Explicit expressions for totally symmetric spherical functions and symmetry-dependent properties of multipoles

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Closed expressions for matrix elements \(\langle lm'|A(G)|lm \rangle\), where \(|lm\rangle\) are spherical functions and \(A(G)\) is the average of all symmetry operators of point group \(G\), are derived for all point groups \((PGs)\) and then used to obtain linear combinations of spherical functions that are totally symmetric under all symmetry operations of \(G\). In the derivation, we exploit the product structure of the groups. The obtained expressions are used to explore properties of multipoles of symmetric charge distributions. We produce complete lists of selection rules for multipoles \(Q_l\) and their moments \(Q_{lm}\), as well as of numbers of independent moments in a multipole, for any \(l\) and \(m\) and for all PGs. Periodicities and other trends in these properties are revealed.

1. Introduction

Totally symmetric spherical functions \(|S;lm\rangle\) are such linear combinations of spherical functions \(|lm\rangle\equiv Y_{lm}(\theta, \phi)\) that are symmetric under all symmetry operations \(P_i\) of point group \(G\). These functions are given by Jacobs [1]

\[
|S;lm\rangle \equiv S_{lm}(\theta, \phi) = A(G)|lm\rangle = \sum_{m'=-l}^{l} |lm'\rangle \langle lm'|A(G)|lm \rangle, \tag{1.1}
\]

where \(A(G)\) is the projection operator to the identity representation \(\Gamma_1\) [1]:

\[
A(G) = \frac{1}{|G|} \sum_{i=1}^{|G|} P_i, \quad P_i \in G, \tag{1.2}
\]
where \(|G|\) is the order of \(G\). For brevity and due to its form as the average of all operators \(P_i\) of group \(G\), we term this operator the group average (it may be compared to the Dirac characters that are defined as the class sums of group operators, see [1], Appendix A2, and [2], §1.3). With equation (1.1), the problem reduces to search of matrix elements \(a_{lm'm}(G) = \langle lm'|A(G)|lm\rangle\), termed here the symmetry factors (SFs).

Functions \(|S;lm\rangle\) are used in theory of molecules [3] and solids [4], electron microscopy [5] and other fields. To obtain these functions, various techniques were developed (see references in [6–9]). Most of them require individual consideration of each \(l\) or use a recursive method over \(l\), which becomes progressively more difficult when applied to higher point groups (PGs) and higher \(l\). At the same time, it is possible to obtain explicit algebraic expressions valid for any \(l\), such as those obtained for I group by Fan et al. [7] using mathematical double-induced technique, eigenfunction method, group chains and reduced projector operators.

In this paper, we propose a different method of finding totally symmetric spherical functions \(|S;lm\rangle\) and then apply them to study properties of multipole moments (MMs). Using this method, we obtain closed expressions for the SFs for all PGs with arbitrarily high order of the principal axis. The essence of the method follows. We start with known expressions for action of rotation \(e_n\), reflection \(\sigma_h\) and rotoreflection \(e_n\sigma_h\) on \(|lm\rangle\) [10]. The SF for a cyclic group (like group \(C_n\) of rotations around the \(z\)-axis) is found as a sum of geometric series formed of such an expression. For non-cyclic groups, we exploit their product structure: if group \(G\) can be presented as the product of its subgroups \(G_1\) and \(G_2\), then it is easy to show that \(A(G) = A(G_1)A(G_2)\). The SFs turn out to be rather simple functions of their indices for polyhedral groups, and especially simple for axial groups. For group \(C_n\), for example, \(a_{lm'm}(C_n)\) equals 1 if \(n\) divides \(m\) and \(m' = m\), and 0 otherwise.

The set of SFs \(a_{lm'm}(G)\) at given \(l\) forms a matrix \(a_l(G)\) representing operator \(A\). In general, this representation, \(\Gamma_l(G)\), is reducible. The trace of this matrix shows the frequency \(n_l\) of \(\Gamma_l\) in \(\Gamma_l(G)\) [1] (the number of times \(\Gamma_l\) appears in \(\Gamma_l(G)\)). We obtained these traces for all PGs, also in closed form.

These results are applied to study the symmetry-dependent properties of MMs. The MMs play an important role in different fields, including molecular spectroscopy, electromagnetism and gravity. Symmetry considerations provide such information about MMs as selection rules and relationships between their components. While \(2^l\)-poles below hexadecapole (\(l = 4\)) are commonly used, progressively higher moments appear in research context. Therefore, a systematic approach to deriving symmetry properties of higher multipoles is desirable.

The principles of deriving selection rules for multipoles \(Q_l\) and for their components, MMs \(Q_{lm}\), are well known; these rules are related to symmetry of charge distribution (see [2,11,12] and references therein). Selection rules for multipoles \(Q_l\) can be derived from the subduction tables showing decomposition of representations of full orthogonal group into PG representations. The tables are provided by Lax [2] for most common PGs and, through recurrence formulae, for any \(l\). Explicit expansions for 48 PGs and for \(l \leq 9\) are given by Gelessus et al. [12,13]. Selection rules for \(Q_{lm}\) can be derived from character tables, where Cartesian bases of irreducible representations of PGs are given. Explicit expressions for Cartesian components of ranks up to 2 are found in, e.g. [1], up to 3 in [14,15], up to 4 in [11] and up to 6 in [16].

On the other hand, in order to advance in \(l\) a recurrence procedure is necessary which becomes cumbersome at high \(l\). To explore groups with higher \(n\)-fold axis, every \(n\) must be considered separately. This makes obtaining results for large \(l\) or \(n\) and studying general trends in \(l\) or \(n\) problematic.

The method advanced in the current paper solves this problem. Consider an MM of a system of point charges \(e_k\) [17]

\[
Q_{lm} = \sqrt{\frac{4\pi}{2l+1}} \sum_{k=1}^{N} e_k r_k^l Y_{lm}(\theta_k, \varphi_k), \quad m = -l, \ldots, l; \quad l = 0, 1, 2, \ldots, (1.3)
\]

where \(e_k\) and \((r_k, \theta_k, \varphi_k)\) are the charge and the spherical coordinates of the \(k\)th particle. For specificity, we will refer to \(e_k\) as the electrical charges and the system as a molecule; however,
Properties of the SFs determine properties of both MMs and symmetrized functions immediately yield the MMs. Owing to the obvious parallelism between equations (1.1) and (1.4), where the former factor encompasses all dependence on symmetry while the latter (the multipole vanishes (selection rule) if and only if \( n I < n \) or \( l \) is odd and \( (n I < n \).

In §3, we present a parallel formalism based on real-valued functions \(|m I \lambda \rangle \langle \lambda | = \pm 1\) instead of \(|m I \rangle\); these functions are actually (up to a factor) the real and imaginary part of \(|m I \rangle\). We introduce the real-valued SFs and MMs and find formulae that express them via their complex-valued counterparts. The final results take more elegant form in this notation.

Properties of the SFs are studied in §4. We prove the multiplication rule for SFs for a PG that is a product of its subgroups. This rule is extensively used in the following section. In addition, we advance an alternative way to obtain the SFs for non-cyclic groups: if the set of elements of group G is presented as a union of the sets of its subgroups, then the SFs are linear combinations of SFs of subgroups of G.

