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Phase-fixed double-group 3-Γ symbols. V. 3-Γ symbols and coupling coefficients for all the octahedral double group-subgroup hierarchies

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For all the subgroup hierarchies descending from the octahedral double group O^*, we have obtained sets of 3-Γ symbols and discuss here their properties. We have entirely real sets of 3-Γ symbols for the tetrahedral and tetragonal hierarchies as well as for $O^* \supset C_3^*$. For the latter hierarchy and the tetragonal ones, formalisms almost as powerful as the classical one for the rotation group may be established. We also discuss results obtained for cases with strict adaption to D_3^* where it is now known that non-real 3-Γ symbols are unavoidable.

The 3-Γ symbols are phase-fixed by the specification of basis functions (or, equivalently, subduction coefficients) generating them.

The significance of the concept of associated representations of O^* is discussed. The problems raised by the two multiplicity triples UT_1U and UT_2U in O^* are given particular attention.

Key words: octahedral double group-subgroup hierarchies—real phase-fixed three-gamma symbols and coupling coefficients—standard irreducible matrix representations—complex conjugation of matrix representations by inner automorphism—non-real trigonally adapted octahedral three-gamma symbols.

1. Introduction

The importance of the octahedral group O and its double group O^* for coordination chemistry is well-known, and these symmetries are also often taken as the

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basis for considerations or calculations in neighboring disciplines such as molecular spectroscopy or solid-state physics. Thus it is clearly of interest to have at one's disposal smoothly working Wigner–Racah algebras for the various group hierarchies of the form $O^* \supset G_1 \supset G_2 \cdots$. The purpose of the present paper is to provide a basis for this by discussing the building-blocks for Wigner–Racah algebra called 3-Γ symbols [1]. The exposition will be based on the general developments made in [1] and the particular remarks concerning double groups made in [2]. We refer to these papers for terminology and notation not explained here.

There exists, of course, a rather vast literature on octahedral symmetry. We do not purport to reference this literature in any complete way here. However, we shall comment on most of the literature from the last decade or so regarding octahedral 3-Γ symbols. This literature includes two earlier publications from this laboratory [3, 4]. We refer to these papers for discussions of most of the relevant literature prior to 1972.

The present work makes use of *basis functions* [2] generating the *standard* matrix forms of the irreps (irreducible representations) of O^*. There is a long record of literature dealing with the determination of such basis functions, especially linear combinations of spherical harmonics or other basis functions for irreps of the full rotation double group R_3^*. For our present purpose it is not of particular relevance to make detailed comparisons with these older works. For a collection of references and still another contribution to that particular subject we refer to a forthcoming publication on cubic harmonics [5]; another useful source of references of this kind is [6].

Most previous papers devoted to octahedral 3-Γ symbols take some or other set of coupling coefficients ([1], Sect. 3.3) as the starting point from which they proceed to a 3-Γ symbol-like construction. This approach in many cases has led to an erroneous or, at the best, very involved treatment of the two multiplicity triples UT_1U and UT_2U in O^*. The approach adopted here [1, 2] does not lead to these difficulties, as will be demonstrated below.

2. General remarks on the representation algebra of O^*

A listing of those O^*-irrep triples $\Gamma_1\Gamma_2\Gamma_3$ for which dim $\mathscr{F}(\Gamma_1\Gamma_2\Gamma_3) > 0$ ([1], Sect. 3.1), that is, for which 3-Γ symbols exist, may be obtained for example from Table 5 of [4]. We shall use the same symbols for the irreps as in [4]; in particular, the totally symmetric irrep will be denoted A_1 rather than 1_{O^*}. Its component will be denoted 0. The component designations for the other irreps depend on the subgroup adaption.

The group O^* is *ambivalent*, that is, all its irreps are of the first or second kind according to the Frobenius–Schur classification [(1], Sect. 5.2; [7]) and thus matrix forms of the irreps always possess conjugating matrices. By our conventions ([1], Sects. 5.1–5.3), the conjugating matrix $\mathbb{U}^\Gamma$ corresponding to the matrix form $\mathbb{\Gamma}$ of an irrep Γ generated by our standard basis functions for Γ is given by the formula

$$(\mathbb{U}^{\Gamma})_{\gamma\gamma'} = \sqrt{\dim \Gamma}\begin{pmatrix} \Gamma & \mathrm{A}_1 & \Gamma \\ \gamma & 0 & \gamma' \end{pmatrix} \quad \text{for all } \gamma, \gamma'. \tag{2.1}$$

We recall that the conjugating matrix satisfies the relation $\mathbb{U}^{\Gamma}\mathbb{\Gamma}(R)(\mathbb{U}^{\Gamma})^{-1} = \overline{\mathbb{\Gamma}(R)}$ for all $R \in O^*$, the overbar denoting complex conjugation. In [4], the 3-Γ symbols $(\Gamma\Gamma A_1/\gamma\gamma'0)$ were used instead of $(\Gamma \mathrm{A}_1 \Gamma/\gamma 0 \gamma')$; if basis functions are identical, the difference in the resulting algebras amounts to a sign change on $\mathbb{U}^{\Gamma}$ when Γ is of the second kind (i.e. when $\Gamma = \mathrm{E}_1$, E_2, or U). However, as will be clear from the sequel, the present formalism is different from that of [4] in several other, more significant respects.

