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Permutation representations in molecular symmetry

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The reducible representations of the point groups are generally studied because of their relevance to molecular orbital and vibration theory. Triple correlations within the polyhedra are described by group-theoretical invariants that are related to the permutation representations and termed polyhedral isoscalar factors. These invariants are applied in theorems on matrix elements referring to the symmetry-adapted bases at different centres. Further invariants or geometrical weight factors inter-relate different types of reduced matrix elements of irreducible tensors (generalization of the Wigner-Eckart theorem to the polycentric case). As a demonstration a complete tabulation is given for the point group C_{4v}.

Keywords: Polycentric molecules — Permutational representations — Symmetry adaption — Irreducible tensors — Wigner-Eckart theorem

1. Introduction

The purpose of this paper is the study of certain representations of molecular symmetry groups. These representations are in general reducible and composed of permutation matrices, i.e. of matrices obtained from the unit matrix by permuting the columns. The equivalent atoms of a P_4 molecule or a Nb_6 cluster, for instance, induce such a permutation representation of the tetrahedral or the octahedral group. It has been shown that the decomposition of these reducible representations plays a central part in finding the symmetry coordinates of the molecule [1–3] as well as the symmetry-adapted molecular orbitals [4]. Moreover, if we consider interactions, chemical bonds, or two-centre integrals, the edges connecting the atomic positions come into question. These edges also form equivalent sets and thus induce permutation representations, too. The same

applies to the triangular faces and more complex substructures of the molecular skeleton involved in the three-centre integrals in MO-LCAO calculations and in the configurations of the valence bond theory. Thus it may be worth studying these representations and their interrelations from the outset.

Since the labelling of equivalent particles and the choice of principal axis frames are arbitrary, the essential aim must be the definition and calculation of symmetry coefficients being invariant to the relabelling of particles and to the transformation of axes. As shown in [5], this is achieved by generalizing the theorem of Wigner and Eckart [6], and the factorization lemma of Racah [7], to the polycentric case. The present paper is a generalization of the ideas outlined in [5].

For the sake of simplicity, the general theory is demonstrated by the small symmetry group C_{4v} acting only in the plane. The extensive results for the frequent symmetry groups T_d and O_h will be published later.

2. The symmetry group

Louck and Galbraith [1] have defined the equivalence of particles in advance of the symmetry group by two criteria: (a) the identity of particles in a certain sense and (b) the existence of a rotation-inversion operator $g \in O(3)$ such that $g\boldsymbol{R}_1 = \boldsymbol{R}_2$. This definition would make the two hydrogen atoms in the molecule $CH_2{=}CFCl$ equivalent. So we have to restrict the operators and prefer to define the symmetry group of a molecule first. Having declared the identity of particles in a certain sense (taking into account mass, charge etc.), we define the symmetry group G as that subgroup of O(3) the elements of which map only identical particles onto each other.

We parametrize the rotation-inversion operators $g \in G$ by a unit vector $\boldsymbol{n}$ pointing in the direction of the rotation axis, by the rotation angle ϕ (in right-handed sense) and by a parity factor p distinguishing the pure rotations ($p = +1$) from the rotary inversions ($p = -1$). The action of g on an arbitrary vector $\boldsymbol{R}$ is given by:

$$g\boldsymbol{R} = p \cdot [\cos\phi \cdot \boldsymbol{R} + (1 - \cos\phi) \cdot (\boldsymbol{n} \cdot \boldsymbol{R}) \cdot \boldsymbol{n} + \sin\phi \cdot (\boldsymbol{n} \times \boldsymbol{R})]. \tag{2.1}$$

The representation of g by a unitary operator $U(g)$ acting on functions is then given by:

$$U(g) f(\boldsymbol{R}) = f(g^{-1}\boldsymbol{R}). \tag{2.2}$$

The inverse operator g^{-1} in this definition guarantees the product relation $U(gg') = U(g)U(g')$, i.e.

$$U(g)U(g')f(\boldsymbol{R}) = U(g)f(g'^{-1}\boldsymbol{R}) = f(g'^{-1}g^{-1}\boldsymbol{R}) = f((gg')^{-1}\boldsymbol{R}) = U(gg')f(\boldsymbol{R}). \tag{2.3}$$

The principal axis frame to which the components of the vector $\boldsymbol{n}$ refer is fixed, once and for all time and for all atomic positions, to the Eckart frame at the centre of mass [1]. This assures the same meaning of the indices of representa-

tion matrices, Clebsch-Gordan coefficients, orbitals, and symmetry-adaption coefficients in all cases, without any recourse to local axis frames.

For the purpose of reference we compile the properties of the point group C_{4v} beginning with the elements and their parameters. In the last columns we add the conjugate class C to which they belong and the effect on the coordinates x and y.

For the decomposition of reducible representations we need the characters of the irreducible representations. Since the representation matrices an $3jm$ symbols refer to certain basis functions we add them here.

For several calculations the full representation matrices are needed. Table 2.3 refers to the basis of Table 2.2.

Table 2.1. The elements of the group C_{4v}

g	n_x	n_y	n_z	ϕ	p	C	x	y
1	0	0	1	0°	1	E	x	y
2	0	0	1	90°	1	C_4	$-y$	x
3	0	0	1	−90°	1	C_4	y	$-x$
4	0	0	1	180°	1	C_2	$-x$	$-y$
5	1	0	0	180°	−1	σ_v	$-x$	y
6	0	1	0	180°	−1	σ_v	x	$-y$
7	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	180°	−1	σ_d	$-y$	$-x$
8	$1/\sqrt{2}$	$1/\sqrt{2}$	0	180°	−1	σ_d	y	x

Table 2.2. The characters $\chi^a(C)$ and bases of the irreducible representations of C_{4v}

a	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Basis $\|a\ p\rangle$
A_1	1	1	1	1	1	$\|A_1 1\rangle = 1$
A_2	1	1	1	−1	−1	$\|A_2 1\rangle = xy(x^2-y^2)$
B_1	1	−1	1	1	−1	$\|B_1 1\rangle = x^2-y^2$
B_2	1	−1	1	−1	1	$\|B_2 1\rangle = xy$
E	2	0	−2	0	0	$\|E1\rangle = x, \|E2\rangle = y$

Table 2.3. The matrices $D^E_{ik}(g_j)$ of representation E

ik	g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8
11	1	0	0	−1	−1	1	0	0
12	0	−1	1	0	0	0	−1	1
21	0	1	−1	0	0	0	−1	1
22	1	0	0	−1	1	−1	0	0

Table 2.4. $3j$ and $3jm$ symbols of C_{4v}

$a\ b\ c$	$\{abc\}$	klm	$3jm$
$A_1A_1A_1$	1	111	1
$A_1A_2A_2$	1	111	1
$A_1B_1B_1$	1	111	1
$A_2B_1B_2$	−1	111	1
$A_1B_2B_2$	1	111	1
A_1EE	1	111	$1/\sqrt{2}$
		122	$1/\sqrt{2}$
A_2EE	−1	112	$1/\sqrt{2}$
B_1EE	1	111	$-1/\sqrt{2}$
		122	$1/\sqrt{2}$
B_2EE	1	112	$1/\sqrt{2}$

The $3jm$ symbols of a group may be calculated as the eigenvectors of the projection operator $P_{iln,kmp} = \text{ord}\, G^{-1} \sum_{g \in G} D^a_{ik}(g) D^b_{lm}(g) D^c_{np}(g)$:

$$\sum_{iln} P_{iln,kmp} \begin{pmatrix} abc \\ iln \end{pmatrix}^{\varepsilon} = \begin{pmatrix} abc \\ kmp \end{pmatrix}^{\varepsilon} \tag{2.4}$$

$$P_{iln,kmp} = \sum_{\varepsilon} \begin{pmatrix} abc \\ iln \end{pmatrix}^{\varepsilon} \cdot \begin{pmatrix} abc \\ kmp \end{pmatrix}^{\varepsilon}. \tag{2.5}$$

The latter equation will later serve as a model for the calculation of other types of coefficients. Since the solution of these equations at least involves an arbitrary choice of phases, we list the non-zero $3jm$ symbols and the permutation phases $\{abc\}$ for the group C_{4v}.

3. Equivalence classes

We now can define the equivalence of particles with respect to the symmetry group G. The particle A_i is equivalent to A_k, if (a) the particles are identical in the afore-mentioned sense and (b) there is at least one rotation-inversion operator $g \in G(!)$ such that

$$g\boldsymbol{A}_j = \boldsymbol{A}_k. \tag{3.1}$$

In this way all particles of a molecule or cluster are divided into disjoint equivalent sets. Because (3.1) is an equivalence relation in the mathematical sense, Louck and Galbraith call the equivalent sets equivalence classes. We prefer to use the latter term in a more general and abstract sense utilizing the following two observations. First, the benzene molecule C_6H_6 tells us that different sets of equivalent particles may be isomorphic in the sense that, by an appropriate labelling, $g\boldsymbol{C}_i = \boldsymbol{C}_k$ implies $g\boldsymbol{H}_i = \boldsymbol{H}_k$ and vice versa. On the other hand, equivalent sites may not be occupied at all. As an example one may compare the tetrahedral molecules P_4 and P_4O_6.

Obviously the site groups which leave invariant the different positions are the main issue. They are defined by:

$$H(A_i) = \{h \in G \text{ with } h\boldsymbol{A}_i = \boldsymbol{A}_i\}. \tag{3.2}$$

Since the site groups are subgroups of G, the number of equivalent sites or the dimension of the equivalence class is given by:

$$\dim A = \text{ord } G/\text{ord } H(A_i) \tag{3.3}$$

Within an equivalent set A the site groups $H(A_i)$ are isomorphic to each other. If $g\boldsymbol{A}_i = \boldsymbol{A}_k$ and $h \in H(A_i)$ then the relation

$$ghg^{-1}\boldsymbol{A}_k = gh\boldsymbol{A}_i = g\boldsymbol{A}_i = \boldsymbol{A}_k \tag{3.4}$$

proves that the isomorphic subgroup

$$H(A_k) = H(g\boldsymbol{A}_i) = gH(A_i)g^{-1} = \{ghg^{-1} \text{ with } h \in H(A_i)\} \tag{3.5}$$

is the site group of $\boldsymbol{A}_k$. Hence we define an equivalence class of a symmetry group G to be a set of site groups (isomorphic subgroups of G) related by the equivalence relation (3.5). The concrete equivalent sets are different realizations of the same equivalence class.

Note that the site groups may share only one, several, or even all elements. The latter case occurs for opposite positions because the inversion operator interchanges with all elements:

$$\boldsymbol{A}_i = -\boldsymbol{A}_k = i\boldsymbol{A}_k, \quad \text{i.e. } H(\boldsymbol{A}_i) = iH(\boldsymbol{A}_k)i = H(\boldsymbol{A}_k). \tag{3.6}$$

Since relation (3.5) also maps the conjugate classes of the group into themselves, the isomorphism of the site groups implies that the equivalent particles lie on equivalent symmetry elements, such as equivalent rotation axes or reflection planes, including for the moment the entire R_3 as a symmetry element of the identity operator.