In §5, we present an example of calculation of the SFs for a cyclic group and explain the route of derivation for each PG. The explicit expressions of the SFs and of their traces for all PGs are collected in tables 1 and 2.
Table 2. Symmetry cofactors $\psi_{lnm,G}(G)$, traces of SF matrices and selection rules for polyhedral PGs. (The standard frame is used: $F_c$ for cubic groups; $F_i$ for icosahedral groups. The symmetry cofactors are defined in equation (5.8) for cubic groups and in equation (5.15) for icosahedral groups. mod(1,3) equals $l / 3$).

<table>
<thead>
<tr>
<th>G</th>
<th>$\psi_{lnm,G}(G)$</th>
<th>$\psi_{lnm,G}(G)$</th>
<th>$\Tr (a_l(G))$</th>
<th>vanishing multipoles</th>
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<tr>
<td>T</td>
<td>[2</td>
<td>l]</td>
<td>[2</td>
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<tr>
<td>T_h</td>
<td>[2</td>
<td>l]</td>
<td>0</td>
<td>[l/2] − [l/3] + 1 − mod(l, 3)</td>
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<tr>
<td>O</td>
<td>[4</td>
<td>m][4</td>
<td>m'][2</td>
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<tr>
<td>T_d</td>
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<tr>
<td>O_h</td>
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</tr>
<tr>
<td>I_h</td>
<td>[2</td>
<td>l]</td>
<td>0</td>
<td>[l/5] + [l/3] − [l/2] + [2</td>
</tr>
</tbody>
</table>

In §§6 and 7, these results are applied to study of the symmetry-dependent properties of MMs. We conclude that selection rules for $Q_{lnm}$ depend on vanishing of SFs; in case of any non-axial or axial group the question reduces to vanishing of a single $a_{lnm}(G)$. In turn, the selection rules for $Q_{l}$ depend on vanishing of the trace of $a_{lnm}(G)$. Exhaustive lists of numbers of independent components of multipoles, as well as of selection rules for MMs and for multipoles, are provided for all PGs (including seven infinite series of axial groups) and for all values of $l$ and $m$. The trends of these properties in $l$ and $n$ are studied.

Relationships between multipole components in polyhedral groups and some sum rules are provided in §8. Section 9 presents the Discussion.

### 2. Expansion of multipole moments

In this section, we transform equation (1.3) for MMs to make the symmetry evident in the terms. Let us split all particles into orbits [18], an orbit $O_p$ being a set of all equivalent particles, i.e. interrelated by symmetry operations of the PG (cf. [1], §16.2). Collecting terms for the same orbits in equation (1.3), we can present MM as

$$Q_{lnm} = \sqrt{\frac{4\pi}{2l+1}} \sum_{p=1}^{N_{orb}} n_p e_p r_p^l S_{lnm}(\theta_p, \phi_p), \quad (2.1)$$

where $n_p$ is the population of the $p$th orbit, $e_p$ and $(r_p, \theta_p, \phi_p)$ are the charge and the spherical coordinates of some particle of the $p$th orbit, which is referred to as the generating particle, $N_{orb}$ is the number of orbits present in the molecule, and functions $S_{lnm}(\theta, \phi)$ are defined in equation (1.1). As we see, only symmetry-unrelated terms are present in this expansion.

By using equations (1.1) and (2.1) and reordering the summation, we can present MMs also in the form given by equation (1.4) where the geometrical factors are

$$q_{lnm} = \sqrt{\frac{4\pi}{2l+1}} \sum_{p=1}^{N_{orb}} n_p e_p r_p^l Y_{lnm}(\theta_p, \phi_p). \quad (2.2)$$

Let us find explicit expressions for the SFs. Action of operator $P$ on a spherical function can be presented in terms of its matrix elements $D_{m'm}(P)$ between spherical functions:

$$P Y_{lnm}(\theta, \varphi) = \sum_{m'} Y_{lm'n'}(\theta, \varphi) D_{m'm}(P) \quad \text{and} \quad R(\alpha, \beta, \gamma) Y_{lnm}(\theta, \varphi) = \sum_{m'} Y_{lm'n'}(\theta, \varphi) D_{m'm}(\alpha, \beta, \gamma). \quad (2.3)$$
If $P$ is a rotation $R(\alpha, \beta, \gamma)$ with Eulerian angles $(\alpha, \beta, \gamma)$, then $D_{m'm}^{l}(R)$ are Wigner’s $D$-functions [10]

$$D_{m'm}^{l}(\alpha, \beta, \gamma) = e^{-im\gamma}d_{m'm}^{l}(\beta)e^{-im\alpha}. \quad (2.4)$$

Factors $d_{m'm}^{l}(\beta)$ are known [10]. They expose various symmetries [10]; we will need the following ones:

$$d_{m'm}^{l}(\beta) = d_{mm}^{l}(-\beta) = (-1)^{m'-m}d_{m-m'}^{l}(\beta). \quad (2.5)$$

It follows from equations (1.2) and (2.3) that SFs

$$a_{lm'm}(G) \equiv \langle lm'|A|lm \rangle = \frac{1}{|G|} \sum_{i=1}^{|G|} D_{m'm}^{l}(P_{i}). \quad (2.6)$$

For groups ($C_{\infty v}, D_{\infty h}$ and $K_{h}$) with axes of infinite order, the sum over $i$ should be replaced with integral(s) over angle(s).

3. Real-valued multipole moments

While we have considered complex-valued MMs (equation (1.3)) so far, it is more convenient to work with real-valued moments $Q_{lm\pm}$. In this section, a summary of respective relationships is presented. The proofs are omitted as they are all straightforward.

The real-valued moments are defined as follows:

$$Q_{lm\pm} = [2(1 + \delta_{m0})]^{-1/2}i^{(\lambda-1)/2}[Q_{lm} + \lambda(-1)^{m}Q_{l-m}]$$

$$= \sqrt{\frac{4\pi}{2l+1}} \sum_{k=1}^{N} \epsilon_{k}Y_{lm\pm}(\theta_{k}, \varphi_{k}), \quad m = 0, \ldots, l; \lambda = \pm 1, \quad (3.1)$$

where $\delta_{m'm}$ is Kronecker’s delta function. In particular,

$$Q_{l0^+} = Q_{l0}; \quad Q_{l0^-} = 0; \quad Q_{lm^+} = 2^{1/2}ReQ_{lm}; \quad Q_{lm^-} = 2^{1/2}ImQ_{lm}, \quad m = 1, \ldots, l.$$

Throughout the paper, $\lambda$ takes values $\pm$ in subscripts or superscripts, and $\pm$ as term in expressions. For the sake of brevity, we sometimes include the term with $(m = 0, \lambda = -)$ in equations but use a convention that any such a term equals zero; e.g. $Q_{l0^+} = 0$. The real-valued spherical functions that appear in equation (3.1) are defined similarly (they differ in notation and, for $m \neq 0$, by a factor $\sqrt{2}$ from those defined in [10], §5.6):

$$Y_{lm\pm}(\theta, \varphi) = [2(1 + \delta_{m0})]^{-1/2}i^{(\lambda-1)/2}[Y_{lm}(\theta, \varphi) + \lambda(-1)^{m}Y_{l-m}(\theta, \varphi)]; \quad m = 0, \ldots, l; \lambda = \pm 1. \quad (3.2)$$

