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Application of coset representations to the construction of symmetry adapted functions

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Summary. A coset representation ($\boldsymbol{G}(/\boldsymbol{G}_i)$), which is defined algebraically by a coset decomposition of a finite group $\boldsymbol{G}$ by its subgroup $\boldsymbol{G}_i$, is shown to be a method for the decomposition of a regular body into its point group orbits. This proof also shows that each member of the $\boldsymbol{G}(/\boldsymbol{G}_i)$ orbit belongs to the $\boldsymbol{G}_i$ site-symmetry. In addition, a general equation concerning the multiplicities of such coset representations is derived and shown to involve Brester's equations and the k-value equations of framework groups as special cases. The relationship of the coset representation and the site-symmetry affords a general procedure for obtaining symmetry adapted functions.

Key words: Coset representation – Regular body – Site-symmetry – Brester's equation – Symmetry adapted functions

1. Introduction

The construction of symmetry adapted linear combinations (SALCs) of basis functions is one of the most important applications of group theory in chemistry [1, 2]. For constructing SALCs, a standard method utilizes projection operators after reducing a matrix representation into irreducible representations [1]. In recent years, several alternative procedures have been suggested to obtain SALCs of highly symmetric non-axial groups. For example, Flurry has reported the use of site-symmetry [3, 4]. Stone has presented the tensor surface harmonic (TSH) theory, which is appropriate for the generation of SALCs [5], Quinn et al. have determined σ-characters as permutation characters, which are then utilized for the construction of σ-, π-, and δ-type SALCs [6–8]. Ceulemans has described an essentially equivalent method [9]. According to these methods, the total set of fragments (or atoms) appearing in a molecule is resolved into orbits containing equivalent fragments, where each orbit is characterized by a site-symmetry group. This characterization contains at least three steps: (1) the resolution into such orbits, (2) the decomposition of permutation characters, and (3) the assignment of the site-symmetry group. These steps are not trivial especially for highly symmetric non-axial groups. In particular, the first task can be

complicated if Brester's method is used [10]. Moreover, step 3 has not been systematized sufficiently to stimulate general applications.

In previous papers, we have used coset representations (CRs) and their subductions to enumerate organic compounds [13–18] and to classify molecular symmetry [19]. The coset representations (CRs) are obtained directly by examining the multiplication tables of groups. The relationship between the CRs and orbits has been proven for the enumeration; however, a more comprehensive discussion is required for the application of this approach to the construction of SALCs. In this paper, the chemical and geometrical meanings of CRs and their relationship to orbits are presented. This analysis reveals the inherent identities of Brester's method [10], the so-called k-values in framework groups [20], the σ-character technique [6], and the site-symmetry method [3] in the light of CRs. A typical procedure for constructing SALCs also is presented.

2. Orbits

Consider a molecule of G-symmetry that consists of several sets (orbits) of equivalent atoms or ligands. Enumeration of such orbits has been done by Brester [10], Jahn and Teller [11], Boyle [12] and Fowler and Quinn [6] for most point groups. Each orbit (O_A) is usually characterized by the site-symmetry group (H_A) that stabilizes (or fixes) one site (A) of the orbit. This characterization can be accomplished without difficulty by using tables presented by Fowler and Quinn [6]. H_A for a non-center atom is shown to be one of C_1, C_s, C_n, or C_{nv} ($n \geqslant 2$) [12]; and several subsymmetries of G cannot be site-symmetry groups. There has been, however, no mathematical rationalization for this selection. The present section aims at providing such a selection within a more logical framework in terms of coset representations.

2.1. Assignment of a coset representation to an orbit

Suppose that a set of subgroups of a finite group G is defined as

$$SSG = \{G_1, G_2, \ldots, G_s\}, \tag{1}$$

each element of which is a representative of respective conjugate subgroups. The elements of the SSG are aligned in the order $|G_1| \leqslant |G_2| \leqslant \cdots \leqslant |G_s|$, wherein G_1 is an identity group and G_s is equal to G. The corresponding set of coset representations (CRs) [21],

$$SCR = \{G(/G_1), G(/G_2), \ldots, G(/G_s)\}, \tag{2}$$

is a full list of transitive permutation representations of the group G, where the representation $G(/G_1)$ is a regular representation (RR) and the symbol $G(/G_s)$ denotes an identity representation.

A coset representation (CR) is constructed algebraically for every subgroup (G_i) by using a multiplication table of G and a coset decomposition of G by G_i [22]. The symbol ($G(/G_i)$) has been introduced to designate the latter fact. For example, Table 1 shows coset representations for D_{2d}, in which each permutation is represented by a product of cycles. Such a CR acts originally on an orbit of cosets, but can be considered to govern an orbit of atoms or ligands. In this sense, an orbit governed by the CR $G(G_i)$ is referred to as an $G(/G_i)$ orbit.

Table 1. Coset representations for D_{2d}

Symmetry operation	Coset representation							
	$D_{2d}(/C_1)$	$D_{2d}(/C_2)$	$D_{2d}(/C_2')$	$D_{2d}(/C_s)$	$D_{2d}(/S_4)$	$D_{2d}(/C_{2v})$	$D_{2d}(/D_2)$	$D_{2d}(/D_{2d})$
I	(1)(2)(3)(4)(5)(6)(7)(8)	(1)(2)(3)(4)	(1)(2)(3)(4)	(1)(2)(3)(4)	(1)(2)	(1)(2)	(1)(2)	(1)
$C_{2(3)}$	(1 2)(3 4)(5 6)(7 8)	(1)(2)(3)(4)	(1 2)(3 4)	(2)(3 4)	(1)(2)	(1)(2)	(1)(2)	(1)
$C_{2(1)}$	(1 3)(2 4)(5 7)(6 8)	(1 2)(3 4)	(1)(2)(3 4)	(1 3)(2 4)	(1 2)	(1 2)	(1)(2)	(1)
$C_{2(2)}$	(1 4)(2 3)(5 8)(6 7)	(1 2)(3 4)	(1 2)(3)(4)	(1 4)(2 3)	(1 2)	(1 2)	(1)(2)	(1)
$\sigma_{d(1)}$	(1 5)(2 6)(3 8)(4 7)	(1 3)(2 4)	(1 3)(2 4)	(1)(2)(3 4)	(1 2)	(1)(2)	(1 2)	(1)
$\sigma_{d(2)}$	(1 6)(2 5)(3 7)(4 8)	(1 3)(2 4)	(1 4)(2 3)	(1 2)(3)(4)	(1 2)	(1)(2)	(1 2)	(1)
S_4^3	(1 7 2 8)(3 6 4 5)	(1 4)(2 3)	(1 4 2 3)	(1 3 2 4)	(1)(2)	(1 2)	(1 2)	(1)
S_4	(1 8 2 7)(3 5 4 6)	(1 4)(2 3)	(1 3 2 4)	(1 4 2 3)	(1)(2)	(1 2)	(1 2)	(1)
Orbit (O_A)	O_8	–	O_4	O_{4d}	–	O_2	–	O_1

The assignment of a CR to an orbit is performed by using a table of marks [23, 24]. Let $\boldsymbol{P}_A$ be an arbitrary permutation representation of $\boldsymbol{G}$, so that $\boldsymbol{P}_A$ acts on a set of points,

$$\Delta = \{\delta_1, \delta_2, \ldots, \delta_{|\Delta|}\}. \tag{3}$$

Then $\boldsymbol{P}_A$ can be expressed

$$\boldsymbol{P}_A = \sum_{i=1}^{s} \alpha_i \boldsymbol{G}(/\boldsymbol{G}_i) \quad (j = 1, 2, \ldots, s). \tag{4}$$