This general concept of equivalence classes covers more complex entities than particles and their positions. The edges and triangular faces of the molecular skeleton which connect the atomic positions form equivalent sets too. In order to be precise we define the edges, triangular faces, pseudo-tetrahedra etc. as ordered (!) pairs, triples, quadruples etc. of the atomic positions. As a degenerate case one position may occur repeatedly in these pairs, triples etc. ("null edges" etc.). Consequently two edges (triangles etc.) are equivalent; if there is one operator of G mapping the first pair (triple etc.) onto the second in the same order, i.e. if $S_i = (A_1, B_m)$ and $S_k = (A_r, B_s)$ then

$$gS_i = S_k \quad \text{implies } g\boldsymbol{A}_l = \boldsymbol{A}_r \quad \text{and} \quad g\boldsymbol{B}_m = \boldsymbol{B}_s. \tag{3.7}$$

Table 3.1. The equivalence classes of C_{4v}

Class	Dim	Site group	Symmetry el.	First position
O	1	C_{4v}	all	$O_1 = (0, 0, 0)$
A	4	C_s	E, σ_v	$A_1 = (1, 0, 0)$
B	4	C_s	E, σ_d	$B_1 = (1, 1, 0)$
C	8	C_1	E	$C_1 = (1, 2, 0)$

Table 3.2. The full classes A, B, and C

Member	Position	Gen. el.	Member	Position	Gen. el.
A_1	1, 0, 0	g_1	C_1	1, 2, 0	g_1
A_2	0, 1, 0	g_2	C_2	−2, 1, 0	g_2
A_3	0, −1, 0	g_3	C_3	2, −1, 0	g_3
A_4	−1, 0, 0	g_4	C_4	−1, −2, 0	g_4
B_1	1, 1, 0	g_1	C_5	−1, 2, 0	g_5
B_2	−1, 1, 0	g_2	C_6	1, −2, 0	g_6
B_3	1, −1, 0	g_3	C_7	−2, −1, 0	g_7
B_4	−1, −1, 0	g_4	C_8	2, 1, 0	g_8

Thus the edges, triangles, pseudo-tetrahedra etc. constitute further realizations of the same equivalence classes. Of course, the labels of these new entities should coincide with the label of the site group leaving invariant the entire ordered pair or triple etc. This rule of labelling stresses topological correlations, which will be discussed in Sect. 5.

As for the group C_{4v}, there are four equivalence classes termed O, A, B, and C. Table 3.1 contains a list of these classes with their dimension, the name of their site groups, and the invariant symmetry elements, an exemplary position vector being labelled as number one.

Further members of the classes are generated by applying certain elements of G to the first member, for instance $A_3 = g_3 A_1$. These further members and their generating elements are given in the Table 3.2. Of course, the choice of the generating elements is not unique. We proceed as follows. The group elements of Table 1.1 are applied to A_1, for instance, one after another. If $g_i A_1$ is a new position, it is given the next index and g_i is taken as its generating element. This is summarized in Table 3.2.

The coincidence of the indices of A_i, B_i and g_i is due to the simplicity of group C_{4v} and not valid in general, except for the classes with the site group C_1, i.e. in the present case class C.

4. Permutation representations

Each equivalence class, or its realization by an equivalent set, induces a representation of the symmetry group G. This is brought out by writing Eq. (3.1) in

a different way. We first introduce a set of matrices $\sigma^A(g)$ belonging to class A by

$$\sigma^A_{ki}(g) = \begin{cases} 1 & \text{if } g\boldsymbol{A}_i = \boldsymbol{A}_k \\ 0 & \text{otherwise.} \end{cases} \tag{4.1}$$

Using this definition Eq. (3.1) reads:

$$g\boldsymbol{A}_i = \sum_l \sigma^A_{li}(g) \cdot \boldsymbol{A}_l. \tag{4.2}$$

Applying a second operator g' demonstrates the product property:

$$g'g\boldsymbol{A}_i = \sum_l \sigma^A_{li}(g) \cdot g'\boldsymbol{A}_l = \sum_{lm} \sigma^A_{li}(g) \cdot \sigma^A_{ml}(g') \cdot \boldsymbol{A}_m.$$

In addition $g'g\boldsymbol{A}_i = \sum_m \sigma^A_{mi}(g'g) \cdot \boldsymbol{A}_m$, so we finally have:

$$\sigma^A_{mi}(g'g) = \sum_l \sigma^A_{ml}(g') \cdot \sigma^A_{li}(g). \tag{4.3}$$

Because of the definition (4.1) the matrices have zero elements except for one unit per row and per column. In this way they represent certain, but not all, permutations of the members of the equivalent set. Therefore, we term them permutation representations of group G. The characters of these representations,

$$\sigma^A(g) = \sum_i \sigma^A_{ii}(g), \tag{4.4}$$

have a simple meaning. They are equal to the number of members of an equivalent set, which are not affected by the operator g.

The permutation representations are decomposed to the irreducible representations of the group in the usual way. The branching rules are calculated by the well-known character formula

$$n(a, A) = \text{ord } G^{-1} \sum_C \lambda(C) \chi^a(C)^* \sigma^A(C). \tag{4.5}$$

We note that the identity representation always occurs once. In addition $n(a, A) \leq \dim a$. The proof of this inequality follows from consideration of Eq. (4.1). $\sigma^A_{ii}(g) = 1$ holds only if the element g belongs to the site group $H(A_i)$. Therefore, the sum for all group elements $\sum_g \sigma^A_{ii}(g)$ is equal to the order of this site group. This order does not depend on the index i. Summing with respect to i then yields the sum of characters $\sum_g \sigma^A(g) = \text{ord } G$. This result is equivalent to

$$n(A_1, A) = \text{ord } G^{-1} \sum_C \lambda(C) \sigma^A(C) = 1. \tag{4.5a}$$

Because of the inequality $|\chi^a(C)| \leq \dim a$ we now can deduce from Eq. (4.5) the required inequality: $n(a, A) \leq \text{ord } G^{-1} \sum_C \lambda(C) \sigma^A(C) \cdot \dim a = \dim a$. In Table 4.1 we list the characters and the branching rules of the permutation representations of group C_{4v}.

Table 4.1. The characters $\sigma^X(C)$ of the permutation representations of C_{4v}

Eq. class X	E	$2C_4$	C_2	$2\sigma_d$	$2\sigma_v$
O	1	1	1	1	1
A	4	0	0	0	2
B	4	0	0	2	0
C	8	0	0	0	0

Table 4.2. The branching rules $n(a, X)$ of C_{4v}

Eq. class X	A_1	A_2	B_1	B_2	E
O	1	0	0	0	0
A	1	0	1	0	1
B	1	0	0	1	1
C	1	1	1	1	2

Table 4.3. SALC coefficients of type $(\mathrm{Ai}\,|\,A\alpha ap)$

αap	$A1$	$A2$	$A3$	$A4$
$1A_11$	1/2	1/2	1/2	1/2
$1B_11$	1/2	−1/2	−1/2	1/2
$1E\_1$	$1/\sqrt{2}$	0	0	$-1/\sqrt{2}$
$1E\_2$	0	$1/\sqrt{2}$	$-1/\sqrt{2}$	0

Table 4.4. SALC coefficients of type $(Bi\,|\,B\alpha ap)$

αap	$B1$	$B2$	$B3$	$B4$
$1A_11$	1/2	1/2	1/2	1/2
$1B_21$	1/2	−1/2	−1/2	1/2
$1E\_1$	1/2	−1/2	1/2	−1/2
$1E\_2$	1/2	1/2	−1/2	−1/2

The unitary matrix decomposing the permutation matrices of σ^A is written as $(A_i\,|\,A\alpha ap)$, where α indicates the repeated representations a occurring in σ^A $(1 \leq \alpha \leq n(a, A))$:

$$\sum_{ik} (A\alpha ap\,|\,A_i)\sigma^A_{ik}(g)(A_k\,|\,A\beta bq) = \delta(\alpha, \beta)\delta(a, b)D^a_{pq}(g) \tag{4.6}$$

The matrix elements $(A_i\,|\,A\alpha ap)$ play the essential role in setting up symmetry-adapted linear combinations (SALCs). The symmetry-adapted molecular orbitals basing on atomic s-orbitals, for instance, are given by:

$$|A\alpha ap\rangle = \sum_k (A_k\,|\,A\alpha ap) \cdot |sAk\rangle, \tag{4.7}$$

with the orbitals $s(\boldsymbol{r} - \boldsymbol{A}_k) = \langle \boldsymbol{r}\,|\,sAk\rangle$.

Therefore, the matrix elements $(A_k\,|\,A\alpha ap)$ are termed SALC coefficients. In [4, 5] the details concerning the orthogonality and the calculation of the coefficients have been worked out. Another way of calculating is inspired by Eq. (2.5). Since the SALC coefficients are the eigenvectors of the projection operator $P_{pi,qk} = \mathrm{ord}\, G^{-1} \sum_{g \in G} D^a_{pq}(g)\sigma^A_{ik}(g)$, the relation analogous to (2.5) reads:

$$P_{pi,qk} = \sum_\alpha (A_i\,|\,A\alpha aq)(A\alpha ap\,|\,A_k). \tag{4.8}$$

Again the coefficients are not fixed uniquely and may be redefined by a unitary transformation:

$$(A_i\,|\,A\alpha ap)' = \sum_\beta U^{Aa}_{\alpha\beta} \cdot (A_i\,|\,A\beta ap). \tag{4.9}$$

Table 4.5. SALC coefficients of type $(Ci|C\alpha ap)$

αap	$C1$	$C2$	$C3$	$C4$	$C5$	$C6$	$C7$	$C8$
$1A_1 1$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$
$1A_2 1$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$
$1B_1 1$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$
$1B_2 1$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$1/\sqrt{8}$	$1/\sqrt{8}$
$1E\_1$	$1/2$	0	0	$-1/2$	$-1/2$	$1/2$	0	0
$1E\_2$	0	$1/2$	$-1/2$	0	0	0	$-1/2$	$1/2$
$2E\_1$	0	$-1/2$	$1/2$	0	0	0	$-1/2$	$1/2$
$2E\_2$	$1/2$	0	0	$-1/2$	$1/2$	$-1/2$	0	0

This transformation can be utilized to impose certain conditions on the SALC coefficients, especially some zeros. In the case $n(a, A) = 2$ we put $(A_1|A2a1) = 0$ and if $n(a, A) = 3$ we further require $(A_1|A3a1) = (A_1|A3a2) = 0$. The orthogonality relations then produce further zeros. For $n(a, A) = \dim a$ we thus get in general $(A_1|A\alpha ap) = \delta(\alpha, p) \cdot (A_1|Apap)$. The main advantage of this transformation is a considerable simplification of the higher coefficients to be defined in Sect.7, which now, in contrast to [5], can all be expressed by $\sqrt{m}/n$ with integer m and n. In Tables 4.3–4.5 we compile the SALC coefficients of the group C_{4v}. For the class O we have in general $(O_1|O1A_1 1) = 1$.

5. Topological correlations

Having found the equivalence classes of a symmetry group all objects in a molecule, i.e. positions or atoms, edges or bonds, faces etc., are related to these classes via their site group. The latter offer an adequate numbering of these objects. The topological correspondences of different objects sharing a site group have already been mentioned in connection with Eq. (3.7). They are represented by topological matrices τ.