Like $Y_{lm}$, functions $Y_{lm\pm}$ form an orthonormal set. Real-valued symmetrised functions $S_{lm\pm}(\theta, \varphi)$ are defined similarly. The inverse relationships to equations (3.1) and (3.2) are

$$Q_{lm} = \left[1 + \frac{\delta_{m0}}{2}\right]^{1/2}i^{m-l}[Q_{lm^+} + i\text{sgn}(m)Q_{lm^-}], \quad m = -l, \ldots, l \quad (3.3)$$

and

$$Y_{lm}(\theta, \varphi) = \left[1 + \frac{\delta_{m0}}{2}\right]^{1/2}i^{m-l}[Y_{lm^+}(\theta, \varphi) + i\text{sgn}(m)Y_{lm^-}(\theta, \varphi)], \quad m = -l, \ldots, l. \quad (3.4)$$

For the real-valued MMs, analogues of expansions (1.2) and (2.1) are valid, with respectively modified symmetrized functions, SFs and geometrical factors:

$$Q_{lm\pm} = \sqrt{\frac{4\pi}{2l+1}} \sum_{p=1}^{N} \epsilon_{p}q_{plm\pm}S_{lm\pm}(\theta_{p}, \varphi_{p}). \quad (3.5)$$

$$Q_{lm\pm} = \sum_{m', \lambda'} q_{lm\pm, \lambda' \text{sgn}(m)\lambda'}(G), \quad (3.6)$$
\[ a_{\ell m' \lambda m}(G) = \frac{1}{|G|} \sum_{i=1}^{|G|} D_{m' \lambda m}^\ell (P_i) = \frac{1}{2} (1 + \delta_{m0})^{-1/2} (1 + \delta_{m'0})^{-1/2} j^{(\lambda - \lambda')/2} \]

\[ \times \{ a_{\ell m'}(G) + \lambda(-1)^m a_{\ell -m'}(G) + \lambda'(-1)^{m'} a_{\ell -m' m}(G) + \lambda \lambda'(-1)^{m+m'} a_{\ell m -m'}(G) \}; \]

\[ m, m' = 0, \ldots, l \]

and

\[ q_{lm\lambda} = [2(1 + \delta_{m0})]^{-1/2} j^{(\lambda - 1)/2} [q_{lm} + \lambda(-1)^m q_{l-m}] \]

\[ = \sqrt{\frac{4\pi}{2l + 1}} \sum_{p=1}^{N_{alp}} n_p e_p r_p Y_{lm\lambda}(\theta_p, \varphi_p), \quad m = 0, \ldots, l; \lambda = \pm 1. \]

The inverse relationship to equation (3.7) is

\[ a_{\ell m'}(G) = \frac{1}{2} (1 + \delta_{m0})^{1/2} (1 + \delta_{m'0})^{1/2} j^{(\lambda + \lambda')/2} \]

\[ \times \{ D_{m' \lambda m}^\ell (P) + \lambda(-1)^m D_{m' -m}^\ell (P) + \lambda'(-1)^{m'} D_{m' -m' m}^\ell (P) + \lambda \lambda'(-1)^{m+m'} D_{m' -m' -m}^\ell (P) \}; \]

\[ m, m' = 0, \ldots, l. \]

The transformations of matrix elements of operators from basis \(|lm\rangle\) to basis \(|lm\lambda \rangle\) and vice versa are given by

\[ D_{m' \lambda m}^\ell (P) = \frac{1}{2} (1 + \delta_{m0})^{-1/2} (1 + \delta_{m'0})^{-1/2} j^{(\lambda - \lambda')/2} \]

\[ \times \{ D_{m' \lambda m}^\ell (P) + \lambda(-1)^m D_{m' -m}^\ell (P) + \lambda'(-1)^{m'} D_{m' -m' m}^\ell (P) + \lambda \lambda'(-1)^{m+m'} D_{m' -m' -m}^\ell (P) \}; \]

\[ m, m' = 0, \ldots, l. \]

(3.10)

\[ D_{m' \lambda m}^\ell (P) = \frac{1}{2} (1 + \delta_{m0})^{1/2} (1 + \delta_{m'0})^{1/2} j^{(\lambda + \lambda')/2} \]

\[ \times \{ D_{m' \lambda m}^\ell (P) + \lambda(-1)^m D_{m' -m}^\ell (P) + \lambda'(-1)^{m'} D_{m' -m' m}^\ell (P) + \lambda \lambda'(-1)^{m+m'} D_{m' -m' -m}^\ell (P) \}; \]

\[ m, m' = 0, \ldots, l. \]

(3.11)

The transformations of \(Y_{lm\lambda}\) under symmetry operations have the form (cf. equation (2.3)):

\[ P Y_{lm\lambda}(\theta, \varphi) = \sum_{m' \lambda'} Y_{lm' \lambda'}(\theta, \varphi) D_{m' \lambda' m \lambda}(P), \]

\[ (3.12) \]

4. **Symmetry factors: properties**

(a) **Idempotence, hermiticity, symmetry**

The set \(a_{\ell m'}(G)\) for fixed \(l\) and \(G\) forms a \((2l + 1) \times (2l + 1)\) matrix \(a_l(G)\) which is a representation of group average operator \(A(G)\) in the basis of spherical functions (see equation (2.6)); hence

\[ A(G) Y_{lm}(\theta, \varphi) = \sum_{m'} Y_{lm'}(\theta, \varphi) a_{lm'}(G). \]

(4.1)

Properties of SFs follow from the properties of the group average operator and of spherical functions. Being a projection operator, \(A(G)\) is idempotent and Hermitian [1]

\[ A(G) A(G) = A(G) \]

(4.2)

and

\[ A(G) = A(G). \]

(4.3)

As a consequence, SFs possess the following properties:

\[ \sum_{m'} a_{lm' m'}(G) a_{lm' m}(G) = a_{lm m}(G); \quad a_l(G) a_l(G) = a_l(G) \]

(4.4)
and

\[ a_{l'm'}^*(G) = a_{l'm'}(G); \quad a_l^+(G) = a_l(G). \quad (4.5) \]

Being an idempotent matrix, \( a_l(G) \) has eigenvalues that are all either 0 or 1 [19]. Its trace

\[ \text{Tr}(a_l(G)) = \sum_m a_{l'm}(G) = \sum_{m\lambda} a_{l'm\lambda}(G) \quad (4.6) \]

equals its rank and equals the geometric multiplicity of the eigenvalue 1.