The presence of the non-trivial one-dimensional irrep A_2 in the irrep algebra of O^* gives rise to the concept of *associated* octahedral representations. Two (equivalence classes of) representations Γ_1 and Γ_2 of O^* are said to be associated if $\Gamma_1 = \Gamma_2 \otimes \mathrm{A}_2$ (or, equivalently, $\Gamma_2 = \Gamma_1 \otimes \mathrm{A}_2$). The irreps A_1 and A_2; T_1 and T_2; and E_1 and E_2 form pairs of associated representations. The irreps E and U are both self-associated. The term "associated" has been used in contexts similar to the present one in early literature on group representations [8, 9], but the usual starting reference in connection with Wigner–Racah algebra is Griffith ([10], App. B), who discussed the phenomenon for the octahedral group *O*. Several later publications deal with the subject, partly in more general settings [11–14]. From our present point of view, association is only of interest if the associated irreps actually have *associated matrix forms*. This is of course not possible for the self-associate irreps, E and U, and it is trivial for A_1 and A_2; but for T_1, T_2 and E_1, E_2 it is a possible and non-trivial restriction on matrix forms of the irreps that they satisfy $\mathbb{T}_1 = \mathbb{T}_2 \otimes \mathrm{A}_2$ and $\mathbb{E}_1 = \mathbb{E}_2 \otimes \mathrm{A}_2$. (Identities like these imply a correspondence between *components* of $\mathbb{T}_1$ and $\mathbb{T}_2$ and a correspondence between those of $\mathbb{E}_1$ and $\mathbb{E}_2$. In [4], it was incorrectly stated that establishing such a correspondence contradicts Schur's lemma; there is, in fact, no contradiction because the construction involves no statement equivalent to claiming that, e.g. $\mathbb{T}_1$ and $\mathbb{T}_2$ are *equivalent*. This error was also noted in [12].) In the case of such associated matrix forms, we may use ([1], Eq. (3.1.5)) to establish certain relations involving 3-Γ symbols in which two irreps are replaced by their associates. E.g., if Γ is any irrep of O^* with standard matrix form $\mathbb{\Gamma}$, one gets

$$\begin{aligned}
&\overline{\begin{pmatrix} \mathrm{T}_2 & \mathrm{T}_2 & \Gamma \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}}\begin{pmatrix} \mathrm{T}_2 & \mathrm{T}_2 & \Gamma \\ \gamma_1' & \gamma_2' & \gamma_3' \end{pmatrix} \\
&= \frac{1}{48} \sum_{R \in O^*} [\mathbb{T}_1 \otimes \mathrm{A}_2](R)_{\gamma_1\gamma_1'} [\mathbb{T}_1 \otimes \mathrm{A}_2](R)_{\gamma_2\gamma_2'} \mathbb{\Gamma}(R)_{\gamma_3\gamma_3'} \\
&= \frac{1}{48} \sum_{R \in O^*} \mathbb{T}_1(R)_{\gamma_1\gamma_1'} \mathbb{T}_1(R)_{\gamma_2\gamma_2'} \mathbb{\Gamma}(R)_{\gamma_3\gamma_3'} \\
&= \overline{\begin{pmatrix} \mathrm{T}_1 & \mathrm{T}_1 & \Gamma \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}}\begin{pmatrix} \mathrm{T}_1 & \mathrm{T}_1 & \Gamma \\ \gamma_1' & \gamma_2' & \gamma_3' \end{pmatrix}
\end{aligned} \tag{2.2}$$

for all components $\gamma_1, \gamma_2, \gamma_3, \gamma_1', \gamma_2', \gamma_3'$ (denoting corresponding components of T_1 and T_2 by the *same* component symbol); it is then an easy exercise to infer from (2.2) that the 3-Γ symbols $(T_2T_2\Gamma/\gamma_1\gamma_2\gamma_3)$ can differ from $(T_1T_1\Gamma/\gamma_1\gamma_2\gamma_3)$ by at most a common complex phase (a sign factor if the 3-Γ symbols are real). When this proportionality phase is known, a reduction in tabulation space for the 3-Γ symbols can be achieved. However, in view of the points made in Sect. 4.1 below, this aspect is not that important, especially considering that the price to be paid is that we have to keep track of the phases in our formalism. Furthermore, matrix irrep association for O^* is incompatible with adaption to D_3^* or D_4^*. The problem is there already for $O \supset D_3$ and $O \supset D_4$. In the trigonal case, this may be appreciated by noting the subduction relations

$$\begin{aligned} &T_1(O) \to A_2(D_3) \oplus E_1(D_3) \\ &T_2(O) \to A_1(D_3) \oplus E_1(D_3) \qquad (2.3) \\ &A_2(O) \to A_2(D_3). \end{aligned}$$

The irreps of D_3 are denoted as in [15]. Since no matrix form $\mathbb{E}_1$ of $E_1(D_3)$ can satisfy $\mathbb{E}_1 = \mathbb{E}_1 \otimes A_2(D_3)$, matrix forms $\mathbb{T}_1$ and $\mathbb{T}_2$ of $T_1(O)$ and $T_2(O)$, respectively, satisfying $\mathbb{T}_1 = \mathbb{T}_2 \otimes A_2(O)$, cannot be $(O \supset D_3)$-adapted. It seems as if Griffith overlooked this problem in his discussion of trigonal symmetry adaption ([10], p. 19). The argument for D_4 is completely analogous.