Let us think of two atoms A_i and B_k with the site groups $H(A_i)$ and $H(B_k)$ respectively. The atoms may belong to the same class $(A = B)$ so $H(A_i) \sim H(B_k)$ or even may be identical $(A_i = B_k)$ so $H(A_i) = H(B_k)$. The edge connecting the ordered (!) pair (A_i, B_k) has the site group $H(A_i) \cap H(B_k)$. If the equivalence classes found in Sect. 4 are complete, this site group must belong to an equivalence class C, for instance. C may be equal to A or B or to both. If the label of the relevant site group in class C is l, we have:

$$H(A_i) \cap H(B_k) = H(C_l). \tag{5.1}$$

In the case of C_{4v} the indices refer to Table 3.2. We thus get an assignment of the pair (A_i, B_k) to the vector C_l sharing the site group:

$$(A_i, B_k) \to C_l. \tag{5.2}$$

The validity or non-validity of Eqs. (5.1)–(5.2) for three arbitrary vectors will be fixed by a topological matrix belonging to the triple ABC. The first idea is to put $\tau\binom{ABC}{ikl}=1$, if (5.1)–(5.2) hold, and zero otherwise. For reasons of normalization we shall take $1/\sqrt{\dim C}$ instead of 1. From (3.5) and (5.1) we derive:

$$H(gA_i)\cap H(gB_k)=gH(A_i)g^{-1}\cap gH(B_k)g^{-1}=g(H(A_i)\cap H(B_k))g^{-1}$$
$$=H(gC_l) \tag{5.3}$$

or in shortened notation with $g\boldsymbol{A}_i=\boldsymbol{A}_{gi}$ etc.:

$$\tau\begin{pmatrix}ABC\\ikl\end{pmatrix}=\tau\begin{pmatrix}A & B & C\\gi & gk & gl\end{pmatrix} \tag{5.4}$$

These equations express the congruence of the geometric figures being composed of the three vectors $\boldsymbol{A}_i$, $\boldsymbol{B}_k$, $\boldsymbol{C}_l$ and $\boldsymbol{A}_{gi}$, $\boldsymbol{B}_{gk}$, $\boldsymbol{C}_{gl}$ respectively.

Non-equivalent correlations, i.e. non-congruent geometric figures, often occur within the same triple ABC. Several correlations must then be distinguished by a multiplicity index. A triple ABC together with the number of the concrete correlation will be termed a triad, $ABCm$ for instance. In the case of the group C_{4v} there are two triads $AAA1$ and $AAA2$ with the correlations $H(A_1)\cap H(A_1)=H(A_1)$ or $(A_1, A_1)\to A_1$ and $H(A_1)\cap H(A_4)=H(A_1)$ or $(A_1, A_4)\to A_1$ (cf. Table 3.2). Since congruent geometric figures contain the same distances, these distances may be used to distinguish the different triads: $D(ABCm)=|\boldsymbol{A}_i-\boldsymbol{B}_k|$. The two triads above yield $D(AAA1)=0$ and $D(AAA2)=2$.

Taking into account the multiplicity of correlations, we are led to the following definition of the topological matrix belonging to the triad $ABCm$:

$$\tau\begin{pmatrix}ABC\\ikl\end{pmatrix}^m=\begin{cases}1/\sqrt{\dim C}\\ \quad \text{if } H(A_i)\cap H(B_k)=H(C_l) \text{ and } |\boldsymbol{A}_i-\boldsymbol{B}_k|=D(ABCm)\\ 0\quad \text{otherwise.}\end{cases} \tag{5.5}$$

Because of (5.3) and the invariance of the distances $D(ABCm)$, the matrix elements referring to one triad $ABCm$ are again related by:

$$\tau\begin{pmatrix}ABC\\ikl\end{pmatrix}^m=\tau\begin{pmatrix}A & B & C\\gi & gk & gl\end{pmatrix}^m. \tag{5.6}$$

The normalization is such that

$$\sum_{ikl}\left|\tau\begin{pmatrix}ABC\\ikl\end{pmatrix}^m\right|^2=1 \tag{5.7}$$

The orthogonality relations of the topological matrices elaborated in Eqs. (6.2 and 3) of [5] can now be re-expressed:

$$\sum_{ik}\tau\begin{pmatrix}ABC\\ikl\end{pmatrix}^m\tau\begin{pmatrix}ABD\\ikp\end{pmatrix}^n=\delta(C,D)\delta(m,n)\delta(l,p)/\dim C \tag{5.8}$$

$$\sum_{Clm} \tau\begin{pmatrix} ABC \\ ikl \end{pmatrix}^m \tau\begin{pmatrix} ABC \\ rsl \end{pmatrix}^m \dim C = \delta(i, r)\delta(k, s) \tag{5.9}$$

The normalization (5.7) is a special case of (5.8).

It is very laborious to find all of the correlation triads of a symmetry group by checking all the positional combinations A_i, B_k, C_l. In order to create a new triad by A_i, B_k, C_l Eq. (5.1) must hold, but the vectors must not be related to a prior combination by the relation (5.6). We therefore postpone the problem until we have learned to calculate the multiplicities of the triads directly.

In connection with Eq. (3.7) we also mentioned triangular faces and pseudo-tetrahedra, which are described by ordered triples and quadruples. In the case of the triangles the relations analogous to (5.1)–(5.2) read:

$$H(A_i) \cap H(B_k) \cap H(C_l) = H(D_m) \quad \text{or} \quad (A_i, B_k, C_l) \to D_m. \tag{5.10}$$

Again we need a multiplicity index in order to distinguish the inequivalent correlations between the triple ABC and the class D. The definition (5.5) is then replaced by:

$$\tau\begin{pmatrix} ABCD \\ iklm \end{pmatrix}^n = \begin{cases} 1/\sqrt{\dim D} & \text{if (5.10) holds and } ikl \text{ belongs to } n \\ 0 & \text{otherwise.} \end{cases} \tag{5.11}$$

These more complex correlations can be reduced to the prior ones by proceeding step by step. In a first step two of the three vertices, A_i and B_k for instance, are assigned to their connecting edge of equivalence class E, number r. In the second step the edge E_r and its opposite vertex C_l are assigned to the triangle D_m. The multiplicity index n is then given by the intermediate class E and the multiplicities of the triads $ABEp$ and $ECDq$. In this way the topological matrix (5.11) is decomposed to:

$$\tau\begin{pmatrix} ABCD \\ iklm \end{pmatrix}^n = \sum_r \tau\begin{pmatrix} ABE \\ ikr \end{pmatrix}^p \tau\begin{pmatrix} ECD \\ rlm \end{pmatrix}^q \sqrt{\dim E} \quad \text{with } n = (Epq). \tag{5.12}$$

It is, of course, possible to start with the pair AC or BC instead of AB, thus giving rise to different coupling schemes, cf. Eq. (7.17), of [5]. These topological matrices and their decomposition resemble the $4jm$ symbols of the theory of angular momentum. This allusion will become clearer in the next section. In the same way the pseudo-tetrahedra involved by the four-centre integrals of MO theory are decomposed by introducing two intermediate edges, cf Eq. (10.10) of [5].

As in all cases involving a multiplicity, the numbering of the triads is arbitrary. In the case of C_{4v} we can interchange, for instance, the triads $AAA1$ and $AAA2$ by setting $D(AAA1) = 2$ and $D(AAA2) = 0$. This also interchanges all the matrices defined by (5.5) and (5.6). Moreover, any unitary transformation of the topological

matrices, i.e.

$$\tau'\begin{pmatrix} ABC \\ ikl \end{pmatrix}^m = \sum_n u_{nm}^{ABC} \cdot \tau\begin{pmatrix} ABC \\ ikl \end{pmatrix}^n, \tag{5.13}$$

will not alter the essential relations (5.6)-(5.9).

6. Product representations

As for any representations there is a direct product of two permutation representations

$$\sigma^A \times \sigma^B = \sigma^{A\times B}, \tag{6.1}$$

the matrix elements of which are given by:

$$\sigma_{ik,lm}^{A\times B}(g) = \sigma_{il}^{A}(g) \cdot \sigma_{km}^{B}(g). \tag{6.2}$$

Obviously the product yields permutation matrices too. The characters are given by:

$$\sigma^{A\times B}(g) = \sigma^{A}(g) \cdot \sigma^{B}(g). \tag{6.3}$$

As is well known, the direct product of irreducible representations is uniquely decomposable into irreducible representations. Although the permutation representations are reducible in general, their products are likewise uniquely decomposable to the basic permutation representations again. In this respect they resemble the irreducible representations of a group $H \supset G$ taken as reducible representations of the subgroup G. This analogy leads to useful concepts in what follows.

The first step is the determination of the branching rules

$$\sigma^{A\times B} = \sum_C n(A\times B, C)\sigma^C. \tag{6.4}$$

Because the involved representations are reducible, the multiplicities cannot be calculated by character formulae. However, there are, of course, the sum rules

$$\sigma^{A\times B}(K) = \sum_C n(A\times B, C) \cdot \sigma^C(K) \tag{6.5}$$

for each class of the group. These sum rules have unique solutions for all point groups.

Preparatory to the proof, we point out a necessary property of the solution. Denoting the equivalence class of the centre of symmetry by O, the permutational representation σ^0 has all characters equal to one. All other permutational representations have some zero characters. Taking this into account, we conclude from (6.5):

$$n(O\times O, O) = 1 \quad \text{and otherwise } n(A\times B, O) = 0. \tag{6.6}$$

This means that σ^0 occurs only once in all the direct products. This observation is helpful in some critical cases, the exceptional groups discussed below.

Now beginning the proof, we turn from (6.5) to another system of conditional equations. We multiply by $\sigma^D(K) \cdot \lambda(K)/\text{ord } G$ and take the sum for all classes of the group. Introducing the matrix

$$M(C, D) = \text{ord } G^{-1} \sum_K \lambda(K)\sigma^C(K)\sigma^D(K) \tag{6.7}$$

and the expression

$$L(A, B, D) = \text{ord } G^{-1} \sum_K \lambda(K)\sigma^A(K)\sigma^B(K)\sigma^D(K), \tag{6.8}$$

we get the system of equations:

$$\sum_C M(C, D) \cdot n(A \times B, C) = L(A, B, D). \tag{6.9}$$

For each pair $A \times B$ this system contains as many equations as unknowns $n(A \times B, C)$. The system has unique solutions if the coefficient determinant does not vanish, i.e. if

$$\det |M(C, E)| \neq 0. \tag{6.10}$$

It has been checked that this sufficient condition is met by all the following point groups: C_n, C_{nh}, C_{nv}, S_{2n}, D_{nh}, D_{nd}, T_d, T_h, O_h, and I_h. In these cases we express the solution by the inverted matrix:

$$n(A \times B, C) = \sum_D M^{-1}(D, C) \cdot L(A, B, D). \tag{6.11}$$

However, there are some groups, i.e. D_n, T, O, and I with $\det M = 0$. These require a more detailed inspection. Since the explication of the permutational character tables and branching rules of all these groups would go beyond the scope of this study, only the main points are summarized. Because of $\det M = 0$, there is one and, as it turns out, only one eigenvector of M with an eigenvalue equal to zero. This implies a linear relation within the character table:

$$\sum_C m(C)\sigma^C(K) = 0. \tag{6.12}$$

The component of the eigenvector $m(C)$ belonging to the equivalence class of the centre of symmetry is always equal to two: $m(0) = 2$. Because of (6.12), the right-hand side of Eq. (6.9) is orthogonal to this eigenvector $m(C)$. Therefore, solutions exist in this case. If now $n'(A \times B, C)$ is a formal solution of (6.9), there are further solutions $n(A \times B, C) = n'(A \times B, C) + \alpha \cdot m(C)$. The factor α is fixed by the conditions (6.6):

$$1 = n'(O \times O, O) + \alpha^{O \times O} \cdot m(O), \qquad 0 = n'(A \times B, O) + \alpha^{A \times B} \cdot m(O)$$

So no ambiguity remains. Further, only the factors α fixed in this way produce non-negative and integer multiplicities. Summing up, the branching rules (6.4) are not affected by the relations (6.12), because the former involve σ^0 once, at most, but the latter always twice.