From equation (4.5) and the gauge condition \( Y_{l-m}(\theta, \phi) = (-1)^{m} Y_{lm}^*(\theta, \phi) \) for spherical functions [10], a symmetry relationship follows:

\[ a_{l'm'}(G) = (-1)^m a_{l-m'}(G). \quad (4.7) \]

(b) Transformations

Let us find how the SFs transform under rotations (or other transformations) of the frame. If all operators \( P_i \) of a group \( G \) are transformed by the same operation \( Q \),

\[ P'_i = Q P_i Q^{-1}, \quad i = 1, 2, \ldots, |G|, \quad (4.8) \]

then for the group \( G' \) formed of operators \( P'_i \) (and isomorphic to \( G \)) we have

\[ a_{l'm'}(G') = \sum_{m''} D_{m'm''}^l(Q) a_{l'm''}(G) D_{m''m'}^l(Q^{-1}) \quad (4.9) \]

and

\[ a_{l'm'\lambda'}(G') = \sum_{m''\lambda''} D_{m'm''\lambda''\lambda'}^l(Q) a_{l'm''\lambda''}(G) D_{m''\lambda''m'\lambda'}(Q^{-1}). \quad (4.10) \]

(c) Multiplication rule

Consider a PG that can be presented as a product of its subgroups \( G_1 \) and \( G_2 \) (may be with repetitions):

\[ G_1 G_2 = G_2 G_1 = kG; \quad k = \frac{|G|}{(|G_1||G_2|)} = |G_1 \cap G_2|, \quad (4.11) \]

where \( k \) is the number of repetitions [20]. Here \( |G| \) is the order of \( G \), and \( |G_1 \cap G_2| \) is the cardinality of the set of common elements of the groups. As stated in equation (4.11), the subgroups \( G_1 \) and \( G_2 \) must commute. They are not required but may happen to intersect only in the identity, and, in addition, one or both subgroups may happen to be a normal subgroup of \( G \). If so, \( G_1 G_2 \) becomes, respectively, a Zappa–Szép product, or a semidirect, or a direct product [20]. These particulars do not influence the following derivations. Therefore, we omit special signs for the direct and semidirect products.

Taking average (as in equation (1.2)) of equation (4.11) consecutively over the first and then over the second subgroup, one can prove the multiplication rule for the group average operators

\[ A(G) = A(G_1) A(G_2), \quad \text{if } G_1 G_2 = kG, \quad (4.12) \]

which implies that \( Q_{lm} \) or \( Q_{l'm'} \) for the resulting group has again the form of expansion (1.4) or (3.6), respectively, with the SFs equal

\[ a_{l'm'}(G) = \sum_{m''} a_{l'm''}(G_1) a_{l'm''}(G_2); \quad a_{l'm'\lambda'}(G) = \sum_{m''\lambda''} a_{l'm''\lambda''}(G_1) a_{l'm''\lambda''}(G_2). \quad (4.13) \]

This is the multiplication rule for SFs. It is used below to evaluate SFs for higher groups when SFs for lower groups are known.
(d) Expansion rule

Alongside equation (4.13), there is another way to find SFs for higher groups when those for simpler ones are known. It is based on presentation of the group average operator of group G as a linear combination of such operators of its subgroups Gs:

\[ A(G) = |G|^{-1} \sum cs A(G_s); \sum cs = |G|, \]

(4.14)

with summation over subgroups. This implies the following expansion rule:

\[ a_{lmn}(G) = |G|^{-1} \sum cs a_{lmn}(G_s); a_{lmn/m\lambda}(G) = |G| \sum cs a_{lmn/m\lambda}(G_s). \]

(4.15)

This rule works for non-cyclic groups G, otherwise equation (4.14) is an identity. Let us show how coefficients cs are determined using C4h as an example. In this paragraph, we use the symbol of a group to denote the set of its elements. C4h is the union of its subgroups C2h, C4, and S4; any two of these subgroups intersect in C2. Using the inclusion–exclusion principle [21] for cardinalities of sets, we get

\[
|C_{4h}| = |C_{2h} \bigcup C_4 \bigcup S_4| = |C_{2h}| + |C_4| + |S_4| - |C_{2h} \cap C_4| - |C_4 \cap S_4| - |C_{2h} \cap S_4| \\
+ |C_{2h} \cap C_4 \cap S_4| = |C_{2h}| + |C_4| + |S_4| - 2|C_2|.
\]

Each term in the result provides a relevant cs (e.g., \(-2|C_2| = -4\) is the prefactor for \(A(C_2)\)), and equation (4.14) takes the form \(A(C_{4h}) = (1/8)(4A(C_{2h}) + 4A(C_4) + 4A(S_4) - 4A(C_2))\).

5. Symmetry factors: evaluation and results

In this section, we give details of the techniques used to evaluate the SFs, introduce notation that makes the appearance of results very compact and present the results for all PGs.

(a) Reference frame

As evident from equation (2.6), the SFs do not depend on specific distribution of charge and depend only on the PG of the molecule and on position and orientation of its symmetry elements (centre, axes and/or planes) in space. Therefore, choice of the reference frame is essential. Our choice, referred hereafter the standard frame, is based only on symmetry considerations. The standard frame is chosen in different ways in case of axial (and Ch), cubic and icosahedral groups.

For the axial PGs, the principal symmetry axis cs or s2n is Oz; the principal horizontal symmetry plane σh, if any, is Oxy. One of the secondary c2 axes (in Dn, D2n, and Dnh) is Ox. One of the vertical planes in Cnv is Oxz. When we need a frame that differs from the standard one, we add a subscript showing the direction of the principal axis and/or of the normal to σh; so, C3h is C3 with the symmetry plane being Oyz. Our choice of the reference frame does not consider positions of specific particles. For certain groups (Cn, Cs, Cn\text{iv}, S2n, Cn\text{hv} and Dn\text{ch}), axes x and y (and z, for C1, Ci and K1) therefore remain arbitrary; they may be chosen so as to meet additional conventions, examples of which can be found in [22,23].

For cubic PGs, the standard frame is chosen as follows. The axes with the maximum even order (that is, C4 in O and Oh, or C2 in T and Th, or S4 in Td) are set along Ox, Oy and Oz; then one of C3 (in T, Td and O groups) or S6 (in Td or Oh) axes is set along the direction a = (1, 1, 1). We denote this reference frame as \(F^c\) (‘c’ for cubic).

For icosahedral groups, we choose a frame (cf. [24]) where Oz goes through a vertex of the icosahedron (and along one of axes cs), and Oy through the midpoint of an edge (and along one of axes c2). Denote this frame as \(F^i\) (‘ic’ for icosahedron); it can be transformed to \(F^c\) (where all the coordinate axes coincide with some of c2 axes of the icosahedron) by a rotation \(R(0, \beta_0, 0)\) about Oy through angle \(\beta_0\) such that \(\tan \beta_0 = \phi = (1/2) (√5 + 1)\) (the golden ratio).
(b) Cyclic groups

Evaluation of SFs is especially easy for a cyclic PG. As an example, take group $C_n$ which is a complete cycle of rotation $c_0$ about $Oz$ by angle $2\pi/n$, with the action $c_0 Y_{lm}(\theta, \varphi) = e^{-2\pi im/n} Y_{lm}(\theta, \varphi)$. Thus, the action of the group average (from equation (1.2), sum of geometric series, and l’Hôpital’s rule) is $A(C_n) Y_{lm}(\theta, \varphi) = [(1/n)(1 - e^{-2\pi im})/(1 - e^{-2\pi im/n})] Y_{lm}(\theta, \varphi) = [n \mid m] Y_{lm}(\theta, \varphi)$. Using equations (3.7) and (4.1),

$$a_{lm'm}(C_n) = [n \mid m] \delta_{mm'} \quad \text{and} \quad a_{lm'm\lambda}(C_n) = [n \mid m] \delta_{mm'} \delta_{\lambda'\lambda}.$$ (5.1)

The results contain a notation known as the Iverson bracket $[P]$; by definition, it equals 1 if condition $P$ is true and 0 otherwise [25,26]. Two types of the condition $P$ appear in our application: $n \mid m$ ($n$ divides $m$) and $n \mid m$ ($n$ does not divide $m$). Here, both $n$ and $m$ takes any integer value excluding $n = 0$. Specifically,

$$[n \mid m] = 1 \text{ if } n \text{ divides } m, \text{ and } = 0 \text{ otherwise}$$ (5.2)

and

$$[n \mid m] = 1 \text{ if } n \text{ does not divide } m, \text{ and } = 0 \text{ otherwise.}$$ (5.3)

Group $S_{2n}$ (including $C_1 = S_2$) can be treated similarly, as the cycle of rotoreflection, $c_{2n}\sigma_h$ and $C_s$ as the cycle of reflection $\sigma_h$.