On this background, we shall not devote any more space to the association phenomenon except for noting later on, in the discussion of the 3-Γ symbols we have generated (Sect. 4), whether or not the involved matrix irreps are associated.

3. The multiplicity triples UT_1U and UT_2U

The irrep triples UT_1U and UT_2U in the octahedral double group – and *only* these, disregarding permutations of the irreps within a triple – have multiplicity; indeed, $\dim \mathscr{F}(UT_1U) = 2 = \dim \mathscr{F}(UT_2U)$. The procedure outlined in [2] leads to the assignment of the j-value triples $\frac{3}{2}1\frac{3}{2}$ and $\frac{3}{2}3\frac{3}{2}$ to UT_1U and $\frac{3}{2}2\frac{3}{2}$ and $\frac{3}{2}3\frac{3}{2}$ to UT_2U. We recall that this implies, for example, that the two sets of 3-Γ symbols which we require for UT_2U are constructed by renormalization with positive proportionality factors N of O^*-adapted 3-j symbols according to the following prescriptions:

$$\begin{pmatrix} U & T_2 & U \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_o = N_o \begin{pmatrix} \frac{3}{2} & 2 & \frac{3}{2} \\ U\gamma_1 & T_2\gamma_2 & U\gamma_3 \end{pmatrix} \qquad (2.4a)$$

and

$$\begin{pmatrix} U & T_2 & U \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_e = N_e \begin{pmatrix} \frac{3}{2} & 3 & \frac{3}{2} \\ U\gamma_1 & T_2\gamma_2 & U\gamma_3 \end{pmatrix}. \qquad (2.4b)$$

For the multiplicity index we have here used the subscripts "o" (for *odd*) and "e" (for *even*), since the 3-Γ symbols defined by (2.4a) are odd ($\frac{3}{2}+2+\frac{3}{2}$ is odd; cf. ([2], Eq. (4.3.7)), while those defined by (2.4b) are even.

In both multiplicity cases, the two fix-vectors obtained by the above procedure form an orthonormal set by the arguments given in [2, Sect. 4.6].

The apparently exceptional character of the triple UT_2U signalized by the asterisk in Table 5 of [4] disappears within the present description.

Having obtained 3-Γ symbols for O^*, we may also construct coupling (Clebsch–Gordan coefficients) by the formulas discussed in ([1], Sect. 5.3.3) or, if relevant, by ([1], Eq. (5.5.10)). In [4] the approach was different: First, a certain class of coupling coefficients for O^* was established by renormalization of coupling coefficients for R_3^* with positive proportionality factors. Then these particular coupling coefficients were used to generate a full set of 3-Γ symbols for O^*, after which the remaining coupling coefficients for O^* could be calculated. This way of proceeding resulted, as far as we know, in a consistent formalism, but the approach is less transparent than the one we are now describing. Since [4] may further be confusing because a set of $\frac{5}{2}(R_3^*)U(O^*)$ basis functions was included which is not necessary for the construction of the 3-Γ symbols or coupling coefficients, we would like to add the following remarks of warning.

When generating coupling coefficients for O^* (rather than 3-Γ symbols) by the use of basis functions, it is not unnatural to suggest to use, for coupling coefficients of the types $\langle T_2\gamma_1U\gamma_2|\beta U\gamma_3\rangle$ and $\langle U\gamma_1T_2\gamma_2|\beta U\gamma_3\rangle$, *two* sets of basis functions for U. If one sticks to the lowest possible j-values, this leads to the involvement of $\frac{5}{2}(R_3^*)U(O^*)$-functions. However, the UT_2U fix-vector generated by the transformed 3-j symbols $(\frac{3}{2}2\frac{5}{2}/U\gamma_1T_2\gamma_2U\gamma_3)$ is *neither symmetric nor antisymmetric* (i.e. it is a mixture of both symmetry types), so from this fix-vector it is *impossible* to construct 3-Γ symbols. For UT_1U, the consequences of using a $\frac{5}{2}$-set of basis functions for one of the U's are less dramatic; in fact, it can easily be shown from the arguments in ([2], Sect. 4.6) that the transformed 3-j symbols of the two types $(\frac{3}{2}1\frac{5}{2}/U\gamma_1T_1\gamma_2U\gamma_3)$ and $(\frac{3}{2}3\frac{3}{2}/U\gamma_1T_1\gamma_2U\gamma_3)$ form proportional fix-vectors for UT_1U.