As usual, the product representations are decomposed by unitary transformations. These are directly related to the topological matrices of the last section; more precisely, the topological matrices play the role of Wigner's $3jm$ symbols. In order to prove this, we write (5.6) more explicitly:

$$\tau\begin{pmatrix} ABC \\ ikl \end{pmatrix}^m = \sum_{rst} \sigma^A_{ri}(g)\sigma^B_{sk}(g)\sigma^C_{tl}(g)\tau\begin{pmatrix} ABC \\ rst \end{pmatrix}^m. \tag{6.13}$$

Taking the sum over all elements of the group shows that the topological matrices are eigenvectors of the projection operator

$$P_{rst,ikl} = \text{ord } G^{-1} \sum_{gG} \sigma^A_{ri}(g)\sigma^B_{sk}(g)\sigma^C_{tl}(g). \tag{6.14}$$

Comparing now

$$\sum_{rst} P_{rst,ikl}\tau\begin{pmatrix} ABC \\ rst \end{pmatrix}^m = \tau\begin{pmatrix} ABC \\ ikl \end{pmatrix}^m. \tag{6.15}$$

with (2.4) proves the statement. In contrast to (2.4) the topological matrices are not the only solutions of Eq. (6.15). Therefore the analogue of (2.5) or of (4.8) does not hold. The decomposition of $\sigma^{A\times B}$ is shown by rearranging (6.13) using the orthogonality relations:

$$\sum_{rsik} \tau\begin{pmatrix} ABD \\ ikt \end{pmatrix}^n \sigma^A_{ri}(g)\sigma^B_{sk}(g)\tau\begin{pmatrix} ABC \\ rsp \end{pmatrix}^m \dim C = \delta(D,C)\delta(n,m)\sigma^C_{tp}(g). \tag{6.16}$$

Of course, it is possible to introduce a Clebsch-Gordan-like coefficient for the permutation representations:

$$(A_n, B_p \,|\, ABmCq) = \tau\begin{pmatrix} ABC \\ npq \end{pmatrix}^m \cdot \sqrt{\dim C}.$$

Since our example, the group C_{4v}, does not belong to the exceptional groups, we can proceed in a straightforward manner. The matrix defined by (6.6) reads

$$M = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 3 & 2 & 4 \\ 1 & 2 & 3 & 4 \\ 1 & 4 & 4 & 8 \end{pmatrix}$$

with $\det M = 3$. From this it follows that:

$$M^{-1} = \frac{1}{3} \cdot \begin{pmatrix} 8 & -4 & -4 & 3 \\ -4 & 5 & 2 & -3 \\ -4 & 2 & 5 & -3 \\ 3 & -3 & -3 & 3 \end{pmatrix}.$$

In both cases the order of rows and columns is according to O, A, B, C. The branching rules are now found by calculating $L(A, B, D)$. Because of its symmetry

Table 6.1. Values of $L(X, Y, Z)$ according to (6.8)

X	$YZ = AA$	AB	AC	BB	BC	CC
A	10	8	16	8	16	32
B				10	16	32
C						64

Table 6.2. The permutational branching rules of C_{4v}

	σ^O	σ^A	σ^B	σ^C
σ^O	σ^O	σ^A	σ^B	σ^C
σ^A		$2\sigma^A + \sigma^C$	$2\sigma^C$	$4\sigma^C$
σ^B			$2\sigma^B + \sigma^C$	$4\sigma^C$
σ^C				$8\sigma^C$

and because $L(A, B, O) = M(A, B)$, there remains the evaluation of ten expressions given in Table 6.1.

Applying now (6.11) gives the branching rules of Table 6.2.

Having learnt the multiplicities of Table 6.2 we look for one positional triple A_i, B_k, C_l of each triad $ABCm$. The result of this investigation is compiled in Table 6.3. In the last column the value of the matrix element $\tau(^{ABC}_{ikl})^m$ is added.

The other triples of these triads follow from the first one by (5.7). In the case of $AAA2$, for instance, we get from $A_1A_4A_1$, or in short 141, the further triples 232, 323, and 414. In the case of $AAC1$ from 121 follow 242, 313, 434, 425, 126, 347, and 218. The common feature of the triples belonging to a triad is that the three vectors subtend the same geometrical figure except for the different orientation in space. The site group of the geometrical figure is given by the first two vectors jointly, as well as by the third one separately.

Referring to site groups instead of concrete positions or geometrical figures, we have reached a point of view superior to that of [5, 8] in several aspects:

(a) In [8] we used the distance vectors $\boldsymbol{A}_i - \boldsymbol{B}_k$ instead of the ordered pairs (A_i, B_k). This made it somewhat artificial to distinguish between (A_i, B_k) and (B_k, A_i) or between (A_i, A_i) and (A_k, A_k) as in [5]. For general correlations or two-point functions this distinction makes sense.

(b) Since the distance vectors $\boldsymbol{A}_i - \boldsymbol{B}_k$ belonging to different triads have different lengths, they were labelled by different symbols, in the case of C_{4v} for instance $O_1^A = \boldsymbol{A}_1 - \boldsymbol{A}_1$ and $\boldsymbol{T}_1^A = \boldsymbol{A}_1 - \boldsymbol{A}_4$. Although the isomorphism of the sets O^A and T^A was noticed, this notation led to the triples AAO^A and AAT^A instead of our triads $AAA1$ and $AAA2$, thus obscuring the multiple correlations between the very same equivalence classes.

(c) Finally, taking the triangular faces and the pseudo-tetrahedra as different objects, we had to describe their correlations with the atomic positions by different

Table 6.3. Topological matrix elements of group C_{4v}

triad		i	k	l	τ
OOO	1	1	1	1	1
OAA	1	1	1	1	1/2
OBB	1	1	1	1	1/2
OCC	1	1	1	1	$1/\sqrt{8}$
AAA	1	1	1	1	1/2
	2	1	4	1	1/2
AAC	1	1	2	1	$1/\sqrt{8}$
ABC	1	1	1	1	$1/\sqrt{8}$
	2	1	2	1	$1/\sqrt{8}$
ACC	1	1	1	1	$1/\sqrt{8}$
	2	1	2	1	$1/\sqrt{8}$
	3	1	3	1	$1/\sqrt{8}$
	4	1	4	1	$1/\sqrt{8}$
BBB	1	1	1	1	1/2
	2	1	4	1	1/2
BBC	1	1	2	1	$1/\sqrt{8}$
BCC	1	1	1	1	$1/\sqrt{8}$
	2	1	2	1	$1/\sqrt{8}$
	3	1	3	1	$1/\sqrt{8}$
	4	1	4	1	$1/\sqrt{8}$
CCC	1	1	1	1	$1/\sqrt{8}$
	2	1	2	1	$1/\sqrt{8}$
	3	1	3	1	$1/\sqrt{8}$
	4	1	4	1	$1/\sqrt{8}$
	5	1	5	1	$1/\sqrt{8}$
	6	1	6	1	$1/\sqrt{8}$
	7	1	7	1	$1/\sqrt{8}$
	8	1	8	1	$1/\sqrt{8}$

topological matrices of a so-called second and third kind. Regarding these geometrical figures as further realizations of the same equivalence classes makes this distinction obsolete. This unification of all kinds of topological matrices has been anticipated by the introduction of "generalized" topological matrices in Chap. 20 of [5]; the concept of equivalence classes of site groups brings out the facts much more clearly.

4. Polyhedral isoscalar factors

Following the analogy of the topological matrices to the $3jm$ symbols of reducible representations we transform the matrices to a symmetry-adapted basis. According to (4.6)–(4.7) we get:

$$\tau\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \\ npq \end{pmatrix}^m = \sum_{rst} \tau\begin{pmatrix} ABC \\ rst \end{pmatrix}^m (A_r \mid A\alpha an)(B_s \mid B\beta bp)(C_t \mid C\gamma cq). \tag{7.1}$$

Using now Racah's factorization lemma [7] we get

$$\tau\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \\ npq \end{pmatrix}^m = \sum_{\varepsilon} PIs\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^m_{\varepsilon} \cdot \begin{pmatrix} abc \\ npq \end{pmatrix}^{\varepsilon}. \tag{7.2}$$

This relation defines the "polyhedral isoscalar factors" or in short "polyhedral isoscalars". These factors are the central invariants of the group theory for polycentric systems. By equating the right-hand sides of (7.1) and (7.2) and rearranging the resulting equation we get the theorem

$$\sum_{rstnp} \tau\begin{pmatrix} ABC \\ rst \end{pmatrix}^m (A_r|A\alpha an)(B_s|B\beta bp)(C_t|C\gamma cq)\begin{pmatrix} abd \\ npk \end{pmatrix}^{\varepsilon}$$
$$= \delta(c, d)\delta(q, k) \dim c^{-1} \cdot PIs\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^m_{\varepsilon}. \tag{7.3}$$

Finally the calculation of the factors is done by:

$$PIs\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^m_{\varepsilon} = \sum_{rst}\sum_{npq} \tau\begin{pmatrix} ABC \\ rst \end{pmatrix}^m (A_r|A\alpha an)(B_s|B\beta bp)(C_t|C\gamma cq)\begin{pmatrix} abc \\ npq \end{pmatrix}^{\varepsilon}. \tag{7.4}$$

The polyhedral isoscalars obey the following orthogonality relations:

$$\sum_{\alpha a\beta b\varepsilon} PIs\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^m_{\varepsilon} PIs\begin{pmatrix} ABD \\ \alpha\beta\delta \\ abc \end{pmatrix}^n_{\varepsilon} = \delta(C, D)\delta(m, n)\delta(\gamma, \delta) \dim c/\dim C \tag{7.5}$$

$$\sum_{Cm\gamma} \dim C \cdot PIs\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^m_{\varepsilon} PIs\begin{pmatrix} ABC \\ \sigma\tau\gamma \\ stc \end{pmatrix}^m_{\eta}$$
$$= \delta(a, s)\delta(\alpha, \sigma)\delta(b, t)\delta(\beta, \tau)\delta(\varepsilon, \eta) \cdot \dim c. \tag{7.6}$$

Note that in both relations the factors must contain the same irreducible representation c, but there is no sum over c in either case. The relations (7.3)–(7.6) are quite analogous to those of the common isoscalars referring to group chains [5, 9].