(c) Axial groups

For other axial groups, the multiplication rule (equation (4.13)) and products $C_{nh} = C_n C_s$; $C_{nv} = C_n C_{sx}$; $D_n = C_n C_{2x}$; $D_{nd} = S_{2n} C_{2x}$; $D_{nh} = D_n C_s$ are useful. SFs for PGs with a non-standard frame, like $C_{sx}$ or $C_{2x}$ which appear here, can be found using equation (4.9) or (4.10).

The derivations show that the real-valued SFs are diagonal in $m$ and $\lambda$ for any axial (and non-axial) PG and thus $[S; lm\lambda]$ and MMs take the form with a single term in the sum (equations (1.1) and (3.6)):

$$a_{lm'\lambda}(G) = a_{lm\lambda}(G) \delta_{mm'} \delta_{\lambda'\lambda},$$ (5.4)

$$S_{lm\lambda}(\theta, \varphi) = a_{lm\lambda}(G) Y_{lm\lambda}(\theta, \varphi)$$ (5.5)

and

$$Q_{lm\lambda} = a_{lm\lambda}(G) q_{lm\lambda}; \quad \lambda = \pm.$$ (5.6)

Moreover, the SFs take only values 0 or 1 for all these PGs. The results for cofactors $a_{lm\lambda}(G)$ are summarized in columns 2 and 3 of table 1. Note that the non-axial groups ($C_1$, $C_s$ and $C_i$) are formally included in the axial case as groups with onefold axis.

(d) Cubic groups

We start consideration with group $T$, which can be presented as a direct product $T = D_2C_{3a}$, where $C_{3a}$ denotes group $C_3$ with the axis set along vector $a = (1 \ 1 \ 1)$. The SFs for $C_3$ in the standard frame are given in table 1; we use equation (4.9) to find them for $C_{3a}$ and get

$$a_{lm'm}(C_{3a}) = \left(\frac{1}{3}\right) \left[\delta_{mm'} + (-1)^m [m^m + i^{-m'}] \delta_{mm'} \left(\frac{\pi}{2}\right)\right], \quad -l \leq m, m' \leq l.$$ (5.7)

We then use equation (4.13) and the known factors for $C_{3a}$ (equation (5.7)) and $D_2$ (table 1) to find the SFs for $T$. Next, any cubic group can be written as a product of $T$ and some other group: $T_h = C_i$; $T_l = (1/2)C_4$; $T_d = (1/2)S_4$; $O_h = C_i$; $O = (1/2)C_{4h}$, and thus again we can use equation (4.13). We omit the derivations and give only the results. In the standard frame, the
real-valued SFs for any cubic group can be presented in the general form

\[ a_{lm'm''}\lambda\lambda'(G) = u_{lm'm''}(T)v_{lm'm''}(G)\delta_{\lambda\lambda'}, \]  

(5.8)

where the first cofactor

\[ u_{lm'm''}(T) = \left( \frac{1}{2} \right) (1 + \delta_{m0})^{-1/2}(1 + \delta_{m'0})^{-1/2}[2 | m][2 | m'] \times \left\{ \delta_{m'm}(1 + \lambda\delta_{m0}) + 4(-1)^{m/2}[4 | m + m']d_{m'm}^{l}(\frac{\pi}{2}) \right\}, \quad m, m' = 0, \ldots, l \]  

(5.9)

is common for all cubic groups, while the second cofactor \( v_{lm'm''}(G) \) is specific for each group and is presented in table 2 (columns 2 and 3).

Having the real-valued SFs on hand, we can find expressions for the original SFs. For example, for group T we have from equations (5.8), (5.9) and (3.9):

\[ a_{lm'm''}(T) = \frac{1}{2}(1 + \delta_{m0})^{1/2}(1 + \delta_{m'0})^{1/2}2^{m'-|m'|-|m|} \times \left\{ u_{|m'||m|}(T)[2 | l] + \text{sgn}(m)\text{sgn}(m')u_{|m'||m|}(T)[2 | l] \right\}, \quad m, m' = -l, \ldots, l. \]  

(5.10)

This explicit form makes it easy to observe the following symmetry properties:

\[ a_{lm'm''}(T) = (-1)^{l+m'}a_{l(-m')m}(T) = (1)^{l+m}a_{l(-m')(-m)}(T) = (-1)^{m+m'}a_{l(-m')(m)}(T). \]  

(5.11)

(e) Icosahedral groups

Group I can be presented as a product \( I = T^c C_5 \), where symmetry axes of all groups are taken in the \( F^c \) frame. The SFs for \( T^c \) can be found by frame rotation \( R(0, -\rho_0, 0) \) from \( F^c \) to \( F^c \) and applying equation (4.9); they are

\[ a_{lm'm''}(T^c) = \sum_{m''''=-l}^{l} d^{l}_{m'm'''}(\rho_0)a_{lm'm''}(T)\delta_{m''''} \]  

(5.12)

It is easy to derive symmetry properties of \( a_{lm'm''}(T^c) \) using equation (5.12) together with symmetry properties of Wigner functions (equation (2.5))) and of factors \( a_{lm'm''}(T) \) (equation (5.11)):

\[ a_{lm'm''}(T^c) = (-1)^{l+m'}a_{l(-m')m}(T^c) = (1)^{l+m}a_{lm'(-m)}(T^c) = (-1)^{m+m'}a_{l(-m')(-m)}(T^c). \]  

(5.13)

The SFs for \( I = T^c C_5 \) follow from equation 35 and §4.7.2 [10] as a product of two SF matrices:

\[ a_{lm'm''}(I) = a_{lm'm''}(T^c)[5 | m][5 | m'], \]  

and their real-valued analogues can be found from equation (3.7) and then simplified using equation (5.13). Next, the SFs for \( I_h = I C_5 \) can be derived using equation (4.13). The final result for \( G = I \) or \( I_h \) is (cf. equation (5.8)):

\[ a_{lm'm''\lambda\lambda'}(G) = u_{lm'm''}(I)v_{lm'm''}(G)\delta_{\lambda\lambda'} \]  

(5.15)

where (cf. equation (5.9))

\[ u_{lm'm''}(I) = \left( \frac{1}{2} \right) (1 + \delta_{m0})^{-1/2}(1 + \delta_{m'0})^{-1/2}[5 | m][5 | m'] \times \left\{ \delta_{m'm}(1 + \lambda\delta_{m0}) + 5(-1)^{m}[d_{m'm}(2\rho_0) + (-1)^{l+m}d_{m'-m}(2\rho_0)] \right\}, \quad m, m' = 0, \ldots, l. \]  

(5.16)

The second cofactors for both groups are listed in table 2.

