

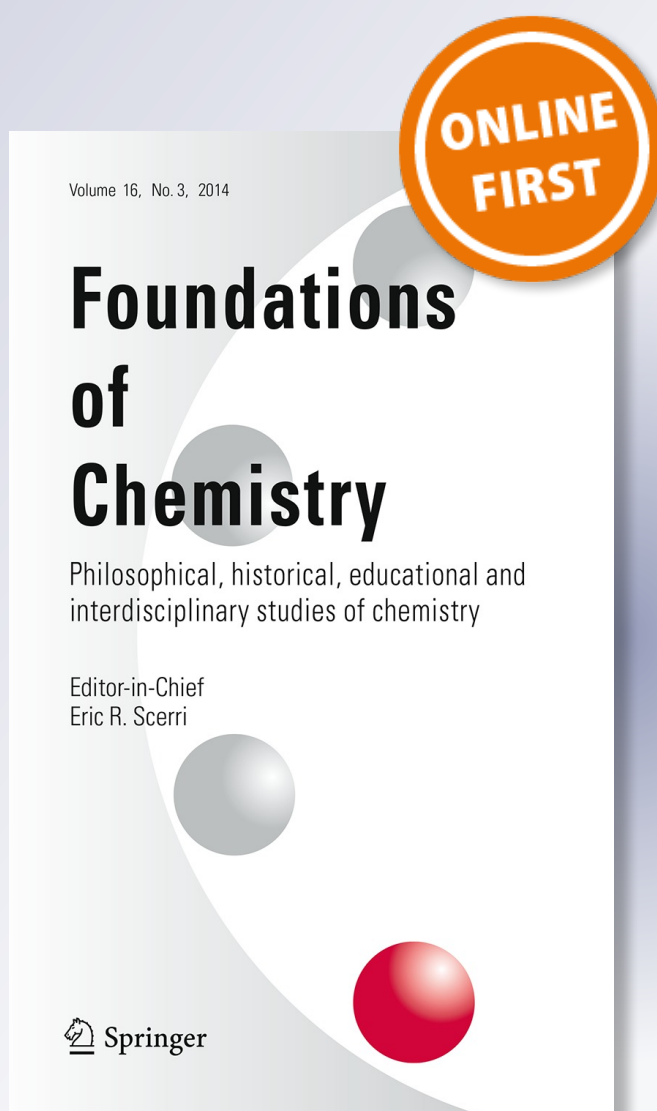
Symmetry and representation in a three dimensional space

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Symmetry and representation in a three dimensional space

Michael Downward¹

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Abstract Schoenflies point groups are presented in terms of spatial partitions and Laue classes based on abstract groups. A much simpler system using only a minimal set of generators for three dimensional groups is then presented in the same form. This simplified treatment allows group operations of a given Laue class to be correlated to a greatly simplified Mulliken-style notation for irreducible representations of that class. Transformation matrix representations of point groups in the simplified style can then be manipulated according to their position in the class or to their sub-groups in very clear procedures. Simple rules can replace the large numbers of tables necessary in the Schoenflies approach. Some applications of the method are described.

Keywords Point groups · Irreducible representations · Matrix reduction · Direct product · Correlation

Introduction

Crystallographic symmetry was fully described in terms of point and space groups in the late nineteenth century following the work of Schoenflies and Federov (Schoenflies 1892; Federov 1891). This treatment preceded the discovery of X-ray diffraction but was later extended to include a fuller treatment of atomic positions in crystalline cells (Schoenflies 1923). Although described in terms of group theory it is important to note that this early work was essentially geometric in its reasoning and, while using group algebra, did not see abstract algebraic structures as a unifying feature. Schoenflies labeled point groups with an ad-hoc collection of geometrical operations then simply numbered space groups corresponding to each of these point groups. C. Hermann and H. Mauguin later developed an approach that incorporated translational operations into a space group notation that became an international

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standard for crystallography. (Hermann 1928; Mauguin 1931). Published work in atomic and molecular structure continued to use a version of the Schoenflies approach augmented to include non-crystallographic rotations because most of the advantages of the International System are limited to descriptions of crystallographic space groups. Typically, point group symmetry is applied to atomic and molecular quantum mechanical problems in order to clarify or simplify computation by reducing representations of groups to their irreducible representations (irreps). (Mulliken 1955). Mulliken notation is derived from a geometrical point group system intended to describe the external morphology of crystals and can only be adapted for atomic use with the aid of large numbers of tables. This complex and convoluted approach not only makes it very difficult to understand the subject but also guarantees mistakes. For example, R.B. Shirts noted that mistakes in group theory tables have been propagated through the literature for periods of 50 years. (Shirts 2007). This article describes point groups in 3D space in terms of the abstract groups to which they belong and presents much simpler, more intuitive notations that facilitate computation. It shows that using the irrep symbols of the defining abstract group in a Laue class for all members of the class allows simple deductions to be made from the point group generator symbols.