As a consequence of the unification of the topological matrices the distinction of several kinds of polyhedral isoscalars in [5] becomes obsolete, too. The polyhedral isoscalars are group-theoretical invariants independent of the special choice of labellings and axis frames. Yet, as often in group theory, different corpora of coefficients may be created because of different choices of phases or because of unitary transformations in the case of multiplicities. The different

Table 7.1. Polyhedral isoscalars $PIs(OAAm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$
111	$A_1A_1A_1$	1/2
111	$A_1B_1B_1$	1/2
111	$A_1E\_E\_$	$1/\sqrt{2}$

Table 7.2. Polyhedral isoscalars $PIs(OBBm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$
111	$A_1A_1A_1$	1/2
111	$A_1B_2B_2$	1/2
111	$A_1E\_E\_$	$1/\sqrt{2}$

Table 7.3. Polyhedral isoscalars $PIs(OCCm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$
111	$A_1A_1A_1$	$1/\sqrt{8}$
111	$A_1A_2A_2$	$1/\sqrt{8}$
111	$A_1B_1B_1$	$1/\sqrt{8}$
111	$A_1B_2B_2$	$1/\sqrt{8}$
111	$A_1E\_E\_$	1/2
112	$A_1E\_E\_$	0
121	$A_1E\_E\_$	0
122	$A_1E\_E\_$	1/2

Table 7.4. Polyhedral isoscalars $PIs(AAAm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$	$m=2$
111	$A_1A_1A_1$	1/4	1/4
111	$A_1B_1B_1$	1/4	1/4
111	$A_1E\_E\_$	$1/\sqrt{8}$	$-1/\sqrt{8}$
111	$B_1A_1B_1$	1/4	1/4
111	$B_1B_1A_1$	1/4	1/4
111	$B_1E\_E\_$	$-1/\sqrt{8}$	$1/\sqrt{8}$
111	$E\_A_1E\_$	$1/\sqrt{8}$	$1/\sqrt{8}$
111	$E\_B_1E\_$	$-1/\sqrt{8}$	$-1/\sqrt{8}$
111	$E\_E\_A_1$	$1/\sqrt{8}$	$-1/\sqrt{8}$
111	$E\_E\_B_1$	$-1/\sqrt{8}$	$1/\sqrt{8}$

Table 7.5. Polyhedral isoscalars $PIs(BBBm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$	$m=2$
111	$A_1A_1A_1$	1/4	1/4
111	$A_1B_2B_2$	1/4	1/4
111	$A_1E\_E\_$	$1/\sqrt{8}$	$-1/\sqrt{8}$
111	$B_2A_1B_2$	1/4	1/4
111	$B_2B_2A_1$	1/4	1/4
111	$B_2E\_E\_$	$1/\sqrt{8}$	$-1/\sqrt{8}$
111	$E\_A_1E\_$	$1/\sqrt{8}$	$1/\sqrt{8}$
111	$E\_B_2E\_$	$1/\sqrt{8}$	$1/\sqrt{8}$
111	$E\_E\_A_1$	$1/\sqrt{8}$	$-1/\sqrt{8}$
111	$E\_E\_B_2$	$1/\sqrt{8}$	$-1/\sqrt{8}$

Table 7.6. Polyhedral isoscalars $PIs(AACm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$
111	$A_1A_1A_1$	1/4
111	$A_1B_1B_1$	−1/4
111	$A_1E\_E\_$	0
112	$A_1E\_E\_$	$1/\sqrt{8}$
111	$B_1A_1B_1$	1/4
111	$B_1B_1A_1$	−1/4
111	$B_1E\_E\_$	0
112	$B_1E\_E\_$	$1/\sqrt{8}$
111	$E\_A_1E\_$	$1/\sqrt{8}$
112	$E\_A_1E\_$	0
111	$E\_B_1E\_$	$1/\sqrt{8}$
112	$E\_B_1E\_$	0
111	$E\_E\_A_1$	0
111	$E\_E\_A_2$	$1/\sqrt{8}$
111	$E\_E\_B_1$	0
111	$E\_E\_B_2$	$1/\sqrt{8}$

Table 7.7. Polyhedral isoscalars $PIs(ABCm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$	$m=2$
111	$A_1A_1A_1$	1/4	1/4
111	$A_1B_2B_2$	1/4	−1/4
111	$A_1E\_E\_$	1/4	−1/4
112	$A_1E\_E\_$	1/4	1/4
111	$B_1A_1B_1$	1/4	1/4
111	$B_1B_2A_2$	1/4	−1/4
111	$B_1E\_E\_$	−1/4	1/4
112	$B_1E\_E\_$	1/4	1/4
111	$E\_A_1E\_$	$1/\sqrt{8}$	$1/\sqrt{8}$
112	$E\_A_1E\_$	0	0
111	$E\_B_2E\_$	0	0
112	$E\_B_2E\_$	$1/\sqrt{8}$	$-1/\sqrt{8}$
111	$E\_E\_A_1$	1/4	−1/4
111	$E\_E\_A_2$	1/4	1/4
111	$E\_E\_B_1$	−1/4	1/4
111	$E\_E\_B_2$	1/4	1/4

Table 7.8. Polyhedral isoscalars $PIs(BBCm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$
111	$A_1A_1A_1$	1/4
111	$A_1B_2B_2$	−1/4
111	$A_1E\_E\_$	−1/4
112	$A_1E\_E\_$	1/4
111	$B_2A_1B_2$	1/4
111	$B_2B_2A_1$	−1/4
111	$B_2E\_E\_$	1/4
112	$B_2E\_E\_$	−1/4
111	$E\_A_1E\_$	1/4
112	$E\_A_1E\_$	1/4
111	$E\_B_2E\_$	−1/4
112	$E\_B_2E\_$	−1/4
111	$E\_E\_A_1$	0
111	$E\_E\_A_2$	$1/\sqrt{8}$
111	$E\_E\_B_1$	$1/\sqrt{8}$
111	$E\_E\_B_2$	0

Table 7.9. Polyhedral isoscalars $PIs(ACCm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$	$m=2$	$m=3$	$m=4$
111	$A_1A_1A_1$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1A_2A_2$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1B_1B_1$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1B_2B_2$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1E_-E_-$	1/4	0	0	−1/4
112	$A_1E_-E_-$	0	1/4	−1/4	0
121	$A_1E_-E_-$	0	−1/4	1/4	0
122	$A_1E_-E_-$	1/4	0	0	−1/4
111	$B_1A_1B_1$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$B_1A_2B_2$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$
111	$B_1B_1A_1$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$B_1B_2A_2$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$B_1E_-E_-$	−1/4	0	0	1/4
112	$B_1E_-E_-$	0	1/4	−1/4	0
121	$B_1E_-E_-$	0	1/4	−1/4	0
122	$B_1E_-E_-$	1/4	0	0	−1/4
111	$E_-A_1E_-$	1/4	1/4	1/4	1/4
112	$E_-A_1E_-$	0	0	0	0
111	$E_-A_2E_-$	0	0	0	0
112	$E_-A_2E_-$	−1/4	−1/4	−1/4	−1/4
111	$E_-B_1E_-$	−1/4	1/4	1/4	−1/4
112	$E_-B_1E_-$	0	0	0	0
112	$E_-B_2E_-$	0	0	0	0
112	$E_-B_2E_-$	1/4	−1/4	−1/4	1/4
111	$E_-E_-A_1$	1/4	0	0	−1/4
121	$E_-E_-A_1$	0	−1/4	1/4	0
111	$E_-E_-A_2$	0	1/4	−1/4	0
121	$E_-E_-A_2$	1/4	0	0	−1/4
111	$E_-E_-B_1$	−1/4	0	0	1/4
121	$E_-E_-B_1$	0	1/4	−1/4	0
111	$E_-E_-B_2$	0	1/4	−1/4	0
121	$E_-E_-B_2$	1/4	0	0	−1/4

Table 7.10. Polyhedral isoscalars $PIs(BCC_s|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$	$m=2$	$m=3$	$m=4$
111	$A_1A_1A_1$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1A_2A_2$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1B_1B_1$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1B_2B_2$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$A_1E_-E_-$	1/4	0	0	−1/4
112	$A_1E_-E_-$	0	1/4	−1/4	0
121	$A_1E_-E_-$	0	−1/4	1/4	0
122	$A_1E_-E_-$	1/4	0	0	−1/4
111	$B_2A_1B_2$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$B_2A_2B_1$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$B_2B_1A_2$	$-1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$
111	$B_2B_2A_1$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$B_2E_-E_-$	0	1/4	−1/4	0
112	$B_2E_-E_-$	1/4	0	0	−1/4
121	$B_2E_-E_-$	1/4	0	0	−1/4
122	$B_2E_-E_-$	0	−1/4	1/4	0
112	$E_-A_1E_-$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
112	$E_-A_1E_-$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
111	$E_-A_2E_-$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$
112	$E_-A_2E_-$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$
111	$E_-B_1E_-$	$-1/\sqrt{32}$	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$
112	$E_-B_1E_-$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$E_-B_2E_-$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
112	$E_-B_2E_-$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
111	$E_-E_-A_1$	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$
121	$E_-E_-A_1$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$
111	$E_-E_-A_2$	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
121	$E_-E_-A_2$	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$
111	$E_-E_-B_1$	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$
121	$E_-E_-B_1$	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$
111	$E_-E_-B_2$	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$-1/\sqrt{32}$
121	$E_-E_-B_2$	$1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$

Table 7.11. Polyhedral isoscalars $PIs(CCCm|\alpha\beta\gamma|abc)$

$\alpha\beta\gamma$	abc	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$	$m=7$	$m=8$
111	$A_1A_1A_1$	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8
111	$A_1A_2A_2$	1/8	1/8	1/8	1/8	−1/8	−1/8	−1/8	−1/8
111	$A_1B_1B_1$	1/8	−1/8	−1/8	1/8	1/8	1/8	−1/8	−1/8
111	$A_1B_2B_2$	1/8	−1/8	−1/8	1/8	−1/8	−1/8	1/8	1/8
111	$A_1E_-E_-$	1/√32	0	0	−1/√32	−1/√32	1/√32	0	0
112	$A_1E_-E_-$	0	1/√32	−1/√32	0	0	0	−1/√32	1/√32
121	$A_1E_-E_-$	0	−1/√32	1/√32	0	0	0	−1/√32	1/√32
122	$A_1E_-E_-$	1/√32	0	0	−1/√32	1/√32	−1/√32	0	0
111	$A_2A_1A_2$	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8
111	$A_2A_2A_1$	1/8	1/8	1/8	1/8	−1/8	−1/8	−1/8	−1/8
111	$A_2B_1B_2$	1/8	−1/8	−1/8	1/8	1/8	1/8	−1/8	−1/8
111	$A_2B_2B_1$	−1/8	1/8	1/8	−1/8	1/8	1/8	−1/8	−1/8
111	$A_2E_-E_-$	0	−1/√32	1/√32	0	0	0	1/√32	−1/√32
112	$A_2E_-E_-$	1/√32	0	0	−1/√32	−1/√32	1/√32	0	0
121	$A_2E_-E_-$	−1/√32	0	0	1//√32	−1/√32	1/√32	0	0
122	$A_2E_-E_-$	0	−1/√32	1/√32	0	0	0	−1//√32	1/√32
111	$B_1A_1B_1$	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8
111	$B_1A_2B_2$	−1/8	−1/8	−1/8	−1/8	1/8	1/8	1/8	1/8
111	$B_1B_1A_1$	1/8	−1/8	−1/8	1/8	1/8	1/8	−1/8	−1/8
111	$B_1B_2A_2$	1/8	−1/8	−1/8	1/8	−1/8	−1/8	1/8	1/8
111	$B_1E_-E_-$	−1/√32	0	0	1/√32	1/√32	−1/√32	0	0
112	$B_1E_-E_-$	0	1/√32	−1/√32	0	0	0	−1/√32	1/√32
121	$B_1E_-E_-$	0	1/√32	−1/√32	0	0	0	1/√32	−1/√32
122	$B_1E_-E_-$	1/√32	0	0	−1/√32	1/√32	−1/√32	0	0
111	$B_2A_1B_2$	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8
111	$B_2A_2B_1$	1/8	1/8	1/8	1/8	−1/8	−1/8	−1/8	−1/8
111	$B_2B_1A_2$	−1/8	1/8	1/8	−1/8	−1/8	−1/8	1/8	1/8
111	$B_2B_2A_1$	1/8	−1/8	−1/8	1/8	−1/8	−1/8	1/8	1/8
111	$B_2E_-E_-$	0	1/√32	−1/√32	0	0	0	−1/√32	1/√32
112	$B_2E_-E_-$	1/√32	0	0	−1/√32	−1/√32	1/√32	0	0
121	$B_2E_-E_-$	1/√32	0	0	−1/√32	1/√32	−1/√32	0	0
122	$B_2E_-E_-$	0	−1/√32	1/√32	0	0	0	−1/√32	1/√32
111	$E_-A_1E_-$	1/√32	1/√32	1/√32	1/√32	1/√32	1/√32	1/√32	1/√32
112	$E_-A_1E_-$	0	0	0	0	0	0	0	0
211	$E_-A_1E_-$	0	0	0	0	0	0	0	0
212	$E_-A_1E_-$	1/√32	1/√32	1/√32	1/√32	1/√32	1/√32	1/√32	1/√32
111	$E_-A_2E_-$	0	0	0	0	0	0	0	0
112	$E_-A_2E_-$	−1/√32	−1/√32	−1/√32	−1√32	1/√32	1/√32	1/√32	1/√32
211	$E_-A_2E_-$	1/√32	1/√32	1/√32	1/√32	−1/√32	−1/√32	−1/√32	−1/√32
212	$E_-A_2E_-$	0	0	0	0	0	0	0	0
111	$E_-B_1E_-$	−1/√32	1/√32	1/√32	−1/√32	−1/√32	−1/√32	1/√32	1/√32
112	$E_-B_1E_-$	0	0	0	0	0	0	0	0
211	$E_-B_1E_-$	0	0	0	0	0	0	0	0
212	$E_-B_1E_-$	1/√32	−1/√32	−1/√32	1/√32	1/√32	1/√32	−1/√32	−1/√32
111	$E_-B_2E_-$	0	0	0	0	0	0	0	0
112	$E_-B_2E_-$	1/√32	−1/√32	−1/√32	1/√32	−1/√32	−1/√32	1/√32	1/√32
211	$E_-B_2E_-$	1/√32	−1/√32	−1/√32	1/√32	−1/√32	−1/√32	1/√32	1/√32
212	$E_-B_2E_-$	0	0	0	0	0	0	0	0
111	$E_-E_-A_1$	1/√32	0	0	−1/√32	−1/√32	1/√32	0	0
121	$E_-E_-A_1$	0	−1/√32	1/√32	0	0	0	−1/√32	1/√32
211	$E_-E_-A_1$	0	1/√32	−1/√32	0	0	0	−1/√32	1/√32