Symmetry properties, equation (5.13), induce, through equation (5.14), similar properties for SFs in groups I and \( I_h \):

\[ a_{lm'm''}(G) = (-1)^{l+m'}a_{l(-m')m}(G) = (1)^{l+m}a_{lm'(-m)}(G) = (-1)^{m+m'}a_{l(-m')(m)}(G); \quad G = I, I_h. \]  

(f) Continuous groups

We use the continuous analogue of equation (2.6) and act as in the case of discrete cyclic groups to obtain SFs for the intermediate PGs \( C_{\infty} \) and \( K \equiv SO(3) \), and then apply the multiplication rule
and products $C_{\infty} = C_{\infty} \ C_{1v}$, $D_{\infty h} = C_{\infty} \ C_{i}$, $K_{h} = K \ C_{i}$. For the results for $C_{\infty} v$ and $D_{\infty h}$, see table 1. The result for $K_{h} \equiv O(3)$ is

$$a_{\lambda m : \lambda m}(K_{h}) = \delta_{\lambda 0}\delta_{m \prime 0}\delta_{m \prime \lambda} + \delta_{\lambda +}\; \text{Tr}(a_{\lambda}(K_{h})) = \delta_{\lambda 0},$$

so that all multipoles excluding monopole vanish in $K_{h}$.

6. Selection rules for multipole moments

(a) Axial groups

For all axial and non-axial groups, vanishing of SFs implies, through equation (5.6), vanishing of MMs: $Q_{\lambda m \lambda}$ vanishes if $a_{\lambda m \lambda} = 0$, $Q_{\lambda m}$ vanishes if both $a_{\lambda m +} = a_{\lambda m -} = 0$. Therefore, the selection rules for components $Q_{\lambda m \lambda}$ in the standard frame are readily evident from expressions for $a_{\lambda m \pm}$ (G) (table 1, columns 2 and 3) and therefore require no additional explicit formulation.

For example, for a charge distribution with $D_{3d}$ symmetry, the general expressions for the SFs of MMs: $Q_{\lambda m \lambda}$ vanish if $a_{\lambda m \lambda} = 0$; $Q_{\lambda m}$ vanishes if both $a_{\lambda m +} = a_{\lambda m -} = 0$. Therefore, the selection rules for components $Q_{\lambda m \lambda}$ in the standard frame are readily evident from expressions for $a_{\lambda m \pm}$ (G) (table 1, columns 2 and 3) and therefore require no additional explicit formulation.

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Periodicity in the MM selection rules for polyhedral groups, when it takes place, follows from periodicity and symmetries of factors $a_{\lambda m \pm}$. As evident from equations (5.9) and (5.16) and table 2, the latter do not change if we change $l$ by 2 and/or we change $m$ and/or $m \prime$ by certain $p$ ($p = 2$ for $T$ and $T_{h}$; $p = 4$ for $T_{d}$, $O$ and $O_{h}$; $p = 5$ for $I$ and $I_{h}$). Repetitive sequences of MMs for cubic groups are shown in the upper part of table 3: we see that the period for non-vanishing
(in at least one cubic group) of MMs is 2 for \( l \) and 4 for \( m \); the series start at \( lm\lambda = 40+, 72-, 62+ \) and \( 13 4- \); several lower terms \((00+, 32-, 94-, 98- )\) appear in addition to the series. The lower part in table 3 refers to the icosahedral groups. Here, the periods are 2 for \( alm \) (because \( \chi \) (equation (4.6)).

If one needs the MMs in a rotated reference frame, their properties as irreducible tensors can be used [10]: MMs behave under symmetry operations like spherical functions (see equation (2.3)), namely

\[
R(\alpha, \beta, \gamma)Q_{lm} = \sum_{m'} Q_{lm'm''} D_{m'm''}^l(\alpha, \beta, \gamma)
\]

(6.3)

and

\[
R(\alpha, \beta, \gamma)Q_{l'm'm''} = \sum_{m\lambda'} Q_{l'm'm'' \lambda'} D_{m'm'' \lambda'}^l(\alpha, \beta, \gamma).
\]

(6.4)

Respectively, the selection rules for MMs change. For example (see table 1, \( C_{11}v \) and \( D_{1h} = C_{2v}x \), \( a_{lm}(C_{2v}x) = 2|m|, a_{lm-}(C_{2v}x) = 0 \), while \( a_{lm+}(C_{2v}x) = 2 |l - m|, a_{lm-}(C_{2v}x) = 0 \).

### 7. Numbers of independent multipole components and selection rules for multipoles

Selection rules for \( Q_l \) can be derived from a set of selection rules for its components. It is possible, however, to obtain an explicit criterion of vanishing of the entire 2\( l \)-pole using the trace of \( a_l(G) \) (equation (4.6)).

(a) Numbers of independent moments, frequencies and traces

Set \( \{Q_{lm}\} \) (at given \( l \)) forms a basis of the \( l \)th irreducible representation \( D^{(l \pm)} \) with signature \((-1)^l \) of the full orthogonal group. During subduction to a lower symmetry group \( G \), this representation becomes, generally speaking, reducible and may be presented as a direct sum of irreducible representations of \( G \). Let us show that frequency \( n_{l1}(G) \) of the totally symmetric representation \( \Gamma_1 \) in this sum equals the trace of matrix \( a_l(G) \):

\[
n_{l1}(G) = \text{Tr}(a_l(G)).
\]

(7.1)

Let \( \chi^{(l)} \) and \( \chi_1 \) be characters of \( D^{(l \pm)} \) and \( \Gamma_1 \), respectively. From equation 4.4.20, [1] we have

\[
n_{l1}(G) = \frac{1}{|G|} \sum_{i=1}^{[G]} \chi^{(l)}(P_i) \chi_1(P_i) = \frac{1}{|G|} \sum_{i=1}^{[G]} \chi^{(l)}(P_i),
\]

(because \( \chi_1(P_i) = 1 \) for any \( i \)). On the other hand, we see from equations (2.6) and (4.6) that \( \text{Tr}(a_l(G)) \) equals exactly the same result, which completes the proof.
The traces provide also selection rules for multipoles and the numbers of independent moments in multipoles. Multipole $Q_l$ does not vanish only if the frequency $n_{11}(G)$ is not zero. By equation (7.1), the trace vanishes together and only together with $n_{11}(G)$, hence (cf. Theorem 3.4.1 [2]):

$$Q_{lm} = 0 \text{ at given } l \text{ and at all } m \text{ if and only if } \text{Tr}(a_l(G)) = 0.$$  
(7.2)

Now let us prove the following statement:

The number of independent $m$-components $Q_{lm}$ of $Q_l$ equals Tr($a_l(G)$).  
(7.3)

Since matrix $a_l(G)$ is idempotent, its trace $n_{11}(G) = \text{Tr}(a_l(G))$ gives the number of linearly independent columns in this matrix, an $m$th column being a set \{$a_{lm'm'}|m' = 0,1,\ldots,l\}$. Select a complete set of linearly independent columns; let their numbers be $m_j$ with $j = 1,2,\ldots,n_{11}(G)$. Any column can be presented as a linear combination of the selected columns: $a_{lm'} = \sum_{j=1}^{n_{11}} c_{lm'm_j}$. Now substitute this in equation (1.4); after changing the order of summation we readily arrive to $Q_{lm} = \sum_{j=1}^{n_{11}} c_{lm'm_j} Q_{lm'}$, which proves the statement.