[The above constructions may be said to effect a *separation of the multiplicities* for the triples UT_1U and UT_2U. The choice of a multiplicity separation has consequences beyond the ones discussed above. For example, sets of recoupling coefficients and 6-Γ symbols calculated on the basis of the 3-Γ symbols will look different depending on the choice of a multiplicity separation. (Work is in progress [16] on 6-Γ symbols for groups with a Wigner–Racah algebra satisfying the conditions discussed in ([1], Sect. 5.5). The concept of 6-Γ symbols generalizes that of 6-j symbols [17, 18] or W coefficients [19] for the rotation group. In [4], 6-Γ symbols were discussed for the octahedral double group and given for the octahedral group. The 6-Γ symbols discussed in [4] were based on the same multiplicity separation as we have here.) One application of the 6-Γ symbols in ligand-field theory is for setting up matrices of the spin-orbit coupling operator [4, 20]. We have checked that for the U part of the quartet spin-orbit coupling matrix within the d^3 electronic configuration, our 6-Γ symbols lead to a set of matrix elements which is *equivalent* to the one given by Griffith ([21], Table A34). For the ${}^4T_1$ terms we get the *same* diagonal matrix as [21]; for the ${}^4T_2$ terms one cannot, like Griffith, obtain a diagonal matrix if one wants to separate the UT_2U multiplicity according to symmetry/antisymmetry. (Piepho [22] has also pointed out that the coupling coefficients on which Griffith's matrix is based mix the symmetric and antisymmetric part.) Butler ([14], pp. 76–77) uses a multiplicity separation for UT_1U based on a certain relation involving the associated irreps concept (see Sect. 2 above) and different from ours; it results in a table of 6-j symbols (in his terminology) for the octahedral double group completely free of factors $\sqrt{5}$, but, on the other hand, leading to a non-diagonal spin-orbit coupling matrix for the $^4T_1$ terms. Still another multiplicity separation is discussed in [23]; although it has interesting properties, it is not useful for our present purpose.]

4. Basis functions and 3-Γ symbols for all the octahedral double group-subgroup hierarchies

4.1. Introductory remarks

In this section we shall list all the subgroup hierarchies of the form $O^* \supset \cdots$ and discuss properties of the standard matrix irreps and the standard basis functions we have chosen and of the resulting octahedral 3-Γ symbols. However, the rather vast tabular material itself is not suitable for reproduction in a paper like the present one. Besides that, in the authors' opinion, when generating 3-Γ symbols by the procedure of [2], the results are not to be communicated as extensive tables. Such tables would inevitably contain errors if they were set manually for printing, and using them without adding further errors would also be difficult. A reasonable approach is to get a set of basis functions with the desired properties and then to generate the 3-Γ symbols (or coupling coefficients) with a computer when they are needed. (The basis function sets referred to below are, consequently, obtainable from the authors until possibly some way of publishing them separately has been decided upon.) Efforts in our laboratory are presently directed at a computer implementation of the whole formalism described in [1, 2] together with the basis functions given here and in [15] for the dihedral double groups, in [24] for the tetrahedral double group, and in [25] for the icosahedral double group. In view of the above remarks, the most important reason for writing the present paper lies in the discussion of the fundamental aspects, to which we shall turn now.

We shall have occasion to refer several times to the particularly convenient formalism described in ([1], Sect. 5.5). We recall that the basis for that formalism was the existence of an inner automorphism of the group carrying all standard matrix irreps into their complex conjugate (see [7, 26] for more of the background). In practical terms, this means that there is a fixed group element R_o so that the relation

$$\begin{pmatrix} \Gamma & A_1 & \Gamma \\ \gamma & 0 & \gamma' \end{pmatrix} = (\dim \Gamma)^{-1/2}\Gamma(R_o)_{\gamma\gamma'} \qquad (4.1.1)$$

is satisfied for all standard matrix irreps Γ. The 3-Γ symbols represented to the left in (4.1.1) are related to our conjugating matrices as described in Sect. 2. In all the cases below where we have the situation (4.1.1), the coordinate system has been chosen in such a way that the element R_o is C_2^{Y*}, the double-group element $\mathscr{D}^{[1/2]}(0, \pi, 0)$ corresponding to the two-fold rotation around the Y axis (cf. [2], Sect. 2). The main advantages of the inner automorphism situation are that all 3-Γ symbols may be chosen real; all Derome–Sharp $\mathbb{A}$ matrices ([1], Sect. 5.4) are unit matrices, i.e. the formula

$$\begin{pmatrix} \bar{\Gamma}_1 & \bar{\Gamma}_2 & \bar{\Gamma}_1 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\beta = \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\beta \tag{4.1.2}$$

holds generally; and that $\mathbb{B}$ matrices ([1], Sect. 5.4) are generally given by $\mathbb{B}^i(\Gamma_1\Gamma_2\Gamma_3)_{\alpha\beta} = \pi(\Gamma_i A_1 \Gamma_i)\delta(\alpha, \beta)$, so that, for example,

$$\begin{pmatrix} \bar{\Gamma}_1 & \Gamma_2 & \bar{\Gamma}_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\beta = \pi(\Gamma_2 A_1 \Gamma_2) \begin{pmatrix} \Gamma_1 & \bar{\Gamma}_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\beta . \tag{4.1.3}$$

Furthermore, the relation between coupling coefficients and 3-Γ symbols discussed in ([1], Sect. 5.3) and fixed there (by convention) assumes the simple form

$$\langle \Gamma_1\gamma_1\Gamma_2\gamma_2 | \beta\Gamma_3\gamma_3 \rangle = \pi(\Gamma_1\Gamma_2\Gamma_3\beta)\pi(\Gamma_2 A_1 \Gamma_2)\sqrt{\dim \Gamma_3} \begin{pmatrix} \Gamma_1 & \Gamma_2 & \bar{\Gamma}_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\beta . \tag{4.1.4}$$

In (4.1.3) and in (4.1.4), the π phases are the permutational characteristics (transposition phases), that is, $\pi(\Gamma_1\Gamma_2\Gamma_3\beta) = +1$ if the 3-Γ symbols $(\Gamma_1\Gamma_2\Gamma_3/\gamma_1\gamma_2\gamma_3)_\beta$ are *even* and $= -1$ if they are *odd* ([1], Sect. 4).