Geometrical point groups in an n -dimensional space belong to partitions labeled by a bracketed set of positive integers with sum n so a 3 dimensional space admits partitions [1,1,1], [2,1] and [3]. Laue classes are sets of groups within partitions that each contain one rotational group, a small number of groups isomorphic to the rotational group together with a centrosymmetric group obtained as the direct product of any of these groups with space inversion. This classification arose in X-ray diffraction because this process adds a centre of symmetry to the crystalline group being observed. It is also of interest in areas such as Raman spectroscopy because the process is also insensitive to space inversion. Table 1

Table 1 Point groups—Schoenflies notation

Partition	System	G	\bar{G}	Gi
[1,1,1]	Triclinic	C_1		C_i
	Monoclinic	C_2		C_s C_{2h}
	Orthogonal	D_2	C_{2v}	D_{2h}
[2,1]	Trigonal	C_3		S_6 D_{3d}
		D_3	C_{3v}	
	Tetragonal	C_4		S_4 C_{4h}
		D_4	C_{4v}	D_{2d} D_{4h}
	Pentagonal	C_5		S_{10} D_{5d}
		D_5	C_{5v}	
	Hexagonal	C_6		C_{3h} C_{6h}
		D_6	C_{6v}	D_{3h} D_{6h}
	Heptagonal	C_7		S_{14} D_{7d}
		D_7	C_{7v}	
	Octagonal	C_8		S_8 C_{8h}
		D_8	C_{8v}	D_{4d} D_{8h}
	Infinite	C_∞		$C_{\infty h}$ $D_{\infty h}$
	D_∞	$C_{\infty v}$		
[3]	Tetrahedral	T		T_h
	Octahedral	O		T_d O_h
	Icosahedral	I		I_h

shows Schoenflies groups arranged in Laue classes with a rotational group (G) in the left column, non-rotational groups (\bar{G}) of the same order in the two middle columns and a centrosymmetric group (Gi) of twice the order on the right. The Schoenflies system labels cyclic and dihedral rotational groups in the [1,1,1] and [2,1] partitions with symbols C_n and D_n , using a notation now generally accepted for the corresponding *abstract* groups. Groups of the [1,1,1] partition contain only those operations in which points on x , y , and z axes are transformed into plus or minus themselves. These are groups in which the only allowed operations are 180° rotations, combinations of such rotations with space inversion and the identity operation. Groups of the [2,1] partition might transform points on two axes into each other while always transforming points on the other axis, usually chosen to be z , into plus or minus itself. Groups in the [3] partition contain operations that transform points on all three axes into each other.

Non-rotational groups in these partitions are described by combinations of rotational motion and mirror reflections in an ad-hoc variety of planes, producing arbitrary and unnecessarily complex descriptions. For example, tetragonal dihedral groups in this table are given symbols D_4 , C_{4v} and D_{2d} , suggesting that they are quite different in character even though they are three instances of the *same abstract group* i.e. they are *isomorphic* groups. All groups in a given row of the table have this property except for the right-hand column which contains centrosymmetric groups that are simple products of the defining group with space inversion. It is the complex use of mirror reflections in horizontal, vertical and diagonal positions together with rotation-reflection combinations that makes the Schoenflies system so impractical and unhelpful. Each group is treated separately, creating for each one a set of distinct rules and labels that have to be applied to its representations through many pages of tables.

A much simpler presentation based on a minimum number of group generators is shown in Table 2. A limited version of this approach was used in the derivation of crystallographic point groups in higher dimensional spaces (Downward 2011) but references to that paper may be unhelpful because of the different conventions used in crystallographic and molecular work. The generator approach is used here to expose an underlying structure in the Schoenflies system and to use that structure to simplify applications of representation theory.