Explicit expressions for $\text{Tr}(a_l(G))$ for all PGs are listed in tables 1 and 2 (column 4); they are obtained from columns 2 and 3 using equation (4.6). The selection rules for multipoles follow from equation (7.2) with traces from tables 1 and 2; the results showing conditions (on $l$) under which $Q_l$ vanishes are presented in the last columns of the tables. For example, for group $D_{3d}$ the multipoles vanish at any odd $l$, while for group $D_{4d}$ only at $l = 1$ and $l = 3$; for group I, there are only 15 values of $l$ such that the multipole vanishes.

(b) Regularities

The expressions for traces can be used to reveal regularities in $n_{11}(G)$ depending on PG and multipole. Some rules are listed below; $n$ starts from 1 ($C_{1h} = C_S$; $C_{1v} = C_{sv}$; $S_2 = C_1$). The continuous groups $C_{∞v}$, $D_{∞h}$ and $K_h$ are not included as the trends are evident in their case.

1. Recurrence relationships over $l$. For each group,

$$n_{l+s,1}(G) = n_{11}(G) + i.$$  
(7.4)

Steps $s$ and increments $i$ are listed in table 4.

It is evident from equation (7.4) and the table that any $n_{11}(G)$ can be found if we know the first $n$ values if the PG is $C_n$, $C_{nh}$ or $C_{nv}$, or 2$n$ values in case of another axial group. These values are controlled by Rule 2.
2. If \( l < n \), then \( n_{l_l}(G) = 1 \) in \( C_n \) and \( C_{nv} \). If PG is \( C_{nh}, S_{2n}, D_{n}, D_{nd} \) or \( D_{nh} \), and \( l < n \), then \( n_{l_l}(G) = 0 \) or 1 for \( l \) odd (even).
   If PG is \( S_{2n}, D_{n}, D_{nd} \) or \( D_{nh} \), and \( n < l < 2n \), then \( l = l'' \) given in table 4.
3. Multipoles with \( l = 6, 10, 12, 16 \) and higher even values do not vanish in any PG.
4. In the axial and non-axial groups, if a \( 2l \)-pole with \( l \) odd does not vanish then all higher multipoles also do not vanish.
5. \( n_{l_l}(G) = 0 \) if \( l \) is odd and the PG has inversion. These conditions become necessary and sufficient (if and only if) for \( l \geq n \) in the axial groups, and for \( l \geq s \) (table 4) in the polyhedral groups.
6. The infinite set of all \( n_{l_l}(G) \) for each PG is unique. Moreover, the set of the first \( f + 1 \) values (starting with \( n_{l_l}(G) \)) is unique for each PG, with \( f = n \) for \( C_n, C_{nh}, C_{inv} ; f = n + 1 \) for \( S_{2n}, D_{n}, D_{nd}, D_{nh} ; f = 6 \) for \( T, T_h, T_d ; f = 9 \) for \( O, O_h \) and \( f = 15 \) for \( I, I_h \).

8. Relationships between multipole components

(a) Linear relationships

We work with irreducible multipole components rather than Cartesian ones; nonetheless, some of them may be mutually dependent. This is not the case for non-axial and axial groups, but happens in polyhedral groups when the number of non-zero components in the standard frame (table 3) exceeds number \( n_{l_l}(G) \) of independent components (column 4 of table 2). For example, for \( l = 6 \) there are two non-zero components, \( l m\lambda = 60+ \) and \( 64+ \), in all cubic groups, and more two, \( l m\lambda = 62+ \) and \( 66+ \), in \( T \) and \( T_h \); but only two of them are independent in \( T \) and \( T_h \), and only one in other cubic groups.

Component \( Q_{lm\lambda} \) is determined (equation (3.6)) by a set of geometrical factors \( [a_{lm\lambda}; m' = 0, 1, \ldots, l] \), which is same for all components of the \( 2l \)-pole, and a set of SFs \( [a_{lm\lambda}; m; m' = 0, 1, \ldots, l] \) forming the \( m \)th column of matrix \( a_l(G) \). Hence, the linear dependence between MMs is the same as between columns of the matrix (which can be easily studied). This, in turn, implies that the dependence is the same in all cubic (or both icosahedral) groups as far as non-zero components are considered.

For example, in all cubic groups \( a_{40;4+}(G)/a_{40;0+}(G) = a_{44;4+}(G)/a_{44;0+}(G) = \sqrt{5/7} \). Hence, \( Q_{44+} = q_{40;4+} + q_{44;4+} + q_{44;4+} + q_{44;0+} + \sqrt{5/7} q_{40;0+} + \sqrt{5/7} q_{44;0+} = \sqrt{5/7} Q_{40;0+} \) in any cubic group.

Relationships between MMs in the standard frame are listed here for \( l \) up to 15.

(i) Cubic groups

Frame \( F_c \).

\[
Q_{44+} = \sqrt{\frac{5}{7}} Q_{40+}; \quad Q_{64+} = -\sqrt{\frac{5}{7}} Q_{60+}; \quad Q_{66+} = -\sqrt{\frac{5}{11}} Q_{62+}; \quad Q_{76+} = \sqrt{\frac{11}{13}} Q_{72+};
\]

\[
Q_{88+} = \frac{1}{2} \sqrt{\frac{5}{7}} \frac{13}{7} Q_{84+}; \quad Q_{86+} = \frac{1}{3} \sqrt{\frac{5}{11}} \frac{13}{11} Q_{80+}; \quad Q_{96+} = -\sqrt{\frac{13}{3}} Q_{92+}; \quad Q_{98+} = -\sqrt{\frac{7}{17}} Q_{94+};
\]

\[
Q_{10,8+} = \frac{1}{2} \sqrt{\frac{7}{17}} Q_{10,4+} = -\sqrt{\frac{11}{5}} \frac{17}{3} Q_{10,6+}; \quad Q_{10,10+} = -\sqrt{\frac{3 \cdot 5}{2 \cdot 19}} Q_{10,6+} = -\sqrt{\frac{3 \cdot 5}{2 \cdot 19}} Q_{10,2+};
\]

\[
Q_{11,10+} = \frac{1}{2} \sqrt{\frac{7}{19}} Q_{11,6+} = \sqrt{\frac{7}{2}} \frac{19}{5} Q_{11,2+}; \quad Q_{12,8+} = \sqrt{\frac{3 \cdot 11}{17}} Q_{12,0+} = 4 \sqrt{\frac{3 \cdot 7}{17}} Q_{12,4+};
\]

\[
Q_{12,10+} = \frac{1}{2} \sqrt{\frac{11}{3 \cdot 7}} Q_{12,6+} = \sqrt{\frac{11}{27}} Q_{12,2+}; \quad Q_{12,12+} = 4 \sqrt{\frac{2 \cdot 13}{17} \cdot 19} Q_{12,0+} + \sqrt{\frac{11}{17} \cdot 19} Q_{12,4+};
\]

\[
Q_{13,12+} = -\frac{1}{2} \sqrt{\frac{11}{2 \cdot 5}} Q_{13,8+} = -\frac{1}{2} \sqrt{\frac{11}{2 \cdot 5}} Q_{13,4+}; \quad Q_{13,10+} = \sqrt{\frac{23}{11}} Q_{13,6+} = \sqrt{\frac{23}{11}} Q_{13,2+};
\]
Table 5. A selection of sums $\sigma_i^{(q)}$ of squared MMs. ($\alpha$ and $\beta$ are the Eulerian angles of rotation $R(\alpha, \beta, \gamma)$) from the standard frame to the laboratory frame. $Q_{lm}^{(0)}$ is the MM that does not vanish in the standard frame.