Table 7.11. (continued)

$\alpha\beta\gamma$	abc	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$	$m=7$	$m=8$
211	$E\_E\_A_1$	$1/\sqrt{32}$	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0
111	$E\_E\_A_2$	0	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$
121	$E\_E\_A_2$	$1/\sqrt{32}$	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0
211	$E\_E\_A_2$	$-1/\sqrt{32}$	0	0	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0
221	$E\_E\_A_2$	0	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0	0	$1/\sqrt{32}$	$-1/\sqrt{32}$
111	$E\_E\_B_1$	$-1/\sqrt{32}$	0	0	$1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0
121	$E\_E\_B_1$	0	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0	0	$1/\sqrt{32}$	$-1/\sqrt{32}$
211	$E\_E\_B_1$	0	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$
221	$E\_E\_B_1$	$1/\sqrt{32}$	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0
111	$E\_E\_B_2$	0	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$
121	$E\_E\_B_2$	$1/\sqrt{32}$	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$	$-1/\sqrt{32}$	0	0
211	$E\_E\_B_2$	$1/\sqrt{32}$	0	0	$-1/\sqrt{32}$	$-1/\sqrt{32}$	$1/\sqrt{32}$	0	0
221	$E\_E\_B_2$	0	$-1/\sqrt{32}$	$1/\sqrt{32}$	0	0	0	$-1/\sqrt{32}$	$1/\sqrt{32}$

corpora are related to each other by:

$$PIs'\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}_{\varepsilon}^{m} = \sum_{\eta n \alpha\beta\gamma} u^1_{\varepsilon\eta} u^2_{mn} u^3_{\alpha\alpha} u^3_{\beta\beta} u^3_{\gamma\gamma} PIs \begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}_{\eta}^{n} \tag{7.6}$$

The unitary transformation represented by u^1 is due to a different choice of the $3jm$ symbols, that represented by u^2 is due to the similar transformation of the triads (5.13). Finally the transformations u^3 result from Eq. (4.9).

As shown in [5], the polyhedral isoscalars play a central part in calculating matrix elements in molecular orbital theory. In the case of orbitals being more complex than atomic s orbitals they occur combined with other invariants like $6j$ or $9j$ symbols and the isoscalar factors of the group chain $SO(3) \subset G$. In the same way as for the latter coefficients, a full tabulation of the polyhedral isoscalar factors of the point groups is needed to make them freely available. Therefore, we now give an exhaustive tabulation of the factors for group C_{4v}. The majority of the factors involving high multiplicities up to eight belong to the triads of low symmetry, i.e. $CCCm$, whereas the symmetrical and more interesting triads like $AAA1$, $AAA2$, and $AAC1$ have only a few factors. In order to save space in the headings of the tables the factors are printed as $PIs(ABCm\,|\,\alpha\beta\gamma\,|\,abc)$. The first trivial factor is $(PIs(0001\,|\,111\,|\,A_1A_1A_1) = 1$.

8. Symmetry adaption

Usually the application of quantitative group theory begins with the symmetry adaption of basic coordinates, functions etc. An example is the transformation from the angular momentum basis or from the cartesian basis to the bases adapted to the irreducible representations of the symmetry group G:

$$|l\alpha ap\rangle = \sum_m \langle lm\,|\,l\alpha ap\rangle \cdot |\,lm\rangle. \tag{8.1}$$

This transformation is not the topic of the present paper and we assume that all bases are already classified according to the group G.

As for the cartesian coordinates Eq. (8.1) implies:

$$x(ap) = \sum_k \langle 1k | 1ap \rangle \cdot x_k. \tag{8.2}$$

In the case of the group C_{4v} this is simply:

$$x(E1) = x_1, \qquad x(E2) = x_2, \qquad x(A_1 1) = x_3. \tag{8.2a}$$

In polycentric systems the basic functions $|l\alpha ap\rangle$ are translated to several centres. These centres may be atomic positions or may be fictitious (floating orbitals). The translated orbitals are marked by the affix A_i etc.:

$$\langle \boldsymbol{r} | Ail\alpha ap \rangle = \langle \boldsymbol{r} - \boldsymbol{A}_i | l\alpha ap \rangle$$

or in short notation using the translation operator $T(\boldsymbol{A}_i)$:

$$|Aiap\rangle = T(\boldsymbol{A}_i) | ap \rangle. \tag{8.3}$$

As already shown in [4], the orbitals $|Aiap\rangle$ transform according to the direct product representation $\sigma^A \times a$. Therefore, the branching rules for the symmetry adaption of these orbitals are calculated by the character formula

$$n(c, A \times a) = \frac{1}{\text{ord } G} \sum_C \lambda(C) \sigma^A(C) \chi^a(C) \chi^c(C)^*. \tag{8.4}$$

Since the permutation representation σ^A is reducible, it may be first decomposed according to the rule (4.5) which implies:

$$\sigma^A(C) = \sum_e n(e, A) \chi^e(C). \tag{8.5}$$

Because of the well-known product rule

$$n(e, a, c) = \frac{1}{\text{ord } G} \sum_C \lambda(C) \chi^e(C) \chi^a(C) \chi^c(C) \tag{8.6}$$

we finally get:

$$n(c, A \times a) = \sum_e n(e, A) \cdot n(e, a, c^+). \tag{8.7}$$

Using Table 4.2 for the relevant group as well as the multiplicities $n(e, a, c)$ given in every book on point groups, one can now calculate the branching rules of the replresentation $\sigma^A \times a$ induced by the atomic orbitals or displacement coordinates. The intermediate representation e serves as a distinguishing index.

Since the decompositions according to the rules (8.5 and 8.6) are achieved by the SALC and the $3jm$ coefficients respectively, the decomposition of the product $\sigma^A \times a$ is carried out by generalized SALC coefficients first introduced in [4]:

$$K(\gamma cq, Ai\varepsilon e, ap) = \{c\} \sqrt{\dim c} \sum_r \begin{pmatrix} e^+ a^+ c \\ r \; p \; q \end{pmatrix}^\gamma \cdot (A_i | A\varepsilon er) \tag{8.8}$$

Table 8.1. Generalized SALC coefficients $K(cq, Ai\varepsilon e, E\_p)$

εe	cp	$ip=11$	12	21	22	31	32	41	42
$1A_1$	E_1	1/2	0	1/2	0	1/2	0	1/2	0
$1A_1$	E_2	0	1/2	0	1/2	0	1/2	0	1/2
$1B_1$	E_1	−1/2	0	1/2	0	1/2	0	−1/2	0
$1B_1$	E_2	0	1/2	0	−1/2	0	−1/2	0	1/2
$1E\_$	$A_1 1$	1/2	0	0	1/2	0	−1/2	−1/2	0
$1E\_$	$A_2 1$	0	1/2	−1/2	0	1/2	0	0	−1/2
$1E\_$	$B_1 1$	−1/2	0	0	1/2	0	−1/2	1/2	0
$1E\_$	$B_2 1$	0	1/2	1/2	0	−1/2	0	0	−1/2

The transformation of the basis then reads:

$$|(A\varepsilon e, a)\gamma cq\rangle = \sum_{ip} K(\gamma cq, Ai\varepsilon e, ap) \cdot |Ai, ap\rangle. \tag{8.9}$$

For the details we refer to [4, 5]. The same decomposition or symmetry adaption applies to the coordinates within a molecule. When the atomic displacements are given by

$$\boldsymbol{X}(A_i) = \boldsymbol{A}_i - \boldsymbol{A}_i^0 \text{ or } X(A_i)_k = A_{ik} - A_{ik}^0 \tag{8.10}$$

they are adapted to the group G by Eq. (8.2), i.e.

$$X(Ai, ap) = \sum_k \langle 1k|1ap\rangle \cdot X(A_i)_k. \tag{8.11}$$

The fact that the displacements $X(Ai, ap)$ induce the direct product representation $\sigma^A \times a$ has been discussed in [1, 3] and indirectly in [2]. Consequently the symmetry coordinates of a molecule are given by

$$Q(A\varepsilon e, a; \gamma cq) = \sum_{ip} K(\gamma cq, Ai\varepsilon e, ap) \cdot X(Ai, ap). \tag{8.12}$$

As an example we calculate the symmetry coordinates of four atoms at the positions A_i of Table 3.2. Because of Eq. (8.2a) we need the decomposition of $\sigma^A \times A_1$ and of $\sigma^A \times E$. In the first case the coefficients are simply $K(eq, Ai\varepsilon e, A_1 1) = (A_i|A\varepsilon eq)$, cf. Table 4.3. In the second case Eq. (8.7) yields the multiplicities $n(A_1, A) = n(A_2, A) = n(B_1, A) = n(B_2, A) = 1$ and $n(E, A) = 2$. The coefficients $K(cq, Ai\varepsilon e, Ep)$ have been calculated by Eq. (8.9) and are compiled in Table 8.1.