[When all of this favorable formalism applies, the only ingredient which is still needed to establish a machinery completely as elegant as the one for the classical case of the rotation group ([1], Sect. 6 and references therein) – or the hierarchy $I^* \supset C_5^*$ discussed in [25] – is a simple explicit and general formula for the matrix elements $\Gamma(R_0)_{\gamma\gamma'}$ in (4.1.1). This would permit us to simplify the formulas for conjugation of irreps in 3-Γ symbols (compare [1], Eq. (6.3) and [25], Eq. (3.2.6)) and establish some internal relations between 3-Γ symbols for a given triple (compare [1], Eq. (6.6)) and ([25], Eq. (3.2.5)). However, in the octahedral cases considered below, the partial or complete adaption to one or several intermediate dihedral double groups in most cases prevents us from establishing in a simple way this last bit of formalism. Luckily, the advantages lost – the ones just indicated above – are not particularly important for computer applications of the 3-Γ symbols, and manipulating them with paper and pencil, one will often see that obvious relations are actually satisfied even though they would have been complicated to express in a generally valid form.]

In all the cases discussed below, the standard matrix irreps of O^* are at least adapted to some cyclic double group $C_n^* \subset O^*$ with $n = 2$, 3, or 4. This adaption forces ([2], Sect. 3.5) corresponding 3-Γ symbols to satisfy a "selection rule" of the form

$$\begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\beta \neq 0 \Rightarrow \gamma_1 + \gamma_2 + \gamma_3 \equiv 0 \pmod{n}, \tag{4.1.5}$$

provided the components γ_i are chosen as numbers that reflect the C_n^*-adaption (γ_i corresponding to eigenvalue $\exp(-i\gamma_i 2\pi/n)$ under the distinguished C_n^* element of O^*).

4.2. Tetragonal hierarchies

The starting point here was the $(O^* \supset C_4^*)$-adapted basis functions given in [4]. Within our new material, they are available with new component designations conforming to the convention stated at the end of Sect. 4.1. They generate matrix irreps of O^* satisfying $\mathbb{T}_1 = \mathbb{T}_2 \otimes A_2$ and $\mathbb{E}_1 = \mathbb{E}_2 \otimes A_2$ and, by our present procedure, 3-Γ symbols obeying the formalism of ([1], Sect. 5.5) – discussed above in Sect. 4.1 – and satisfying (4.1.5) with $n = 4$.

By rather trivial alterations of these basis functions, it was possible to produce a series of related basis function sets with the common property of being adapted to a D_4^* subgroup of O^*. As noted above, adaption to D_4^* excludes the possibility of having the *matrix* forms of T_1 and T_2 to be associated. All the tetragonal basis functions to be described now are real linear combinations of the $|jm\rangle$ functions and generate real 3-Γ symbols which satisfy the ([1], Sect. 5.5)-formalism.

The groups D_n^*, and in particular D_4^*, were discussed in [15]. Standard matrix irreps adapted to two general dihedral subgroup hierarchies were considered: $D_n^* \supset C_n^*$ and $D_n^* \supset C_2^*$, the C_2^* in the latter case corresponding to a two-fold rotation about an axis perpendicular to the main C_n axis. Imbedding D_4^* into O^*, we get the hierarchies $O^* \supset D_4^* \supset C_4^*$ and $O^* \supset D_4^* \supset C_2^*$.

For $O^* \supset D_4^* \supset C_4^*$ we have two sets of basis functions corresponding to the two choices of a coordinate system shown in Figs. 1a and 1b, that is, differing in whether the element C_2^{Y*} corresponds to a two-fold rotation about a four-fold symmetry axis of the regular octahedron (Fig. 1a) or one about a two-fold symmetry axis (Fig. 1b). For short, we shall denote these two possibilities "*Y*

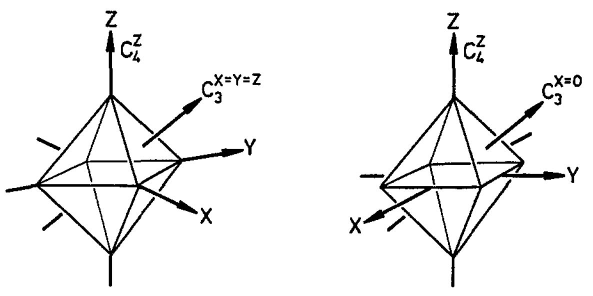

Fig. 1a (left). First choice of a coordinate system (*Y* axis of the vertex type, see main text Sect. 4.2) for applications in an octahedral-tetragonal symmetry hierarchy. The counterclockwise rotation $C_3^{X=Y=Z}$ of $2\pi/3$ about the indicated three-fold symmetry axis of the regular octahedron has Euler angles $(0, \pi/2, \pi/2)$. **b** (right). Second choice of a coordinate system (*Y* axis of the edge type) for applications in an octahedral-tetragonal symmetry hierarchy. The counterclockwise rotation $C_3^{X=0}$ of $2\pi/3$ about the indicated three-fold axis in the *YZ* plane has Euler angles $(\pi/4, \pi/2, \pi/4)$

vertex" and "Y edge" (for obvious reasons). One set of basis functions may be generated from the other by the procedure described in ([12], Sect. 4.5) and they thus generate the same *total* set of 3-Γ symbols. Nevertheless it is practical to actually store both sets. For one thing, the transformation from one set to the other interchanges certain irreps and components so that keeping track of which 3-Γ symbols to use for which irreps and components may be tedious (this mixing of irreps under a coordinate system rotation resembles the one discussed for the icosahedral hierarchy $I \supset D_2$ in [27]). Another reason is that *all* our basis functions have had their signs fixed by the rules given in ([2], Sect. 4.4); thus the "rotation relation" between two such function sets may have been destroyed when fixing their individual signs.