The multiplicities α_i's are obtained by solving the following equations:

$$\mu_j = \sum_{i=1}^{s} \alpha_i m_{ij} \quad (j = 1, 2, \ldots, s). \tag{5}$$

These equations can be expressed by matrices,

$$F = EM, \tag{6}$$

or

$$E = FM^{-1}, \tag{7}$$

wherein

$$E = (\alpha_1 \alpha_2 \cdots \alpha_s), \tag{8}$$

$$F = (\mu_1 \mu_2 \cdots \mu_s), \tag{9}$$

and

$$M = \begin{pmatrix} m_{11} & m_{12} & \cdots & m_{1s} \\ m_{21} & m_{22} & \cdots & m_{2s} \\ \vdots & \vdots & & \vdots \\ m_{s1} & m_{s2} & \cdots & m_{ss} \end{pmatrix}. \tag{10}$$

The matrix (M) is a table of marks and M^{-1} is its inverse; E is referred to as a multiplicity vector (MV) and F as a fixed-point vector (FPV). Such tables of marks play important roles in the present approach. Table 2 is constructed from the data of Table 1, where fixed points are counted for every subgroup [22]. Table 3 shows the inverse of the mark table for $\boldsymbol{D}_{2d}$, which is also useful to the application of Eq. (7).

Tables 4 to 6 are other examples of mark tables.

Table 2. Mark table of $\boldsymbol{D}_{2d}$

	$\boldsymbol{C}_1$	$\boldsymbol{C}_2$	$\boldsymbol{C}_2'$	$\boldsymbol{C}_s$	$\boldsymbol{S}_4$	$\boldsymbol{C}_{2v}$	$\boldsymbol{D}_2$	$\boldsymbol{D}_{2d}$
$\boldsymbol{D}_{2d}(/\boldsymbol{C}_1)$	8	0	0	0	0	0	0	0
$\boldsymbol{D}_{2d}(/\boldsymbol{C}_2)$	4	4	0	0	0	0	0	0
$\boldsymbol{D}_{2d}(/\boldsymbol{C}_2')$	4	0	2	0	0	0	0	0
$\boldsymbol{D}_{2d}(/\boldsymbol{C}_s)$	4	0	0	2	0	0	0	0
$\boldsymbol{D}_{2d}(/\boldsymbol{S}_4)$	2	2	0	0	2	0	0	0
$\boldsymbol{D}_{2d}(/\boldsymbol{C}_{2v})$	2	2	0	2	0	2	0	0
$\boldsymbol{D}_{2d}(/\boldsymbol{D}_2)$	2	2	2	0	0	0	2	0
$\boldsymbol{D}_{2d}(/\boldsymbol{D}_{2d})$	1	1	1	1	1	1	1	1

Table 3. The inverse of the mark table for D_{2d}

	$D_{2d}(/C_1)$	$D_{2d}(/C_2)$	$D_{2d}(/C_2')$	$D_{2d}(/C_s)$	$D_{2d}(/C_4)$	$D_{2d}(/C_{2v})$	$D_{2d}(/C_2)$	$D_{2d}(/D_{2d})$
C_1	1/8	0	0	0	0	0	0	0
C_2	−1/8	1/4	0	0	0	0	0	0
C_2'	−1/4	0	1/2	0	0	0	0	0
C_s	−1/4	0	0	1/2	0	0	0	0
S_4	0	−1/4	0	0	1/2	0	0	0
C_{2v}	1/4	−1/4	0	−1/2	0	1/2	0	0
D_2	1/4	−1/4	−1/2	0	0	0	1/2	0
D_{2d}	0	1/2	0	0	−1/2	−1/2	−1/2	1

Table 4. Mark table of D_2

	C_1	C_2	C_2'	C_2''	D_2
$D_2(/C_1)$	4	0	0	0	0
$D_2(/C_2)$	2	2	0	0	0
$D_2(/C_2')$	2	0	2	0	0
$D_2(/C_2'')$	2	0	0	2	0
$D_2(/D_2)$	1	1	1	1	1

Table 5. Mark table of T_d

	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$T_d(/C_1)$	24	0	0	0	0	0	0	0	0	0	0
$T_d(/C_2)$	12	4	0	0	0	0	0	0	0	0	0
$T_d(/C_s)$	12	0	2	0	0	0	0	0	0	0	0
$T_d(/C_3)$	8	0	0	2	0	0	0	0	0	0	0
$T_d(/S_4)$	6	2	0	0	2	0	0	0	0	0	0
$T_d(/D_2)$	6	6	0	0	0	6	0	0	0	0	0
$T_d(/C_{2v})$	6	2	2	0	0	0	2	0	0	0	0
$T_d(/C_{3v})$	4	0	2	1	0	0	0	1	0	0	0
$T_d(/D_{2d})$	3	3	1	0	1	3	1	0	1	0	0
$T_d(/T)$	2	2	0	2	0	2	0	0	0	2	0
$T_d(/T_d)$	1	1	1	1	1	1	1	1	1	1	1

Table 6. Mark table for D_{3h} point group

	C_1	C_2	C_s	C_s'	C_3	C_{2v}	C_{3v}	C_{3h}	D_3	D_{3h}
$D_{3h}(/C_1)$	12	0	0	0	0	0	0	0	0	0
$D_{3h}(/C_2)$	6	2	0	0	0	0	0	0	0	0
$D_{3h}(/C_s)$	6	0	2	0	0	0	0	0	0	0
$D_{3h}(/C_s')$	6	0	0	6	0	0	0	0	0	0
$D_{3h}(/C_3)$	4	0	0	0	4	0	0	0	0	0
$D_{3h}(/C_{2v})$	3	1	1	3	0	1	0	0	0	0
$D_{3h}(/C_{3v})$	2	0	2	0	2	0	2	0	0	0
$D_{3h}(/C_{3h})$	2	0	0	2	2	0	0	2	0	0
$D_{3h}(/D_3)$	2	2	0	0	2	0	0	0	1	0
$D_{3h}(/D_{3h})$	1	1	1	1	1	1	1	1	1	1

2.2. Regular body

Table 1 indicates the correspondence between CRs of the D_{2d} group and O_A-notations [6] for orbits. By the inspection of this table, there naturally emerges a question: Why are the orbits corresponding to $D_{2d}(/C_2)$ etc. absent? In order to answer this question, it is necessary to explain the geometrical meaning of a coset representation (CR) by introducing the concept of a *regular body*.

Let G be a finite point group of order $|G|$ acting on a set of $|G|$ points in a 3D-space:

$$\Delta^R = \{\delta_1, \delta_2, \ldots, \delta_{|G|}\}. \tag{11}$$

Suppose that there is only one stabilizer of the point (δ_1) which is an identity group, i.e., $G_{\delta_1} = G_1 = \{I\}$. If g_i $(\in G)$ transforms the point δ_1 to δ_i, we can obtain a coset decomposition represented by

$$\begin{aligned} G &= G_{\delta_1} g_1 + G_{\delta_1} g_2 + \cdots + G_{\delta_1} g_{|G|} \\ &= G_1 g_1 + G_1 g_2 + \cdots + G_1 g_{|G|}. \end{aligned} \tag{12}$$

Hence, each point δ_i corresponds to the coset $G_1 g_i$ (i.e., g_i itself) in one-to-one fashion. Since $G(/G_1)$ is the regular representation (RR), Δ^R defines the regular orbit about δ_1. We call this 3D-object (Δ^R) *a regular body*.