9. The theorem on molecular matrices

The essential quantitative theorem of monocentric group theory is the Wigner–Eckart theorem, which applies to tensor operators or tensor matrices having the property:

$$\underline{U}(g)\underline{T}_i^c\underline{U}(g)^{-1} = \sum_k D_{ki}^c(g)\underline{T}_k^c. \tag{9.1}$$

The theorem reads:

$$\langle ap \,|\, T_i^c \,|\, bq\rangle = \sum_{\varepsilon} \langle a \,\|\, T^c \,\|\, b\rangle_{\varepsilon} \cdot \begin{pmatrix} a^+ & c & b \\ p & i & p \end{pmatrix}^{\varepsilon}. \tag{9.2}$$

As a special case Eq. (9.1) includes the invariant or scalar matrices with

$$\underline{U}(g)\underline{T}\underline{U}(g)^{-1} = \underline{T}. \tag{9.3}$$

In this case the theorem reduces to:

$$\langle ap \,|\, T \,|\, bq\rangle = \delta(a, b)\delta(p, q)\langle a \,\|\, T \,\|\, a\rangle / \sqrt{\dim a}. \tag{9.4}$$

Except for a dimensional factor the diagonal elements of a scalar matrix are equal to the reduced matrix element. Because of the deltas, this special case is sometimes called the non-combination theorem.

With respect to a basis of atomic or floating orbitals and displacement coordinates, such matrices are in general bicentric in the sense that the indices in the bras and kets refer to different centres. An example is the matrix $\underline{F}$ of the molecular force constants. Using the symmetry-adapted displacements of Eq. (8.11) it is derived from the scalar molecular potential by

$$(Ai, ap \,|\, F \,|\, Bk, bq) = \partial^2 V / \partial X(Ai, ap)\, \partial X(Bk, bq). \tag{9.5}$$

Writing down Eq. (9.3) explicitly shows the involvement of the permutation representations:

$$\sum_{lmnq} \sigma_{li}^{A}(g) D_{np}^{a}(g) (Ai, ap \,|\, F \,|\, Bk, bq) \sigma_{mk}^{B}(g) D_{rq}^{b}(q) = (Al, an \,|\, F \,|\, Bm, br).$$

In [5] it has been shown that there is an analogue of the Wigner-Eckart theorem for this bicentric case. The theorem gains advantage from the fact that the pair A_i, B_k in Eq. (9.5) shares its site group with a certain C_l according to Eq. (5.5). The theorem reads:

$$\begin{aligned}(Ai, ap \,|\, F \,|\, Bk, bq) &= \sum_{\delta m C\varepsilon} \sum_{erl} (Aa \,\|\, F \,\|\, Bb)_{C\varepsilon e}^{\delta m} \begin{pmatrix} a^+ & b & e^+ \\ p & q & r \end{pmatrix}^{\delta} \\ &\times \tau \begin{pmatrix} ABC \\ ikl \end{pmatrix}^{m} \sqrt{\dim C / \dim e} \cdot (C_l \,|\, C\varepsilon er).\end{aligned} \tag{9.6}$$

Keeping close to the terminology of the Wigner-Eckart theorem $(Aa \,\|\, F \,\|\, Bb)_{C\varepsilon e}^{\delta m}$ is called the bicentric reduced matrix element (BRM).

As an example let us calculate the BRMs for a molecule of a set A of equivalent atoms. For the sake of simplicity we assume harmonic forces between the atoms. Of course, the force constant between two atoms A_i and A_k depends on the kind of edge connecting A_i and A_k, i.e. on the equivalence class C given by $\tau\binom{ABC}{ikl}^m$. Thus the constant must be designated by $k(AACm)$. If we always choose $\tau\binom{AAA}{111}^1 = 1/\sqrt{\dim A}$, the lack of self-interaction causes $k(AAA1) = 0$. Using

Eq. (8.2) the entire potential reads:

$$V = \tfrac{1}{4} \sum_{ikr} \sum_{Xm} k(AAXm) \sqrt{\dim X} \cdot \tau \begin{pmatrix} AAX \\ ikr \end{pmatrix}^m \cdot \sum_{ap} (X(Ai, ap) - X(Ak, ap))^2. \tag{9.7}$$

The factor 1/4 results from the unlimited sums for i and k. From Eq. (9.5) we now get:

$$\begin{aligned} &(Ai, ap|F|Ak, bq) \\ &\quad = \delta(a, b)\delta(p, q) \sum_{Xm} k(AAXm) \\ &\qquad \cdot \left[\delta(i, k) N(AAX) - \sqrt{\dim X} \cdot \sum_r \tau \begin{pmatrix} AAX \\ ikr \end{pmatrix}^m \right] \end{aligned} \tag{9.8}$$

where

$$N(AAX) = \sum_{kr} \tau \begin{pmatrix} AAX \\ jkr \end{pmatrix}^m \sqrt{\dim X} = \dim X / \dim A \tag{9.9}$$

gives the number of edges of class X connecting one atom A_j with its several neighbours.

In the derivation of Eq. (9.8) the symmetry

$$\sum_r \tau \begin{pmatrix} AAX \\ ikr \end{pmatrix}^m = \sum_r \tau \begin{pmatrix} AAX \\ kir \end{pmatrix}^m$$

has been used.

The most reliable way to evaluate the BRMs is to first invert Eq. (9.6) by the orthogonality relations. This yields:

$$\begin{aligned} &(Aa \| F \| Bb)^{\delta m}_{C\varepsilon e} \\ &\quad = \sum_{ikl} \sum_{pqr} (C\varepsilon er | C_l) \sqrt{\dim C \cdot \dim e} \\ &\qquad \cdot \begin{pmatrix} a^+ & b & e^+ \\ p & q & r \end{pmatrix}^\delta \tau \begin{pmatrix} ABC \\ ikl \end{pmatrix}^m (Ai, ap|F|Bk, bq). \end{aligned} \tag{9.10}$$

As for our example inserting (9.8) into Eq. (9.10) yields:

$$\begin{aligned} (Aa \| F \| Ab)^{\delta m}_{C\varepsilon e} &= \delta(a, b)\delta(e, 1)\delta(\delta, 1)\delta(\varepsilon, 1) \sqrt{\dim a \cdot \dim C} \\ &\quad \cdot \left[\delta(C, A)\delta(m, 1) \sum_{Xn} k(AAXn) NAAX) - k(AACm) \right]. \end{aligned} \tag{9.11}$$

This means that the only non-zero BRMs are:

$$(Aa \| F \| Aa)^{11}_{A11} = \sqrt{\dim a \cdot \dim A} \cdot \sum_{Xn} k(AAXn) N(AAX)$$

$$(Aa \| F \| Aa)^{1m}_{C11} = -\sqrt{\dim a \cdot \dim C} \cdot k(AACm) \quad \text{for } Cm \neq A1.$$

Finally, we come to the paradigmatic group C_{4v} with four atoms of equivalence class A. In the case we have $N(AAA1)=1$ (irrelevant because of $k(AAA1)=0$), $N(AAA2)=1$, and $N(AAC1)=2$. Using the abbreviation $k(AAA2)=k_1$ and $k(AAC1)=k_2$ the non-zero BRMs are:

$$\begin{aligned}
&(AA1\|F\|AA_1)^1_{A1A1}=2(k_1+2k_2) && (AE\|F\|AE)^1_{A1A_1}=\sqrt{8}(k_1+2k_2)\\
&(AA_1\|F\|AA_1)^2_{A1A_1}=-2k_1 && (AE\|F\|AE)^2_{A1A_1}=-\sqrt{8}\cdot k_1\\
&(AA_1\|F\|AA_1)^1_{C1A_1}=-\sqrt{8}\cdot k_2 && (AE\|F\|AE)^1_{C1A_1}=-4k_2.
\end{aligned} \tag{9.12}$$

In the more general case of a tensor operator with respect to an atomic orbital basis, the theorem on the bicentric matrix elements reads:

$$\begin{aligned}
&\langle Ai, ap|T^c_j|Bk, bq\rangle\\
&\quad=\sum_{ds\delta\eta}\sum_{C\varepsilon er}\sum_{ml}(Aa\|T^c\|Bb)^{d\delta\eta m}_{C\varepsilon e}\begin{pmatrix}a^+ & b & d\\ p & q & s\end{pmatrix}^{\delta}\\
&\quad\times\begin{pmatrix}d^+ & c & e^+\\ s & j & r\end{pmatrix}\eta\sqrt{\dim C}\,\tau\begin{pmatrix}ABC\\ ikl\end{pmatrix}^m(C_l|C\varepsilon er).
\end{aligned} \tag{9.13}$$

In [5] more details have been given regarding the calculation of the BRMs in the case of spherical atomic orbitals.

10. The geometrical theorem

The purpose of the symmetry adaption of atomic orbitals and coordinates is the diagonalization of scalar matrices as far as possible by group-theoretical means (quasi-diagonalization), and the calculation of reduced matrix elements. In the case of a bicentric matrix the quasi-diagonalization is given by (cf. 8.12):

$$\begin{aligned}
&(A\varepsilon e, a;\ \gamma cr|F|B\phi f, b;\ \delta ds)\\
&\quad=\sum_{ikpq}K(\gamma cr, Ai\varepsilon e, ap)(Ai, ap|F|Bk, bq)K(\delta ds, Bk\phi f, bq).
\end{aligned} \tag{10.1}$$

Since the matrix elements with respect to the symmetry-adapted basis are subject to the Wigner–Eckart theorem (9.2)–(9.4), there is a relation of the reduced matrix elements to the BRMs of Eq. (9.6). Such a relation between different symmetry invariants is well known from multi-electron theory. The reduced multi-electron and the reduced one-electron matrix elements are interrelated geometrically by weight factors. The relating coefficients have been termed g factors by Griffith [10] and Schatz and Piepho [11]. The concept of geometrical factors introduced in [5] is quite analogous.

Introducing now the factors

$$GEO_1(AaBbg\,|\,\varepsilon e\gamma c,\ \phi f\delta d,\ \alpha\,|\,h\eta\theta Cm\sigma k)$$

$$= \{c^+ dg\alpha\} \cdot \sqrt{\dim C \cdot \dim c \cdot \dim d} \cdot \sum_{\beta} \begin{Bmatrix} c^+ & d & g \\ e & f^+ & k^+ \\ a & b^+ & h^+ \\ \gamma & \delta & \theta \end{Bmatrix} \begin{matrix} \alpha \\ \beta \\ \eta \end{matrix}$$

$$\cdot PIs \begin{pmatrix} A & B & C \\ \varepsilon & \phi & \sigma \\ e^+ & f & k \end{pmatrix}^m_\beta . \tag{10.2}$$

the geometrical theorem expressing the reduced matrix elements in terms of the BRMs reads:

$$\langle (A\varepsilon e,\ a)\gamma c \| T^g \| (B\phi f,\ b)\delta d \rangle_\alpha$$

$$= \sum_{h\eta\theta} \sum_{Cm\sigma k} GEO_1(AaBbg\,|\,\varepsilon e\gamma c,\ \phi f\delta d,\ \alpha\,|\,h\eta\theta Cm\sigma k) \cdot (Aa \| T^g \| Bb)^{h\eta\theta m}_{Cmk}.$$

As already mentioned above, the polyhedral isoscalar factors enter this key theorem combined with other invariants, the $9j$ symbols in this case. If $a = b = 1$, for instance, the geometrical factors are reduced to the polyhedral isoscalars. In the case of simply reducible groups, C_{4v}, O_h, and T_d for instance, the indices α, β, γ, δ, η, and θ are dropped. The arrangement of the indices is such that the geometrical factors belonging to $x = (AaBbg)$ form a unitary or orthogonal matrix with respect to the collective indices $y = (\varepsilon e\gamma c,\ \phi f\delta d,\ \alpha)$ and $z = (h\eta\theta Cm\sigma k)$:

$$\sum_y \dim h \cdot GEO_1(x, y, z) \cdot GEO_1(x, y, z')^* = \delta(z, z')$$

$$\sum_z \dim h \cdot GEO_1(x, y, z) \cdot GEO_1(x, y', z)^* = \delta(y, y'). \tag{10.4}$$

This means that the number of reduced matrix elements and of BRMs is equal and that Theorem (10.3) may be inverted.