For $O^* \supset D_4^* \supset C_2^*$, the two-fold axis corresponding to the C_2^* subgroup of D_4^* may be of the vertex or the edge type, and we thus again have two sets of basis functions which we this time denote "$C_2^\perp$ vertex" and "$C_2^\perp$ edge". Of course, $R_o = C_2^{Y^*}$, too, will then correspond to a vertex-type axis and an edge-type axis, respectively. Figs. 1a and 1b and the rest of the above discussion apply again.

There is yet a possibility, however, for hierarchies involving $O^* \supset D_4^*$, namely the further adaption to a D_2^* subgroup of D_4^* and to a C_2^* subgroup of the D_2^* subgroup chosen. The D_2^* subgroup may be imbedded in two ways corresponding to whether the two two-fold axes it singles out among the 4 perpendicular ones of D_4^* are of the vertex or the edge type; the coordinate system is then again chosen as in Fig. 1a or in Fig. 1b, respectively, so that $C_2^{Y^*} \in D_2^*$ in both cases. Afterwards, the C_2^* subgroup of D_2^* may be chosen to be generated by the element $(C_4^{Z^*})^2$ or by an element corresponding to a two-fold rotation about either the X axis or the Y axis; our choice in [15] was $C_2^{X^*}$. In all, we get 4 sets of basis functions for $O^* \supset D_4^* \supset D_2^* \supset C_2^*$.

In all cases corresponding to Fig. 1a, the group O^* is generated within R_3^* by the element $C_4^{Z^*} = \mathscr{D}^{[1/2]}(\pi/2, 0, 0)$ and the element $(C_3^{X=Y=Z})^* = \mathscr{D}^{[1/2]}(O, \pi/2, \pi/2)$ and in all cases corresponding to Fig. 1b, by $C_4^{Z^*}$ and $(C_3^{X=0})^* = \mathscr{D}^{[1/2]}(\pi/4, \pi/2, \pi/4)$. (Cf. discussion of double groups in ([2], Sect. 2).)

The following list summarizes our sets of tetragonally adapted octahedral basis functions:

$O^* \supset C_4^*$ ([4]; note that these functions are not phase-fixed according to the rules in [2]);

$O^* \supset D_4^* \supset C_4^*$ (Y vertex), $O^* \supset D_4^* \supset C_4^*$ (Y edge);

$O^* \supset D_4^* \supset C_2^*$ ($C_2^\perp$ vertex), $O^* \supset D_4^* \supset C_2^*$ ($C_2^\perp$ edge);

$$O^* \supset D_4^* \supset D_2^* \supset C_2^* \ (D_2 \text{ vertex}, C_2^{X^*} \in C_2^*), \tag{4.2.1}$$

$O^* \supset D_4^* \supset D_2^* \supset C_2^*$ (D_2 vertex, $C_2^{Z^*} \in C_2^*$),

$O^* \supset D_4^* \supset D_2^* \supset C_2^*$ (D_2 edge, $C_2^{X^*} \in C_2^*$),

$O^* \supset D_4^* \supset D_2^* \supset C_2^*$ (D_2 edge, $C_2^{Z^*} \in C_2^*$).

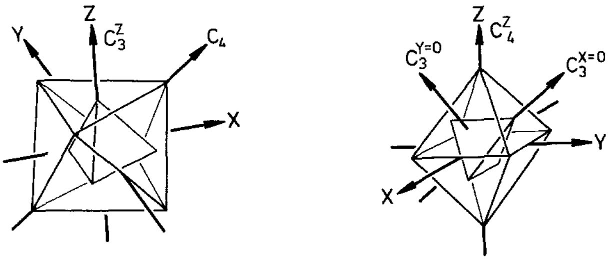

Fig. 2a (left). Coordinate system chosen for the hierarchy $O^* \supset T^* \supset C_3^*$ (main text, Sect. 4.3). The Z axis is a three-fold symmetry axis for the regular octahedron shown and for the regular tetrahedron inscribed in it as well; the Y axis is a two-fold axis for the octahedron, but not a symmetry axis for the tetrahedron; and the X axis is not a symmetry axis for the octahedron. The counterclockwise rotation C_4 of $\pi/2$ about the indicated four-fold axis has Euler angles ($5\pi/3$, Arccos (1/3), $2\pi/3$); its axis is a four-fold symmetry axis for the octahedron and a two-fold axis for the tetrahedron. **b** (right). Coordinate system chosen for the hierarchy $O^* \supset T^* \supset C_2^*$. With respect to the octahedron, the coordinate system is placed as was the one shown in Fig. 1b. The Z axis is a two-fold symmetry axis of the inscribed tetrahedron; the axes of the rotations $C_3^{X=0}$ (see legend to Fig. 1b) and $C_3^{Y=0}$ are three-fold symmetry axes for the tetrahedron