Let us consider a subset of the regular body (Δ^R), which belongs to a subgroup G_i $(\leqslant G)$. We call this set a *block of G_i symmetry* or *a G_i-block*. This selection is realized by considering a subduction of the RR [13],

$$G(/G_1) \downarrow G_i = \frac{|G|}{|G_i|} G_i(/G_{i1}), \tag{13}$$

where $G_i(/G_{i1})$ is a regular representation of the subgroup G_i. This equation indicates that the regular body (Δ^R) is divided into $|G|/|G_i|$ blocks of G_i symmetry, the sizes of which are equal to $|G_i|$. We represent these blocks by the symbols,

$$\omega_1, \omega_2, \ldots, \omega_r,$$

where $r = |G|/|G_i|$. Since we can select an arbitrary block from these blocks, we examine ω_1 as a representative case. Let us consider a cost decomposition of G by G_i,

$$G = G_i g_1 + G_i g_2 + \cdots + G_i g_r, \tag{14}$$

where $g_1 = I$. If we operate the representatives, $\{g_1, g_2, \ldots, g_r\}$, onto the block ω_1, we obtain r imprimitive blocks,

$$\Omega_1 = g_1 \omega_1 = \omega_1, \qquad \Omega_2 = g_2 \omega_1, \ldots, \Omega_r = g_r \omega_1.$$

Since each Ω_k corresponds to the coset $G_i g_k$ through g_k in one-to-one fashion, the coset representation $G(/G_i)$ based on Eq. (14) governs a set of imprimitive blocks,

$$\Omega = \{\Omega_1, \Omega_2, \ldots, \Omega_r\}. \tag{15}$$

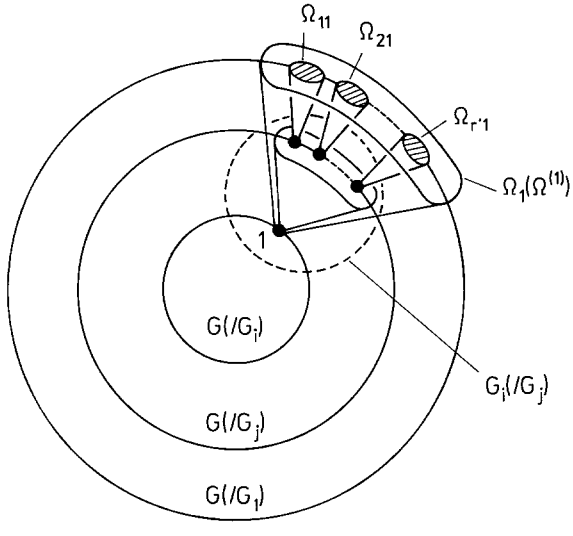


Fig. 1. Imprimitive blocks in a regular body

Figure 1 illustrates these blocks (Ω_k; $k = 1, 2, \ldots, r$), where we pay our attention to the relationship between $\boldsymbol{G}(/\boldsymbol{G}_i)$ and $\boldsymbol{G}(/\boldsymbol{G}_1)$. Since each of the blocks (Ω_k) belongs to $\boldsymbol{G}_i(/\boldsymbol{G}_{i1})$, we arrive at

Lemma 1 (site-symmetry in a regular body). *Suppose that a regular body of* $\boldsymbol{G}$ *symmetry is subject to* $\boldsymbol{G}(/\boldsymbol{C}_1)$. *Then, the coset representation* $\boldsymbol{G}(/\boldsymbol{G}_i)$ *governs a* $\boldsymbol{G}_i$ *block that has a* $\boldsymbol{G}_i(/\boldsymbol{G}_{i1})$ *orbit.*

Note that the $\boldsymbol{G}(/\boldsymbol{G}_{i1})$ representation is an RR of $\boldsymbol{G}_i$.

2.3. A regular body for a subgroup

Let us now consider a regular body which corresponds to $\boldsymbol{G}_i(/\boldsymbol{G}_{i1})$. If an appropriate group $\boldsymbol{G}_j$ satisfies $\boldsymbol{G}_j \leqslant \boldsymbol{G}_i \leqslant \boldsymbol{G}$, we can consider a subduction of $\boldsymbol{G}_i(/\boldsymbol{G}_{i1})$ in terms of

$$\boldsymbol{G}_i(/\boldsymbol{G}_{i1}) \downarrow \boldsymbol{G}_j = \frac{|\boldsymbol{G}_i|}{|\boldsymbol{G}_j|} \boldsymbol{G}_j(/\boldsymbol{G}_{j1}) . \tag{16}$$

According to this equation, the orbit (ω_p) governed by the RR ($\boldsymbol{G}_i(/\boldsymbol{G}_{i1})$) is divided into r' blocks,

$$\omega_{1p}, \omega_{2p}, \ldots, \omega_{r'p},$$

where $r' = |\boldsymbol{G}_i|/|\boldsymbol{G}_j|$ and $p = 1, 2, \ldots, r$. Let us consider a coset decomposition,

$$\boldsymbol{G}_i = \boldsymbol{G}_j h_1 + \boldsymbol{G}_j h_2 + \cdots + \boldsymbol{G}_j h_{r'}, \tag{17}$$

where $h_1 = I$. Then the same discussion as above holds for this case. If we consider ω_{11} only (i.e., $p = 1$), the set of blocks

$$\boldsymbol{\Omega}^{(1)} = \{\Omega_{11}, \Omega_{21}, \ldots, \Omega_{r'1}\} \tag{18}$$

is subject to a CR $G_i(/G_j)$, where

$$\Omega_{11} = h_1\omega_{11} = \omega_{11}, \qquad \Omega_{21} = h_2\omega_{21}, \ldots, \Omega_{r'1} = h_{r'}\omega_{r'1}.$$

Note here that all of these blocks belong to G_j symmetry. Figure 1 depicts the relationship between these blocks, where $\mathbf{\Omega}^{(1)}$ represents a subdivision of Ω_1. Because a block encircled with a broken line is associated with $\mathbf{\Omega}^{(1)}$ on the $G(/G_1)$ orbit, and because $\mathbf{\Omega}^{(1)}$ is subject to $G_i(/G_j)$, the encircled block is concluded to be subject to $G_i(/G_j)$. In other words, the coset representation $G(/G_i)$ governs a G_i-block that has a $G_i(/G_j)$ suborbit if $G_j \leqslant G_i \leqslant G$.

