M) \). The operation \( (12)^* \) has the trace \( -(-1)^{|m'|/2} \), and consequently the functions span \( F_1 \) if \( (-1)^{|m'|/2} = 1 \) and \( F_2 \) otherwise.

7. Conclusion

We summarize the final equations. We present formulae for unnormalized symmetry-adapted functions that are expressed in terms of real-valued and normalized functions \( A_{lm} \) and \( B_{lm} \), which are linear combinations of spherical harmonics, see equations (1)–(2). The spherical harmonics, which have Racah's phase, are obtained from the more usual Condon and Shortley (C&S) spherical harmonics by multiplying with \( i \), thus

\[ Y_{lm}^{\text{Racah}} = (i)^l Y_{lm}^{\text{C&S}}. \]
The quantum number $m$ is even in all cases. The constants $\xi_{m'm}$ are Wigner’s small $d'$ functions for argument $\beta = \pi/2$, see equation (5). The $A_{1,2}$ functions are

$$\left| l, m, T_d, A_{1,2} \right> = A_{lm} + (2 - \delta_{m0})^{1/2} \times \sum_{m' \geq 0 \text{ even}} (2 - \delta_{m'0})^{1/2} \times A_{lm} \xi_{m'm} \{(-1)^{m/2} + (-1)^{m'/2}\}.$$ 

The functions are $A_1$ of the group $O$ if $m \equiv 0 \pmod{4}$ and $A_2$ if $m \equiv 2 \pmod{4}$. The $E$ functions are

$$\left| l, m, T_d, E, 1 \right> = 2A_{lm} - (2 - \delta_{m0})^{1/2} \times \sum_{m' \geq 0 \text{ even}} (2 - \delta_{m'0})^{1/2} A_{lm} \xi_{m'm} \{(-1)^{m/2} + (-1)^{m'/2}\},$$

$$\left| l, m, T_d, E, 2 \right> = (2 - \delta_{m0})^{1/2} \times \sum_{m' \geq 0 \text{ even}} (2 - \delta_{m'0})^{1/2} A_{lm} \xi_{m'm} \{(-1)^{m/2} - (-1)^{m'/2}\}.$$ 

The $F_{1,2}$ functions are

$$\left| l, m, T_d, F_{1,2}, 1 \right> = B_{lm}$$

$$\left| l, m, T_d, F_{1,2}, 2 \right> = (-1)^{m/2} \sqrt{\frac{2 - \delta_{m0}}{2}} \sum_{m' \text{ odd}} A_{lm} \xi_{m'm} B_{lm'}$$

$$\left| l, m, T_d, F_{1,2}, 3 \right> = \sqrt{\frac{2 - \delta_{m0}}{2}} \sum_{m' \text{ odd}} (-1)^{m'/2} \xi_{m'm} A_{lm'}.$$ 

The functions are $F_1$ of the group $O$ if $m \equiv 0 \pmod{4}$ and $F_2$ if $m \equiv 2 \pmod{4}$.

Finally, we emphasize that the present work gives functions carrying the irreps of the point group $T_d$ as well, provided the labels on $A_{1,2}$ and $F_{1,2}$ in the tables are interchanged in the case of odd $l$. This is due to the fact that the equivalent rotations [11], which we considered in this work, actually constitute the point group $O$. Note that the operations in $T(M)$ are in one-to-one correspondence with those in $T$. The order of the sub-group elements determines the isomorphism. Thus, for instance, one of the rotations $C_3 \in T$ corresponds to $(123) \in T(M)$, both elements being of order 3. The coset $T_d(M)/T(M)$ is, as we have seen, generated by $(12)^3$. This element corresponds to the reflection $\sigma_d \in T_d$ in a mirror plane that contains the $z$ axis and the hydrogens $h_3$ and $h_4$. The element $S = C_3^4 \in T_d$ corresponds to $(1324)^3 \in T_d(M)$, where $i$ is the point group inversion. The relation $Y_{lm} = (-1)^{l}Y_{lm}$ is the reason that the subscripts on $A_{1,2}$ and $F_{1,2}$ must be interchanged between $O$ and $T_d$ for odd $l$.

Tables 2-4, listing normalized tetrahedral/octahedral harmonics, were prepared with the aid of Matlab-6 scripts. These scripts are available upon request at pwormer@theochem.kun.nl

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References