4.3. Tetrahedral hierarchies

This class consists of two sets of basis functions, one adapted to $O^* \supset T^* \supset C_3^*$ and one adapted to $O^* \supset T^* \supset C_2^*$. Figs. 2a and 2b show the choices of coordinate systems we have made. For $O^* \supset T^* \supset C_3^*$, the octahedral group has been chosen as the subgroup of R_3^* generated by the elements $C_3^{Z^*} = \mathscr{D}^{[1/2]}(2\pi/3, 0, 0)$ and $C_4^* = \mathscr{D}^{[1/2]}(5\pi/3, \text{Arccos}\,(1/3), 2\pi/3)$; for $O^* \supset T^* \supset C_2^*$, the elements $C_4^{Z^*}$ and $(C_3^{X=0})^*$ (see Sect. 4.2) generate O^*. In each case, the tetrahedral subgroup is generated by the C_3^* element and the square of the C_4^* element. The element $-C_3^*$ chosen as one of the generators for T^* in the discussion of $T^* \supset C_2^*$ in [24] corresponds to the three-fold rotation $C_3^{Y=0}$ also shown in Fig. 2b.

For both sets, (4.1.1) is satisfied with $R_o = C_2^{Y^*}$. The basis functions are all real linear combinations of the $|jm\rangle$ functions and accordingly generate real 3-Γ symbols. For each of the hierarchies $T^* \supset C_3^*$ and $T^* \supset C_2^*$, the set of basis functions in [24] is a subset of the present set for $O^* \supset T^*$, and thus the present matrix irreps of O^* subduce to the ones chosen as standards for T^* in [24].

The matrix irreps of O^* in both cases satisfy $\mathbb{T}_1 = \mathbb{T}_2 \otimes A_2$ and $\mathbb{E}_1 = \mathbb{E}_2 \otimes A_2$.

The $(O^* \supset T^*)$-adpation may not be as important for applications in, say, molecular spectroscopy or ligand-field theory as are the tetragonal hierarchies considered in Sect. 4.2 and the trigonal ones to be discussed in Sect. 4.4. The tetrahedral ones do have a fundamental interest in connection with [24], though. In the present cases, the inner automorphism $R \to C_2^{Y^*} R (C_2^{Y^*})^{-1}$ of O^*, as explained above, carries all standard matrix irreps into their complex conjugate. The subgroup T^* is easily seen to be invariant under this automorphism; on the other hand its restriction to T^* cannot be an inner automorphism of T^*, because

T^* has irreps of the third kind (cf. [7, 26]). Thus we have spotted an *outer* automorphism of T^* carrying its standard matrix irreps of [24] into their complex conjugates. It has recently been proved (combine arguments given in [26] with the result in [28]) that the existence of a full set of real 3-Γ symbols is always associated with a (unique) automorphism which effects complex conjugation of the matrix irreps.]

4.4. Trigonal hierarchies

After the present authors had put a great deal of effort into attempts at preparing real 3-Γ symbols for $O^* \supset D_3^*$, it was recently proved [28] that this is impossible. However, considering the great importance of the trigonal hierarchies in coordination chemistry, we have prepared three different sets of trigonally adapted O^*-basis functions, each with its merits and drawbacks. These will now be described.

4.4.1. Basis functions strictly adapted to $O^* \supset D_3^* \supset C_2^*$

The coordinate system chosen is shown in Fig. 3a. The group O^* is generated by the R_3^*-elements $C_3^{Z^*}$ (see Sect. 4.3) and $\tilde{C}_4^* = \mathscr{D}^{[1/2]}(\pi/6, \text{Arccos}\,(1/3), \pi/6)$; the D_3^* subgroup by $C_3^{Z^*}$ and $C_2^{X^*} = \mathscr{D}^{[1/2]}(\pi, \pi, 0)$; and the latter element finally generates the C_2^* subgroup. Thus the set-up for D_3^* is our standard one for D_3^* as described in [15], and the present basis functions generate the irreps of D_3^* in the standard matrix form (ii) for $D_3^* \supset C_2^*$ given there. The basis functions are *not* all real linear combinations of the $|jm\rangle$ functions. However, for all the vector irreps of $O^*(\mathrm{A_1, A_2, E, T_1, T_2}$, cf. [2], Sect. 2), the matrix representatives of the above-mentioned generators of O^* are *symmetric* matrices, and, indeed, all 3-Γ symbols for triples of three vector irreps are real (cf. [2], Sect. 3.2).