When we introduce Eq. (17) into Eq. (14), we can obtain

$$\begin{aligned} G = {} & G_jh_{11} + G_jh_{12} + \cdots + G_jh_{1r} + \\ & G_jh_{21} + G_jh_{22} + \cdots + G_jh_{2r} + \\ & \vdots \quad + \quad \vdots \quad + \quad + \quad \vdots \quad + \\ & G_jh_{r'1} + G_jh_{r'2} + \cdots + G_jh_{r'r}, \end{aligned} \tag{19}$$

where $h_qg_p = h_{qp}\,(p = 1, 2, \ldots, r;\ q = 1, 2, \ldots, r')$. This is a coset decomposition of G by G_j. If we transform ω_{11} by means of $h_{qp}\,(p = 1, 2, \ldots, r;\ q = 1, 2, \ldots, r')$ to produce $r'r$ blocks,

$$\hat{\mathbf{\Omega}} = \begin{bmatrix} \Omega_{11} & \Omega_{12} & \cdots & \Omega_{1r} \\ \Omega_{21} & \Omega_{22} & \cdots & \Omega_{2r} \\ \vdots & \vdots & & \vdots \\ \Omega_{r'1} & \Omega_{r'2} & \cdots & \Omega_{r'r} \end{bmatrix}, \tag{20}$$

where $\Omega_{qp} = h_{qp}\omega_{11}\,(p = 1, 2, \ldots, r;\ q = 1, 2, \ldots, r')$, then this equation indicates the one-to-one correspondence between Ω_{pq} and the coset (G_jh_{pq}) via h_{qp}. Hence, the set of blocks $\hat{\mathbf{\Omega}}$ is concluded to the subject to the CR $(G(/G_j))$. Note that $\mathbf{\Omega}^{(1)}$ is identical with the first column of $\hat{\mathbf{\Omega}}$. Since $h_{qp}\omega_1 = h_qg_p\omega_1 = h_q\Omega_p$, the remaining pth column of $\hat{\mathbf{\Omega}}$ is associated with Ω_p $(p = 1, 2, \ldots, r)$. These discussions can be summarized by

Lemma 2 (site-symmetry of a $G(/G_i)$ orbit having one suborbit). (*a*) *If $G_i \leqslant G_i \leq G$, the coset representation $G(/G_i)$ governs a G_i-block that has a $G_i(/G_j)$ suborbit.*
(*b*) *The orbit that is produced by all of such blocks as equivalent to the G_i-block is subject to $G(/G_j)$.*

This lemma describes the mode of substitution in which a G_i-block having a $G_i(/G_j)$ suborbit is introduced onto every point of a $G(/G_i)$ orbit. Obviously, a similar discussion can generalize this lemma so it is applicable to the case in which the G_i-block has a given set of suborbits. Hence, we obtain

Theorem 1 (site-symmetry of $G(/G_i)$ orbit having several suborbits). (*a*) *If $G_j \leqslant G_i \leqslant G$, the coset representation $G(/G_i)$ governs a G_i-block that has a set of suborbits represented by*

$$\sum_j \beta_j G_i(/G_j), \tag{21}$$

where the summation is over a given set of subgroups satisfying the above condition; and β_j's are non-negative integers.

(b) The orbit that is produced by all of such blocks as equivalent to the G_i-block is subject to the CR represented by

$$\sum_j \beta_j G(/G_j). \tag{22}$$

The first proposition of this theorem means that an orbit (a set of equivalent atoms or ligands) appearing in a given molecule corresponds to a coset representation, $G(/G_i)$, in one-to-one fashion and that each member of the orbit belongs to a site-symmetry of G_i. This theorem affords mathematical foundations to the subduction of coset representation (SCR) notation [19] and to the concept of chirality fittingness [25].

Figure 2 illustrates orbits and CRs for the T_d group, in which a set of atoms marked with open circles in a molecule are the members of each orbit. The orbit (1) contains 24 hydrogen atoms, which construct a regular body of the T_d symmetry. This orbit is governed by RR ($T_d(/C_1)$). The other orbits (2–5) can be determined to correspond to the respective CRs. The assignment of each orbit to a coset representation is conducted easily as follows. Consider orbit (3) of Fig. 2, the six-membered orbit of T_d found in adamantane. When we use all the symmetry operations concerning every subsymmetry of T_d on (3), we obtain an FPV: $F = (6\,2\,2\,0\,0\,0\,2\,0\,0\,0\,0)$, the elements of which are aligned according to $SSG_{T_d} = \{C_1, C_2, C_s, C_3, S_4, D_2, C_{2v}, C_{3v}, D_{2d}, T, T_d\}$. Since this vector is identical with the $T_d(/C_{2v})$ row of Table 5, we can conclude that the orbit (3) is subject to the CR $T_d(/C_{2v})$.

Figure 2 also exemplifies the interrelation of these orbits, which has been shown generally in Fig. 1. The twelve methylene carbons of (1), each of which is attached by a pair of hydrogens selected from the 24 hydrogen atoms of the $T_d(/C_1)$ orbit, construct a $T_d(/C_s)$ orbit. Note that this orbit is equivalent to the orbit (2) in a geometrical sense. This fact is an example of Lemma 1, since each pair of hydrogens in the methylene group is considered to be a C_s-block governed by $C_s(/C_1)$.

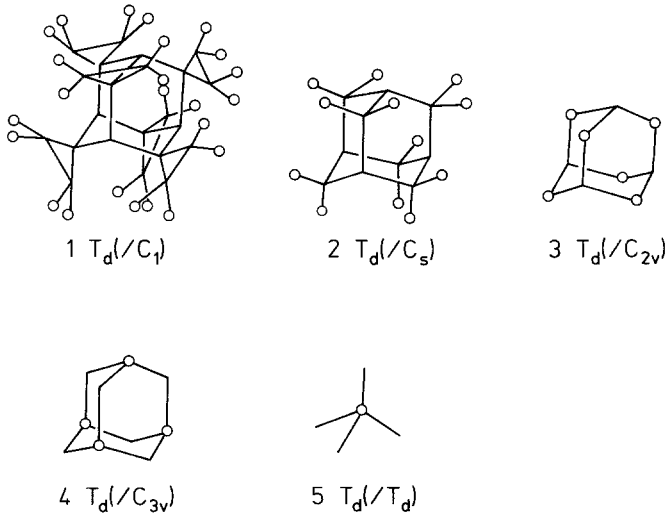


Fig. 2. Orbits of the T_d point group

These methylene carbons (belonging to the 12-membered $T_d(/C_s)$ orbit) are, in turn, divided into six pairs (C_{2v}-blocks) if every cyclopropane ring is taken into consideration. Each pair in the cyclopropane ring is considered to link to the remaining cyclopropane carbon at each spiro-position. Then, the latter six carbon atoms at the spiro-positions are concluded to belong to a $T_d(/C_{2v})$ orbit, which is equivalent to the orbit (3). This fact exemplifies Lemma 2, since the pair in such a cyclopropane ring is regarded as a C_{2v}-block having a $C_{2v}(/C_s)$ orbit.

From an alternative point of view, each of the six cyclopropane rings as a whole can be considered to be a C_{2v}-block that contains four hydrogen atoms ($C_{2v}(/C_1)$), two carbon atoms ($C_{2v}(/C_s)$) and one carbon atom ($C_{2v}(/C_{2v})$). Six such blocks construct a $T_d(/C_{2v})$ orbit. This fact verifies Theorem 1. The relationship between the 24 hydrogens ($T_d(/C_1)$) and the 4 bridgehead carbons ($T_d(/C_{3v})$) can be also recognized by inspection.

It is worthwhile mentioning the differences between our approach and the Fowler–Quinn one [6]. Fowler and Quinn consider that each orbit (O_A) is characterized by a site-symmetry group, H_A, a subgroup of G which describes the symmetry of a given molecule, and that the reducible representation of G generated by a σ function on each member of the orbit is a permutation representation. Thus, their concept of orbit, site-symmetry, and permutation representation are presented rather separately. On the other hand, our approach indicates that an orbit is governed by a coset representation $G(/H)$ which comes from a coset decomposition of G by a subgroup H. The assignment of a CR to such an orbit can be algebraically accomplished by means of a mark table. Moreover, each fragment of the orbit belongs to the H site-symmetry which appears in the symbol $G(/H)$. Hence, our concepts of orbit, site-symmetry, and CR are closely unified in terms of such a key concept the CR.