In the important case of scalar operators ($g = 1$), for example the identity, the Hamiltonian, and the force constants of the molecule, the geometrical factors are reduced to an expression involving $6j$ symbols:

$$GEO_{1\,red}(AaBb\,|\,\varepsilon e\gamma c,\ \phi f\delta c\,|\,\eta Cm\sigma k)$$

$$= \{bfc^+\delta\}\{b^+ak\eta\}\sqrt{\dim C \cdot \dim c/\dim k} \cdot \sum_{\beta} \begin{Bmatrix} e & f^+ & k^+ \\ b^+ & a^+ & c^+ \end{Bmatrix}_{\gamma\delta\eta\beta}$$

$$\cdot PIs \begin{pmatrix} A & B & C \\ \varepsilon & \phi & \sigma \\ e^+ & f & k \end{pmatrix}^m_\beta \tag{10.5}$$

The theorem for the quasi-diagonal elements of the operator then reads:

$$\langle (A\varepsilon e, a)\gamma c \| T \| (B\phi f, b)\delta c \rangle = \sum_{\eta C m \sigma k} GEO_{1red}(AaBb \,|\, \varepsilon e \gamma c, \phi f \delta c \,|\, \eta C m \sigma k) \cdot (Aa \| T \| Bb)^{\eta m}_{C \sigma k} \tag{10.6}$$

We finally come back to the example C_{4v} and calculate the diagonal elements of the matrix of the force constants by Theorem (10.6). As shown in Sect. 8, the atomic displacement coordinates transform according to the irreducible representations A_1 and E. Thus the displacements of the atoms at the site A induce the following irreducible representations:

$x_3 = x(A_1 1)$ induces A_1, B_1, and E (cf. Table 4.3)

$x_1 = x(E1)$ and $x_2 = x(E2)$ induce A_1, A_2, B_1, B_2, and E twice (Table 8.1).

The reduced matrix elements of $\underline{F}$ with respect to these normal coordinates now follow from (10.6). Because C_{4v} is simply reducible the indices γ, δ, and η become obsolete and are omitted. Further, in the present case, the multiplicity indices ε, ϕ, and σ are limited to 1. The reduced matrix elements are given by the three relations:

$$\langle (A1e, A_1)c \| F \| (A1f, A_1)c \rangle = \sum_{Cmk} GEO_{1red}(AA_1AA_1 \,|\, 1ec, 1fc \,|\, Cm1k)(AA_1 \| F \| AA_1)^{m}_{C1k} \tag{10.7a}$$

Table 10.1. Geometrical factors $GEO_{1red}(AA_1AA_1 \,|\, \varepsilon ec, \phi fc \,|\, Xm\sigma k)$

εec	$\phi f c$	$Xm\sigma k =$ $A11A_1$	$A21A_1$	$C11A_1$
$1A_1A_1$	$1A_1A_1$	1/2	1/2	$1/\sqrt{2}$
$1B_1B_1$	$1B_1B_1$	1/2	1/2	$-1/\sqrt{2}$
$1E\_E\_$	$1E\_E\_$	$1/\sqrt{2}$	$-1/\sqrt{2}$	0

Table 10.2. Geometrical factors $GEO_{1red}(AE\_AE\_ \,|\, \varepsilon ec, \phi fc \,|\, Xm\sigma k)$

$\varepsilon e c$	$\phi f c$	$Xm\sigma k =$ $A11A_1$	$A11B_1$	$A21A_1$	$A21B_1$	$C11A_1$	$C11A_2$	$C11B_1$	$C11B_2$
$1A_1E\_$	$1A_1E\_$	1/2	0	1/2	0	$1/\sqrt{2}$	0	0	0
$1A_1E\_$	$1B_1E\_$	0	1/2	0	1/2	0	0	$-1/\sqrt{2}$	0
$1B_1E\_$	$1A_1E\_$	0	1/2	0	1/2	0	0	$1/\sqrt{2}$	0
$1B_1E\_$	$1B_1E\_$	1/2	0	1/2	0	$-1/\sqrt{2}$	0	0	0
$1E\_A_1$	$1E\_A_1$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$1/\sqrt{8}$	0	1/2	0	1/2
$1E\_A_2$	$1E\_A_2$	$1/\sqrt{8}$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	0	1/2	0	−1/2
$1E\_B_1$	$1E\_B_1$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	$1/\sqrt{8}$	0	−1/2	0	−1/2
$1E\_B_2$	$1E\_B_2$	$1/\sqrt{8}$	$1/\sqrt{8}$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	0	−1/2	0	1/2

Table 10.3. Geometrical factors $GEO_{1red}(AA_1AE_-|\varepsilon ec, \phi fc|Xm\sigma k)$

$\varepsilon e c$	$\phi f c$	$Xm\sigma k =$ $A1\,1E_-$	$A2\,1E_-$	$C1\,1E_-$	$C1\,2E_-$
$1A_1A_1$	$1E_-A_1$	$1/\sqrt{8}$	$-1/\sqrt{8}$	0	1/2
$1B_1B_1$	$1E_-B_1$	$-1/\sqrt{8}$	$1/\sqrt{8}$	0	1/2
$1E_-E_-$	$1A_1E_-$	$1/\sqrt{8}$	$1/\sqrt{8}$	1/2	0
$1E_-E_-$	$1B_1E_-$	$-1/\sqrt{8}$	$-1/\sqrt{8}$	1/2	0

$$\langle (A1e, E)c \| F \| (A1f, E)c\rangle = \sum_{Cmk} GEO_{1red}(AE\,AE\,|\,1ec, 1fc\,|\,Cm1k)(AE\|F\|AE)^m_{C1k} \tag{10.7b}$$

$$\langle (A1e, A_1)c \| F \| (A1f, E)c\rangle = \sum_{Cmk} GEO_{1red}(AA_1AE\,|\,1ec, 1fc\,|\,C1nk)(AA_1\|F\|AE)^m_{C1k}. \tag{10.7c}$$

The geometrical factors of these relations are calculated by (10.5) and compiled in the Tables 10.1–10.3.

Using these tables and the BRMs of the preceding section we get the final results for the reduced matrix elements. With Table 10.1:

$$\langle (A1A_1, A_1)A_1 \| F \| (A1A_1, A_1)A_1\rangle = 0$$

$$\langle (A1B_1, A_1)B_1 \| F \| (A1B_1, A_1)B_1\rangle = 4k_2$$

$$\langle (A1E, A_1)E \| F \| (A1E, A_1)E\rangle = \sqrt{8}(k_1 + k_2).$$

With Table 10.2:

$$\langle (A1A_1, E)E \| F \| (A1A_1, E)E\rangle = 0,$$

$$\langle (A1B_1, E)E \| F \| (A1B_1, E)E\rangle = 4\sqrt{2}k_2,$$

$$\langle (A1A_1, E)E \| F \| (A1B_1, E)E\rangle = 0,$$

$$\langle (A1E, E)A_1 \| F \| (A1E, E)A_1\rangle = 2(k_1 + k_2),$$

$$\langle (A1E, E)A_2 \| F \| (A1E, E)A_2\rangle = 2(k_1 + k_2),$$

$$\langle (A1E, E)B_1 \| F \| (A1E, E)B_1\rangle = 2(k_1 + k_2),$$

$$\langle (A1E, E)B_2 \| F \| (A1E, E)B_2\rangle = 2(k_1 + k_2).$$

Finally with Table 10.3 the non-diagonal elements:

$\langle (A1e, A_1)c \| F \| (A1f, E)c\rangle = 0$ for all combinations of e, f, and c.

If m_A is the mass of the particles at the positions A, the molecular vibration frequencies are given by:

$$\nu_c^2 = \frac{\langle (A1e, a)c \| F \| (A1f, a)c\rangle}{m_A \cdot \sqrt{\dim C}}. \tag{10.8}$$

The two resulting values $\nu^2 = 4k_2/m_A$ and $\nu^2 = 2(k_1 + k_2)/m_A$ have an artificial degeneracy due to the over-simplified model of the molecular forces (9.7). This does not affect the demonstration of the group-theoretical methods.

Because of the identical transformation property of atomic p orbitals and of cartesian coordinates, Tables 10.1–10.3 also apply to the matrix elements of the electronic Hamiltonian with respect to these p orbitals. We only have to replace F by H in (10.7a–c).

As a final example involving the general geometrical factors defined by (10.2), we think of an electronic transition (charge transfer) between d orbitals of the central atom (d_{xz}, d_{yz} belong to E) and molecular orbitals built from p_x and p_y orbitals at the positions A. The linear momentum operator transforms according to A_1 and E. In the first case the special factors apply again. In the latter case we get the relation

$$\langle (01A_1, E) \| p^E \| (A1f, E) d \rangle = \sum_{hCmk} GEO_1(OEAEE \,|\, 1A_1E, 1fd \,|\, hCm1k) \cdot (OE \| p^E \| AE)^{hm}_{C1k} \qquad (10.9)$$

with the factors compiled in Table 10.4. Table 10.5 contains the factors for a similar transition between atoms of the equivalent sets A and B. The orbitals at the latter positions belong to the representation A_1, i.e. s, p_z or d_{z^2}.

Table 10.4. Geometrical factors $GEO_1(OE\_AE\_E\_ \,|\, \varepsilon ec, \phi fd \,|\, hXm\sigma k)$

$\varepsilon e c$	$\phi f d$	$hXm\sigma k =$ $A_1A1\,1E\_$	$A_2A1\,1E$	$B_1A1\,1E\_$	$B_2A1\,1E\_$
$1A_1E\_$	$1E\_A_1$	1/2	1/2	1/2	1/2
$1A_1E\_$	$1E\_A_2$	−1/2	−1/2	1/2	1/2
$1A_1E\_$	$1E\_B_1$	1/2	−1/2	1/2	−1/2
$1A_1E\_$	$1E\_B_2$	1/2	−1/2	−1/2	1/2

Table 10.5. Geometrical factors $GEO_1(AE\_BA_1E\_ \,|\, \varepsilon ec, \phi fd \,|\, hXm\sigma k)$

εec	ϕfd	$hXm\sigma k =$ E_C11A_1	E_C11A_2	E_C11B_1	E_C11B_2	E_C21A_1	E_C21A_2	E_C21B_1	E_C21B_2
$1A_1E\_$	$1A_1A_1$	1/2	0	0	0	1/2	0	0	0
$1A_1E\_$	$1B_2B_2$	0	0	0	1/2	0	0	0	−1/2
$1B_1E\_$	$1A_1A_1$	0	0	1/2	0	0	0	1/2	0
$1B_1E\_$	$1B_2B_2$	0	−1/2	0	0	0	1/2	0	0
$1E\_A_1$	$1E\_E\_$	1/4	1/4	−1/4	1/4	−1/4	1/4	1/4	1/4
$1E\_A_2$	$1E\_E\_$	−1/4	−1/4	−1/4	1/4	1/4	−1/4	1/4	1/4
$1E\_B_1$	$1E\_E\_$	1/4	−1/4	−1/4	−1/4	−1/4	−1/4	1/4	−1/4
$1E\_B_2$	$1E\_E\_$	1/4	−1/4	1/4	1/4	−1/4	−1/4	−1/4	1/4

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