<table>
<thead>
<tr>
<th>PGs</th>
<th>$l$</th>
<th>$Q_{lm}^{(0)}$</th>
<th>$\sigma_i^{(2)}$</th>
<th>$\sigma_i^{(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_3$, $D_3d$, $T$, $T_d$</td>
<td>3</td>
<td>$Q_{32}^{-}$</td>
<td>4</td>
<td>$16 + 15 (\sin^2 2\beta + \sin^4 \beta \sin^2 2\alpha)$</td>
</tr>
<tr>
<td>$D_3$, $D_3h$</td>
<td>3</td>
<td>$Q_{33}^{+}$</td>
<td>$(3/2)(5 \cos^2 \beta + 1)$</td>
<td>$(3/2)(15 \cos^4 \beta + 35 \cos^2 \beta + 2)$</td>
</tr>
<tr>
<td>$T$, $T_d$, $T_h$, $0$, $0_h$</td>
<td>4</td>
<td>$Q_{44}^{-} = \sqrt{5/7}Q_{44}^{+}$</td>
<td>$20/3$</td>
<td>$(320/3) + 35 (\sin^2 2\beta + \sin^4 \beta \sin^2 2\alpha)$</td>
</tr>
<tr>
<td>$I$, $I_h$</td>
<td>6</td>
<td>$Q_{65}^{+} = -\sqrt{4/11}Q_{60}^{+}$</td>
<td>14</td>
<td>350</td>
</tr>
</tbody>
</table>

$Q_{14,12} = \sqrt{5/23}Q_{14,8}^{+} = \frac{1}{3} \sqrt{5/19}Q_{14,4}^{+} = -\frac{1}{2} \sqrt{5/19}Q_{14,0}^{+}$;
$Q_{14,14} = -3\sqrt{7/13}Q_{14,10}^{+} = -\sqrt{3/5}Q_{14,6}^{+} = -3\sqrt{5/19}Q_{14,2}^{+}$;
$Q_{15,10} = 2\sqrt{3/19}Q_{15,2}^{+} = 3\sqrt{7/11}Q_{15,6}^{+} = -\frac{1}{2} \sqrt{5/19}Q_{15,8}^{+} = -\frac{1}{2} \sqrt{5/19}Q_{15,4}^{+}$;
$Q_{15,14} = \frac{3}{11} \sqrt{7/19}Q_{15,2}^{+} + 2\sqrt{13/29}Q_{15,6}^{+}.$

Note 2-term expressions for $Q_{12,8}^{+}$ and $Q_{12,12}^{+}$. They manifest that these MMs, together with $Q_{12,0}^{+}$ and $Q_{12,4}^{+}$, belong to non-separated bases of two different copies of the identity representation. Similar situation is with $Q_{15}$.

(ii) Icosahedral groups
Frame $F_{ic}$:

$Q_{65}^{+} = -\sqrt{14/11}Q_{60}^{+}$; $Q_{10,10} = \sqrt{17/3}Q_{10,5}^{+} = \sqrt{2/11}Q_{10,9}^{+}$;
$Q_{12,10} = -\sqrt{3/19}Q_{12,5}^{+} = \sqrt{2/19}Q_{12,0}^{+}$;
$Q_{15,15} = -\sqrt{7/2}Q_{15,10}^{+} = \sqrt{7/3}Q_{15,5}^{+}$.

(b) Sum rules
It is also possible to obtain useful expressions for certain sums of squared MMs in an arbitrary frame. Define

$$\sigma_i^{(q)} = \sum_{m=-l}^{l} m^q|Q_{lm}|^2 / \|Q_l\|^2 = \sum_{m=1}^{l} m^q \frac{[(Q_{lm}^+)^2 + (Q_{lm}^-)^2]}{\|Q_l\|^2}; \quad q = 2, 4, \ldots, \quad (8.1)$$

where

$$\|Q_l\|^2 = (Q_l \cdot Q_l) = \sum_{m=0}^{l} [(Q_{lm}^+)^2 + (Q_{lm}^-)^2]. \quad (8.2)$$

$\|Q_l\|$ is the scalar norm of the multipole. Sums $\sigma_i^{(q)}$ can be found in an arbitrary frame by applying transformation (6.3) to MMs and using explicit expressions for $d_{lm}^{i}(\beta)$ [10]. If for the specific $l$ and PG there is only one independent component of the multipole ($m_1(G) = 1$), then the sums depend only on the angles of the rotation. Moreover, each sum takes the same value in all PGs where the MM that does not vanish in the standard frame is the same. Some of the sums (at lower $q$) are rotational invariants. Several examples of such sums are presented in Table 5.
9. Discussion

We propose a novel method of finding totally symmetric spherical functions $|S; lm\rangle$ and then apply them to study properties of MMs. The method is developed for all three-dimensional PGs possible for a scalar field, like an electrical charge or a mass. Not only molecular symmetry groups but the entire seven infinite series of axial groups are included.

Some ideas underlying our method appeared in previous literature. Wigner’s functions in the basis of real spherical functions were studied in [27]. Factoring the projection operator was considered in [9] under restriction that group $G$ is presented as product of an invariant subgroup and a quotient set of operators. By contrast, the only weak restriction imposed in our equation (4.11) is commutability of the subgroups in the product.

Expressions for the SFs, selection rules for MMs and for entire multipoles, as well as numbers $n_{l 1}(G)$ of independent components of a multipole are either obtained in explicit form, or tabulated (selection rules for MMs in polyhedral groups). These results cover all PGs and all values of $l$ and $m$. Although some of these results for most or all molecular PGs can in principle be derived from [2] (for all $l$), Gelessus et al. [12] (for several $l$) and other works, the analytical expressions we present here offer a useful alternative as they cover arbitrarily large $l$ and $n$ while do not require recurrence calculations.

Comparison of our results for selection rules and $n_{l 1}(G)$ shows agreement with results derived from [2,11–13] (for PGs $l$ and $m$ values covered in each of the works; work [12] contains a few errors that are corrected in [13]). Our approach seems to be more stable against computational mistakes, which in the conventional method could arise during the iterative derivations while constructing the subduction tables.

The proposed approach provides an insight in the studied properties of multipoles and trends in their dependence on $l$ and $n$. Our results confirm or, in some cases, enhance the results of others. For example, Rule 1 can be derived from the subduction tables given in [2]. The first part of Rule 2 ($l < n$) is a theorem proved in [23]. Rule 3 for $l = 6$, Rule 4 for $l = 1$, and the first part of Rule 5 were formulated in [12].

Our technique allowed also finding out dependence between components of the same multipole in polyhedral groups, as well studying certain sums of squared MMs. It turned out, in particular, that some of the sums are rotational invariants.

Acknowledgements. The authors are grateful to our late friend Prof. P. W. M. Jacobs for his attention to our work. The authors are indebted to Dr A. Gelessus for sending a reprint of his paper. Part of the analytical derivations was performed using MathCad 2001 Professional; B.Z. thanks Dr Ruvin Deych for his help with MATHCAD software.

Funding statement. P.Z. is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-06CH11357.

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