2.4. Selection rules for coset representations

Lemmas 1 and 2 clarify whether a coset representation is allowed or forbidden to govern a set of points as a 3D object.

Theorem 2 (forbidden CRs). *The coset representation $G(/G_j)$ is forbidden,*
(a) if G_j ($< G$) has S_n ($n \geqslant 2$) as a symmetry operation,
(b) if G_j ($< G$) is one of polyhedral groups (T, O and I) or of dihedral groups (D_n),
(c) if G_j ($< G_i \leqslant G$) is C_n ($n \geqslant 2$) and G_i ($\leqslant G$) is C_{nv}, or
(d) if G_j ($< G_i \leqslant G$) is $C_{n(v)}$ ($n \geqslant 2$) and G_i ($\leqslant G$) is $C_{m(v)}$.

The rule (a) can be proven as follows. Consider a regular body of G symmetry. Lemma 1 indicates that the CR $G(/G_j)$ governs $\Omega = \{\Omega_1, \Omega_2, \ldots, \Omega_r\}$, each element of which has a $G_j(/G_{j1})$ orbit. The problem may be restated: Can every element correspond to a different point at a general position or not? The condition described in (a) requires that the center of each G_j object (Ω_p; $p = 1, 2, \ldots,$ or r) is identical with the origin of the G-body. This means that none of the G_j objects corresponds to points at general positions. Hence, $G(/G_j)$ is forbidden. If G_j is equal to G, then $G(/G_j)$ is allowed to govern the origin as an orbit. Obviously, the same restriction gives rise to the rule (b).

If (c) is true, Lemma 2 indicates that $\Omega^{(1)} = \{\Omega_{11}, \Omega_{12}\}$ is subject to $C_{nv}(/C_n)$. The symmetries of Ω_{11} and Ω_{12} are both C_n. In addition, they are antipodal with each other. This means the centers of the two blocks are identical with each

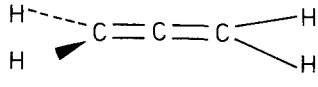
other. Since the total effect is represented by the CR $G(/C_n)$ according to Lemma 2, the CR $G(/C_n)$ is forbidden.

If (d) holds, Lemma 2 shows that $G(/C_{mv})$ governs $\mathbf{\Omega}$, that $C_{mv}(/C_{nv})$ governs $\mathbf{\Omega}^{(1)}$, and that $G(/C_{nv})$ governs $\hat{\mathbf{\Omega}}$. The symmetry of Ω_1 ($\in \mathbf{\Omega}$) is C_{mv}, while that of subblocks (Ω_{11} etc. $\in \mathbf{\Omega}^{(1)}$) is C_{nv}. This means that the center of the former block is identical with those of the latter subblocks. Hence, the CR $G(/C_{nv})$ is forbidden. The same situation holds for the case of C_n and C_m.

In order to illustrate Theorem 2, consider the set of coset representations for T_d described in Table 5. The rule (a) of Theorem 2 forbids $T_d(/S_4)$ and $T_d(/D_{2d})$. The rule (b) indicates the absence of $T_d(/D_2)$ and $T_d(/T)$. The rule (c) does not allow $T_d(/C_2)$ and $T_d(/C_3)$. There are no cases avoided by the rule (d). As a result, there remain allowed five CRs: $T_d/(C_1)$, $T_d(/C_s)$, $T_d(/C_{2v})$, $T_d(/C_{3v})$, and $T_d(/T_d)$. Figure 2 depicts the allowed CRs for the T_d group.

Application of Theorem 2 to D_{2d} gives $D_{2d}(/C_2)$ (rule c), $D_{2d}(/S_4)$ (rule a), and $D_{2d}(/D_2)$ (rule b) as forbidden CRs. The remaining CRs are allowed: $D_{2d}(/C_1)$, $D_{2d}(/C_2')$, $D_{2d}(/C_s)$, $D_{2d}(/C_{2v})$, and $D_{2d}(/D_{2d})$. This result is identical with that collected in Table 1. The following example illustrates a more algebraic method than the assignments described for Fig. 2.

Example 1 (orbits of allene (6)).



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Allene (6) has D_{2d} symmetry and is composed of 3 carbon and 4 hydrogen atoms. When we operate on (6) with the symmetry operations of each subsymmetry of the D_{2d} and count fixed points, we obtain an FPV: $F = (7\ 3\ 1\ 5\ 1\ 3\ 1\ 1)$ according to Eq. (9). The vector is then introduced into Eq. (7) [or equivalently Eqs. (5) or (6)]. The use of Table 3 as M^{-1} affords an MV: $E = (0\ 0\ 0\ 1\ 0\ 1\ 0\ 1)$ (or solutions: $\alpha_{C_s} = 1$, $\sigma_{C_{2v}} = 1$ and $\alpha_{D_{2d}} = 1$). This vector means that there is a $D_{2d}(/C_s)$ orbit, a $D_{2d}(/C_{2v})$ orbit, and a $D_{2d}(/D_{2d})$ orbit. These are determined by inspection to be the 4 hydrogens; the 2 carbons; and 1 central carbon. At the same time, we conclude that the site symmetries of the $D_{2d}(/C_s)$, $D_{2d}(/C_{2v})$, and $D_{2d}(/D_{2d})$ orbits are C_s, C_{2v}, and D_{2d}, respectively. Equation (4) for this case is represented by

$$P_{D_{2d}} = D_{2d}(/C_s) + D_{2d}(/C_{2v}) + D_{2d}(/D_{2d}). \tag{23}$$

This situation is denoted by the SCR notation: $D_{2d}[/C_s(H_4); /C_{2v}(C_2); /D_{2d}(C)]$ [19].

In terms of Theorem 2, we can determine the allowance of CRs for every point group. Note that this theorem holds only for an orbit containing atoms or ligands (not for an orbit containing bonds or faces). Tables 8 to 10 indicate allowed CRs for D_2, D_{2d}, T_d and D_{3h} point groups.