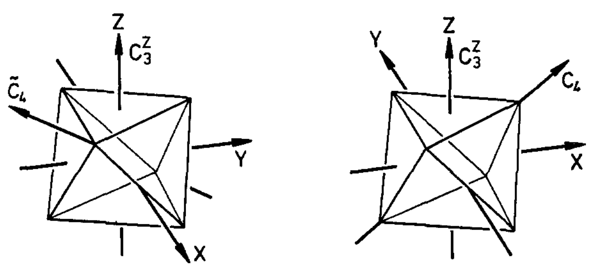

Fig. 3a (left). Coordinate system chosen for the two considered hierarchies $O^* \supset D_3^* \supset C_2^*$ and $O^* \supset D_3^* \supset C_3^*$ with strict adaption of the octahedral irreps to D_3^* (main text Sect. 4.4). The two-fold rotation about the X axis is an element of the octahedral as well as the trigonal dihedral group. The Y axis is not a symmetry axis for the octahedron. The counterclockwise rotation $\tilde{C}_4$ of $\pi/2$ about the indicated four-fold axis has Euler angles ($\pi/6$, Arccos (1/3), $\pi/6$). **b** (right). Coordinate system chosen for the set of basis functions adapted to $O^* \supset C_3^*$, but not strictly to D_3^* (main text Sect. 4.4.3). The two-fold rotation about the Y axis is an element of the octahedral as well as the trigonal dihedral group. The X axis is not a symmetry axis for the octahedron. The four-fold rotation indicated is C_4 described also in the legend to Fig. 2a

4.4.2. Basis functions strictly adapted to $O^* \supset D_3^* \supset C_3^*$

Except for the fact that the hierarchy terminates with the group C_3^* generated by $\boldsymbol{C}_3^{Z^*}$ rather than with C_2^*, the whole description given in Sect. 4.4.1 is valid also for the present set of basis functions.

4.4.3. Basis functions adapted to $O^*(\supset D_3^*) \supset C_3^*$

In the cases we discussed in Sects. 4.4.1 and 4.4.2, the price we had to pay for strict adaption to D_3^* was the presence of non-real 3-Γ symbols. Here, we have a set of basis functions leading to a very convenient algebra with real 3-Γ symbols, but not strictly adapted to D_3^*.

The coordinate system adopted is shown in Fig. 3b. The group O^* is generated by $\boldsymbol{C}_3^{Z^*}$ and the R_3^*-element C_4^* defined in Sect. 4.3. The elements $\boldsymbol{C}_3^{Z^*}$ and $\boldsymbol{C}_2^{Y^*}$ generate the subgroup D_3^* and $\boldsymbol{C}_3^{Z^*}$ the subgroup C_3^*.

The matrix irreps of O^* this time *all* have symmetric generator representatives, so that real 3-Γ symbols should exist, and in fact all the functions are real linear combinations of the $|jm\rangle$ functions and thus generate real 3-Γ symbols. Further, (4.1.1) is satisfied with $R_0 = \boldsymbol{C}_2^{Y^*}$.

The deviation from strict adaption to D_3^* lies mainly in the fact that the irreps $R_1(D_3^*)$ and $R_2(D_3^*)$ (see [15]) are not separated. In addition, we have here $\boldsymbol{C}_2^{Y^*} \in D_3$ with the representative matrices

$$\mathbb{E}_\lambda(\boldsymbol{C}_2^{Y^*}) = \begin{pmatrix} 0 & (-1)^{2\lambda} \\ 1 & 0 \end{pmatrix} \tag{4.4.3.1}$$

in the D_3^*-irreps E_λ, $\lambda = 1/2$ and 1, which was not the standard chosen in [15]; this latter difference is, of course, not as serious as the first one.

4.4.4. Concluding remarks on trigonal hierarchies

The choices of coordinate system made in the three cases discussed above were dictated by the desire to keep the set-up for D_3^* introduced in [15] when adapting the O^*-irreps strictly to D_3^*, but, on the other hand, to have $R_0 = \boldsymbol{C}_2^{Y^*}$ in (4.1.1) in the third case, where the inner automorphism approach is realizable and there is no strict adaption to D_3^* anyway. Furthermore, in the third case, the basis functions assumed more simple expressions in terms of the $|jm\rangle$ functions in the coordinate system chosen.

If it is desired to shift to some coordinate system rotated about the Z axis relative to the one used here, the procedure discussed in ([2], Sect. 4.6) may be applied.

4.5. A note on the figures

The octahedra and tetrahedra in Figs. 1–3 are only drawn to facilitate the visualization of the axes of the selected point group generators. Their full symmetry is of course O_h and T_d, respectively, whereas above we have only been concerned with the double groups O^* and T^* of the proper rotation groups O and T. Double groups of O_h and T_d have been defined ([2], Sect. 2; [29]).

5. Further remarks on the literature

We shall only comment here on literature dealing with the octahedral *double* group (as opposed to just the octahedral group itself); see also the reservations made in Sect. 1 above. The paper [4] has been dealt with in previous sections.

A series of papers by B. and T. Lulek [11, 12, 30, 31] describe a basis function approach to the construction of "$3j\Gamma\gamma$-symbols" for O^*. Their whole exposition is, however, very different from ours, and for the permutational properties, in particular those related to the triples UT_1U, we think it is much too involved, partly because of the way coupling coefficients are drawn into the discussion. A recent paper by Błaszak [32] discusses Wigner–Racah algebra for $O^* \subset SU(2)$. The exposition lies very close to partly that of the Lulek papers, partly that of [4].

Kibler et al. [6] have prepared some tables for $R_3^* \supset O^* \supset D_4^* \supset D_2^*$, but the discussion of how to use them is incomplete. The UT_1U and UT_2U problems are not mentioned at all.

Butler has given tables of "3-*jm* factors" relating to various octahedral subgroup hierarchies [14]. The whole approach of [14] is very different from the present one, as already noted in [2]. One consequence of this is that in [14], the features "coördinate system chosen" and "generator irrep matrices", rather than being at the basis of the material, are properties which can only be determined by an elaborate series of arguments.

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