2.5. Derivation of Brester's equations and of the k-value equations of framework groups

Equation (4) provides a partition of Δ into $\sum_{i=1}^{s} \alpha_i$ orbits,

$$\Delta_{i\alpha} \quad (i = 1, \ldots, s; \alpha = 1, 2, \ldots, \alpha_i),$$

where α_i of the orbits are subject to $\boldsymbol{G}(/\boldsymbol{G}_i)$. Since the size of an orbit ($|\Delta_{i\alpha}|$) is equal to $|\boldsymbol{G}|/|\boldsymbol{G}_i|$, then

$$|\Delta| = \sum_{i=1}^{s} \alpha_i |\boldsymbol{G}|/|\boldsymbol{G}_i|. \tag{24}$$

Theorem 2 indicates that α_i is equal to 0 for a forbidden $\boldsymbol{G}_i$. Hence, Eq. (24) contains the Brester equation [10] and an equivalent framework-group equation [20] as special cases, although they are different in their explicit forms. In order to illustrate this equivalency, we here refer to the $\boldsymbol{T}_d$ symmetry as an example. Since $|\boldsymbol{T}_d|/|\boldsymbol{C}_1| = 24$, $|\boldsymbol{T}_d|/|\boldsymbol{C}_2| = 12$, and so on, Eq. (24) can be written as

$$\begin{aligned} |\Delta| = {} & 24\alpha_{\boldsymbol{C}_1} + 12\alpha_{\boldsymbol{C}_2} + 12\alpha_{\boldsymbol{C}_s} + 8\alpha_{\boldsymbol{C}_3} + 6\alpha_{\boldsymbol{S}_4} + 6\alpha_{\boldsymbol{D}_2} + 6\alpha_{\boldsymbol{C}_{2v}} \\ & + 4\alpha_{\boldsymbol{C}_{3v}} + 3\alpha_{\boldsymbol{D}_{2d}} + 2\alpha_{\boldsymbol{T}} + \alpha_{\boldsymbol{T}_d}. \end{aligned} \tag{25}$$

The above discussion on the allowability of CRs for the $\boldsymbol{T}_d$ group indicates that

$$\alpha_{\boldsymbol{C}_2} = 0, \quad \alpha_{\boldsymbol{C}_3} = 0, \quad \alpha_{\boldsymbol{S}_4} = 0, \quad \alpha_{\boldsymbol{D}_2} = 0, \quad \alpha_{\boldsymbol{D}_{2d}} = 0, \quad \text{and } \alpha_{\boldsymbol{T}} = 0,$$

for the forbidden CRs. With respect to the allowed CRs, we denote the corresponding terms as

$$\alpha_{\boldsymbol{C}_1} = m = k_1, \quad \alpha_{\boldsymbol{C}_s} = m_d = k_2, \quad \alpha_{\boldsymbol{C}_{2v}} = m_2 = k_3,$$
$$\alpha_{\boldsymbol{C}_{3v}} = m_3 = k_4, \quad \text{and } \alpha_{\boldsymbol{T}_d} = m_0 = k_5.$$

Thereby, Eq. (25) is converted into

$$N = 24m + 12m_d + 6m_2 + 4m_3 + m_0, \tag{26}$$

where $N = |\Delta|$, and into

$$\Sigma = 24k_1 + 12k_2 + 6k_3 + 4k_4 + k_5, \tag{27}$$

where $\Sigma = |\Delta|$. These equations are identical with those derived alternatively by Brester's method [10] and the framework-group method [20].

For practical purposes, however, it is unnecessary to consider such allowability of CRs in an explicit fashion. Thus, Theorem 2 is satisfied *spontaneously* upon solving Eqs. (5) to (7). For example, Eq. (23) derived in Example 1 proves to satisfy the selection rule of Theorem 2. According to this equation, we obtain

$$7 = 4\alpha_{\boldsymbol{C}_s} + 2\alpha_{\boldsymbol{C}_{2v}} + \alpha_{\boldsymbol{D}_{2d}}, \tag{28}$$

where $\alpha_{\boldsymbol{C}_s} = 1$, $\alpha_{\boldsymbol{C}_{2v}} = 1$ and $\alpha_{\boldsymbol{D}_{2d}} = 1$. Although this equation is the counterpart of the Brester expression of this case, the present approach obviously affords more detailed information. Since the solution of Eq. (5) or the related equations is quite easy, the present approach has several advantages over the Brester approach, as well as over the framework-group approach.

3. Symmetry adapted functions

3.2. Character tables for coset representations

A reducible representation of $\boldsymbol{G}$ by ligand σ-orbital combinations is called a permutation representation of $\boldsymbol{G}$. The character of this representation (σ-character) is important in the construction of SALCs. The σ-character has been obtained by several methods: (a) inspecting the effect of symmetry orbitals on the set of points in the orbit [1], (b) using the matching technique [6–8], and so on. The discussion in the preceding section indicates that the σ-representation is equivalent to a coset representation, which is formulated originally as acting on a set of cosets. This fact affords an alternative method of calculating σ-characters; these are equal to the characters of coset representations.

We have so far treated the CR as a permutation representation; however, they can be manipulated in the form of a matrix representation. Suppose a permutation of the CR is represented by

$$\boldsymbol{G}(/\boldsymbol{G}_i)_g = \begin{pmatrix} 1 & 2 & \cdots & k & \cdots & r \\ a_1 & a_2 & \cdots & a_k & \cdots & a_r \end{pmatrix}, \tag{29}$$

where $g \in \boldsymbol{G}$ and $\boldsymbol{G}(/\boldsymbol{G}_i)_g \in \boldsymbol{G}(/\boldsymbol{G}_i)$. We then construct a matrix in which the intersecting element of the a_k th column and the kth row is unit and others of the a_k th column and of the kth row are all zero, i.e.,

$$A^{\boldsymbol{G}(/\boldsymbol{G}_i)}(g) = \begin{array}{c} \\ 1 \\ \vdots \\ \\ k \\ \\ \vdots \\ r \end{array} \begin{array}{c} \begin{array}{ccccccccc} & & \cdots & & a_k & & \cdots & & \end{array} \\ \begin{pmatrix} & & & & 0 & & & & \\ & & & & \vdots & & & & \\ & & & & 0 & & & & \\ 0 & \cdots & 0 & 1 & 0 & \cdots & 0 & & \\ & & & & 0 & & & & \\ & & & & \vdots & & & & \\ & & & & 0 & & & & \end{pmatrix} \end{array}. \tag{30}$$

The matrix representation:

$$\boldsymbol{A}^{\boldsymbol{G}(/\boldsymbol{G}_i)} = \{A^{\boldsymbol{G}(/\boldsymbol{G}_i)}(g) \,|\, \forall g \in \boldsymbol{G}\} \tag{31}$$

corresponds to the CR ($\boldsymbol{G}(/\boldsymbol{G}_i)$) in one-to-one fashion. Since any coset representation is available as a kind of permutation representation by examining a coset decomposition as shown in Table 1, the corresponding matrix (Eq. 31) is easily constructed.

The trace of each matrix (Eq. 30) of $\boldsymbol{A}^{\boldsymbol{G}(/\boldsymbol{G}_i)}$ constructs the corresponding σ-character, which is represented by $\gamma^{\boldsymbol{G}(/\boldsymbol{G}_i)}$. Obviously, the trace of the matrix (Eq. 30) is equal to the number of fixed points during the permutation (Eq. 29). Thereby, we can calculate the character $\gamma^{\boldsymbol{G}(/\boldsymbol{G}_i)}$. This calculation is easy if such a permutation is represented in the form of a product of cycles as shown in Table 1. From the data of Table 1, we obtain the character table of CRs for the $\boldsymbol{D}_{2d}$ group (Table 7). Table 7 also contains allowed CRs marked by an asterisk as well as irreducible representations (IR) for every CR. Similarly, we construct several character tables of CRs (Tables 8 to 10).

Table 7. Character table of CRs for D_{2d}

	I	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	Allowed	IR
$D_{2d}(/C_1)$	8	0	0	0	0	*	$A_1+A_2+B_1+B_2+2E$
$D_{2d}(/C_2)$	4	0	4	0	0		A_1+A_2+E
$D_{2d}(/C_2')$	4	0	0	2	0	*	A_1+B_1+E
$D_{2d}(/C_s)$	4	0	0	0	2	*	A_1+B_2+E
$D_{2d}(/S_4)$	2	2	2	0	0		A_1+A_2
$D_{2d}(/C_{2v})$	2	0	2	0	2	*	A_1+B_2
$D_{2d}(/D_2)$	2	0	2	2	0		A_1+B_1
$D_{2d}(/D_{2d})$	1	1	1	1	1	*	A_1

Table 8. Character table of CRs for D_2

	I	$C_{2(z)}$	$C_{2(x)}$	$C_{2(y)}$	Allowed	IR
$D_2(/C_1)$	4	0	0	0	*	$A+B_1+B_2+B_3$
$D_2(/C_2)$	2	2	0	0	*	$A+B_1$
$D_2(/C_2')$	2	0	2	0	*	$A+B_2$
$D_2(/C_2'')$	2	0	0	2	*	$A+B_3$
$D_2(/D_2)$	1	1	1	1	*	A

Table 9. Character table of CRs for T_d

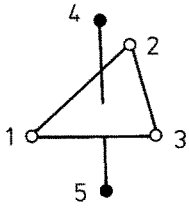
	I	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Allowed	IR
$T_d(C_1)$	24	0	0	0	0	*	$A_1+A_2+2E+3T_1+3T_2$
$T_d(C_2)$	12	0	4	0	0		$A_1+A_2+2R+T_1+T_2$
$T_d(C_s)$	12	0	0	0	2	*	$A_1+E+T_1+2T_2$
$T_d(C_3)$	8	2	0	0	0		$A_1+A_2+T_1+T_2$
$T_d(S_4)$	6	0	2	2	0		A_1+E+T_1
$T_d(D_2)$	6	0	6	0	0		A_1+A_2+2E
$T_d(C_{2v})$	6	0	2	0	2	*	A_1+E+T_2
$T_d(C_{3v})$	4	1	0	0	2	*	A_1+T_2
$T_d(D_{2d})$	3	0	3	1	1		A_1+E
$T_d(T)$	2	2	2	0	0		A_1+A_2
$T_d(T_d)$	1	1	1	1	1	*	A_1

Table 10. Character table of CRs for D_{3h} point group

	I	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Allowed	IR
$D_{3h}(/C_1)$	12	0	0	0	0	0	*	$A_1'+A_2'+2E'+A_1''+A_2''+2E''$
$D_{3h}(/C_2)$	6	0	2	0	0	0		$A_1'+E'+A_1''+E''$
$D_{3h}(/C_s)$	6	0	0	0	0	2	*	$A_1'+E'+A_2''+E''$
$D_{3h}(/C_s')$	6	0	0	6	0	0	*	$A_1'+A_2'+2E'$
$D_{3h}(/C_3)$	4	4	0	0	0	0		$A_1'+A_2'+A_1''+A_2''$
$D_{3h}(/C_{2v})$	3	0	1	3	0	1	*	$A_1'+E'$
$D_{3h}(/C_{3v})$	2	2	0	2	2	0	*	$A_1'+A_2''$
$D_{3h}(/C_{3h})$	2	2	0	2	2	0		$A_1'+A_2'$
$D_{3h}(/D_3)$	2	2	2	0	0	0		$A_1'+A_1''$
$D_{3h}(/D_{3h})$	1	1	1	1	1	1	*	A_1'

A mark table for a CR is closely related to a character table for the same CR. They are both concerned with invariants on symmetry operations. Compare Table 2 with Table 7; and Tables 4 to 6 with Table 8 to 10. As a result, we can assign a CR to an orbit by using a character table in place of the corresponding mark table. This procedure is illustrated as follows.

Example 2 (orbits and onset representations appearing in a trigonal bipyramid (7)).



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A trigonal bipyramid (7) has 5 positions, which are divided into two orbits, $\Delta_1 = \{1, 2, 3\}$ and $\Delta_2 = \{4, 5\}$. Each symmetry operation of $\boldsymbol{D}_{3h}$ fixes several positions of Δ_1, the number of which is counted by inspection, being 3 for I, 0 for the two operations concerning a C_3 axis, 1 for each of the three C_2 axes, 3 for σ_h, 0 for the two operations concerning a S_3 axis, and 1 for the three σ_v planes. These values are identical with those colleced in the $\boldsymbol{D}_{3h}(/\boldsymbol{C}_{2v})$ row of Table 10. Hence, the Δ_1 orbit is subject to the CR $\boldsymbol{D}_{3h}(/\boldsymbol{C}_{2v})$. This assignment, at the same time, allows us to conclude that each member of this orbit belongs to the site-symmetry of $\boldsymbol{C}_{2v}$. In a similar way, the Δ_2 orbit is concluded to be governed by the CR $\boldsymbol{D}_{3h}(/\boldsymbol{C}_{3v})$ and to have a $\boldsymbol{C}_{3v}$ site-symmetry. This method is effective if each orbit can be recognized by inspection. Compare this feature with that of the method described in Example 1.

3.2. A procedure for obtaining SALCs

In the preceding section, σ-characters are given in the form of character tables of CRs. We can thereby obtain π- and δ-representations in the light of the method presented by Quinn et al. [6–8] or of the TSH theory [5, 9]. We here follow the standard method [1] except in the calculation of characters.

We have clarified the relationship between the CR $\boldsymbol{G}(/\boldsymbol{G}_i)$ on $\boldsymbol{\Omega}$ and the RR $\boldsymbol{G}(/\boldsymbol{G}_1)$ on Δ. The CR and RR are here manipulated in the form of matrix representations rather than that of permutation representations. Let $\boldsymbol{B}^{\boldsymbol{G}_i}$ be a matrix representation of $\boldsymbol{G}_i$. Suppose that g_q and g_p are selected from the transversal in Eq. (14). We define $D_{qp}(g)$ using $B^{G_i}(g) \in \boldsymbol{B}^{\boldsymbol{G}_i}$ as being

$$D_{qp}(g) = B^{G_i}(g_q g g_p^{-1}), \tag{32}$$

where $D_{qp}(g) = 0$ if $g_q g g_p^{-1} \notin \boldsymbol{G}_i$. Then, a matrix for an induced representation is

expressed by

$$B^G(g) = \begin{pmatrix} D_{11}(g) & D_{12}(g) & \cdots & D_{1r}(g) \\ D_{21}(g) & D_{22}(g) & \cdots & D_{2r}(g) \\ \vdots & \vdots & & \vdots \\ D_{r1}(g) & D_{r2}(g) & \cdots & D_{rr}(g) \end{pmatrix} . \tag{33}$$

This matrix is rewritten according to Eq. 30 to be

$$B^G(g) = \begin{array}{c} \\ 1 \\ \vdots \\ \\ k \\ \vdots \\ r \end{array} \begin{array}{c} \begin{array}{ccccccc} & \cdots & & a_k & & \cdots & \end{array} \\ \begin{pmatrix} & & & 0 & & & \\ & & & \vdots & & & \\ & & & 0 & & & \\ 0 & \cdots & 0 & D_{ka_k} & 0 & \cdots & 0 \\ & & & \vdots & & & \\ & & & 0 & & & \end{pmatrix} \end{array} , \tag{34}$$

which constructs an induced representation,

$$\boldsymbol{B}^G = \{B^G(g) \,|\, \forall g \in \boldsymbol{G}\} . \tag{35}$$

A non-zero matrix appears once in every row and once in every column. Moreover, as shown in Eq. (34), a non-zero $D_{qp}(g)$ in Eq. (32) corresponds to the unit at the intersection of the qth ($= k$th) row and the pth ($= a_k$th) column in Eq. (30). If the representation $\boldsymbol{B}^{G^i}$ is the RR of $\boldsymbol{G}_i$, Eq. (35) is an alternative form of the RR.

The character of the representation $\boldsymbol{B}^G$ is obtained to be

$$\Gamma^G(g) = \sum_{p=1}^{r} \mathrm{tr}(D_{pp}(g)), \tag{36}$$

wherein $\mathrm{tr}(D_{pp}(g))$ is the trace of $D_{pp}(g)$. Note that $D_{pp}(g) = 0$ if $g_p g g_p^{-1} \notin \boldsymbol{G}_i$. If any conjugate class of $\boldsymbol{G}$ is not divided into two or more conjugate classes of $\boldsymbol{G}_i$, any non-zero $\mathrm{tr}(D_{pp}(g))$ is equal to $\chi^{G_i}(g)$ which is a character of $\boldsymbol{B}^{G_i}$. Because of the correspondence between Eq. (30) and Eq. (34) (or Eq. 33), the number of non-zero D_{pp} is equal to the character of $\mathbf{A}^{G(/G_i)}$, which is represented by $\gamma^{G(/G_i)}$. Thereby, Eq. (36) can be converted into a more convenient form:

$$\Gamma^G(g) = \gamma^{G(/G_i)}(g) \times \chi^{G_i}(g), \tag{37}$$

where $\chi^{G_i}(g)$ is equal to 0 if $g \notin \boldsymbol{G}_i$. The $\boldsymbol{B}^G$ representation can be reduced into irreducible representations by applying the orthogonality theorem [1] to the character $(\Gamma^G(g))$.

In the following paragraphs, a systematic application of the present method will be outlined stepwise. We will construct the molecular orbitals starting from the p-type atomic orbitals on the ligands in a tetrahedral complex (Fig. 3).

Step 1 is the recognition of orbits in this complex (8). This molecule is determined to have two orbits, $\Delta_1 = \{1, 2, 3, 4\}$ and $\Delta_2 = \{5\}$. We only take the Δ_1 orbit into consideration for simplicity of discussion.

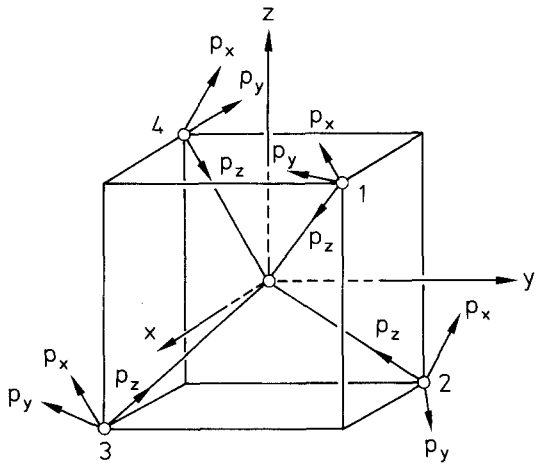

Fig. 3. Orbitals of a tetrahedral complex (8)

In step 2, we assign a CR to this orbit. Thus, the FPV of A_1 is obtained to be $F = (4\,0\,2\,1\,0\,0\,0\,1\,0\,0\,0)$, which is identical to the $T_d(/C_{3v})$ row of the mark table for T_d (Table 5). This means that the A_1 orbit is subject to the CR $T_d(/C_{3v})$. This step can be effected alternatively in an algebraic fashion by using Eq. (6) (see Example 1). It should be emphasized that *this assignment spontaneously determines the site-symmetry of each member of* A_1 *as being* C_{3v}.

Step 3 is an application of Eq. (37) to this case. First, we consider p_z orbitals of the four ligand positions. The character table of the CR (Table 9) affords the $\gamma^{T_d(/C_{3v})}$ values. According to the C_{3v} site-symmetry, we select an A_1 representation for the p_z orbit from a character table for the C_{3v} point group [1]. Thereby, we calculate the character of this case.

	I	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\gamma^{T_d(/C_{3v})}$	4	1	0	0	2
A_1 for C_{3v}	1	1	(0)	(0)	1
$\Gamma_{p\sigma}$	4	1	0	0	2

The character $\Gamma_{p\sigma}$ can be reduced by means of a character table of the T_d point group [1]. It follows that

$$\Gamma_{p\sigma} = A_1 + T_2. \tag{38}$$

Obviously, this result is identical to that of Table 9 which is obtained by using the character of $T_d(/C_{3v})$ itself. Since this relationship holds for general cases, Tables 8 to 10 list such reductions, as pre-estimated from the characters of CRs.

Since p_x and p_y are degenerated forming an E representation under the C_{3v} site-symmetry, step 3 is expressed by

	I	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\gamma^{T_d(/C_{3v})}$	4	1	0	0	2
E for C_{3v}	2	−1	(0)	(0)	0
$\Gamma_{p\pi}$	8	−1	0	0	0

This means that

$$\Gamma_{p\pi} = E + T_1 + T_2. \tag{39}$$

Step 4 is the construction of SALC(s) for each irreducible representation. This is accomplished by using projection operators [1]. For example, we construct SALCs concerning T_2 or $\Gamma_{p\sigma}$. Projection operators for this irreducible representation are calculated as follows:

$$\hat{P}_{11}^{(T_2)} = (3/24)\{I + C_{2(1)} - C_{2(2)} - C_{2(3)} - \sigma_{d(2)} - \sigma_{d(4)} + S_{4(1)} + S_{4(1)}^3\}, \tag{40}$$

$$\hat{P}_{22}^{(T_2)} = (3/24)\{I - C_{2(1)} + C_{2(2)} - C_{2(3)} - \sigma_{d(3)} - \sigma_{d(5)} + S_{4(2)} + S_{4(2)}^3\} \tag{41}$$

and

$$\hat{P}_{33}^{(T_2)} = (3/24)\{I - C_{2(1)} - C_{2(2)} - C_{2(3)} - \sigma_{d(1)} - \sigma_{d(6)} + S_{4(3)} + S_{4(3)}^3\}. \tag{43}$$

When we apply these projection operators on the $p_z^{(1)}$ orbit, we obtain (unnormalized):

$$\hat{P}_{11}^{(T_2)} p_z^{(1)} = p_z^{(1)} - p_z^{(2)} + p_z^{(3)} - p_z^{(4)}, \tag{44}$$

$$\hat{P}_{22}^{(T_2)} p_z^{(1)} = p_z^{(1)} + p_z^{(2)} + p_z^{(3)} - p_z^{(4)} \tag{45}$$

and

$$\hat{P}_{33}^{(T_2)} p_z^{(1)} = p_z^{(1)} - p_z^{(2)} - p_z^{(3)} + p_z^{(4)}. \tag{46}$$

The SALCs are identical with those reported previously [1]. SALCs for the other irreducible representations can be obtained in a similar way.

4. Conclusion

The correspondence between an orbit of a given molecule and a coset representation $G(/G_i)$ was clarified in terms of a regular body. This correspondence affords a general equation that contains Brester's equations and k-value equations of framework groups as special cases. In addition, a $G(/G_i)$ orbit was proved to have a G_i site-symmetry. The method of assigning a CR to an orbit by using a mark table or a character table of CRs also is described. The assigned CR is a basis for a general procedure of obtaining symmetry adapted linear combinations of atomic orbitals.

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