Rotational cyclic groups of order n in the [1,1,1] and [2,1] sections of the table are labeled n and are produced by repeated applications of a generator $c = 2\pi/n$ radians about the z axis producing a series $c, c^2, c^3, \dots, c^n = E$. Dihedral rotational groups of order $2n$ require a second generator u , consisting of a 2-fold rotation about the y axis that does not generally commute with cyclic rotations about the z axis. These groups are labeled by adding letter u to the cyclic group to give symbol nu . Rotational groups of the [1,1,1] partition contain only 2-fold rotations but it is convenient to consider them as part of a continuous series of cyclic and dihedral groups which, in the [2,1] partition have greater than 2-fold symmetry about the z -axis. Rotational groups in the [3] partition are limited to tetrahedral, octahedral and icosahedral groups labeled 23, 43, 53 with orders 12, 24 and 60. Tetrahedral and octahedral groups 23 and 43 are related in much the same way as cyclic and dihedral groups in the lower partitions.

Space inversion (parity inversion) i inverts points on all three axes and this generator forms a group of order 2. This is the only negative generator necessary to describe point groups and their representations and, because it commutes with every other operation, it is the best possible choice. There are two distinct procedures for forming non-rotational groups from rotational groups

- multiply one rotational group generator by space inversion to give groups \bar{G}
- as direct product groups Gi of a rotational group G and the space inversion group.

Table 2 Point groups—generator notation

Partition	System	G	\bar{G}	Gi	
[1,1,1]	Triclinic	1		i	
	Monoclinic	2	$\bar{2}$	$2i$	
	Orthogonal	$2u$	$2\bar{u}$	$2ui$	
[2,1]	Trigonal	3		$3i$	
		$3u$	$3\bar{u}$	$3ui$	
	Tetragonal	4		$\bar{4}$	$4i$
		$4u$	$4\bar{u}$	$\bar{4}u$	$4ui$
		Pentagonal	5		$5i$
	Hexagonal	$5u$	$5\bar{u}$		$5ui$
		6		$\bar{6}$	$6i$
	Heptagonal	$6u$	$6\bar{u}$	$\bar{6}u$	$6ui$
		7			$7i$
	Octagonal	$7u$	$7\bar{u}$		$7ui$
		8		$\bar{8}$	$8i$
	Infinite	$8u$	$8\bar{u}$	$\bar{8}u$	$8ui$
		∞			∞i
		∞u	$\infty \bar{u}$		∞ui
	[3]	Tetrahedral	23		$23i$
Octahedral		43		$\bar{4}3$	
Icosahedral		53		$53i$	

Table 3 Multiplication table for group 4

	E	c	c^2	c^3
E	E	c	c^2	c^3
c	c	c^2	c^3	E
c^2	c^2	c^3	E	c
c^3	c^3	E	c	c^2

Generator c of cyclic group n may be multiplied by space inversion to produce a negated generator \bar{c} as follows $\bar{c} = ic = ci$ and the group generated shown as \bar{n} . Take as an example, the 4-fold cyclic group multiplication table shown in Table 3. When the rotational 4-fold generator (c) is negated to give generator $\bar{c} = ci$ a series of elements $\bar{c}, c^2, \bar{c}^3, \dots, E$ is produced. Space inversion commutes with all other operations and does not therefore change the structure of the group so groups n and \bar{n} are distinct representations of the same abstract group. Consequently, the multiplication table for group $\bar{4}$ shown in Table 4 is structurally identical to that of group 4 in Table 3 and this will be true for any two cyclic groups n and \bar{n} . Notice that space inversion cancels out in even numbered applications of the generator because even applications of space inversion cancel out as follows: $\bar{c}\bar{c} = cici = ccii = c^2$

Rotational dihedral groups nu have two generators that can be negated, producing isomorphic dihedral groups $n\bar{u}$ and $\bar{n}u$ belonging to the same Laue class and the same row of the table. In the [3] partition only the octahedral Laue class contains a non-rotational isomorph $\bar{4}3$, this being the group that chemists usually describe as tetrahedral because of its misleading Schoenflies label.

Table 4 Multiplication table for group 4

	E	\bar{c}	c^2	\bar{c}^3
E	E	\bar{c}	c^2	\bar{c}^3
\bar{c}	\bar{c}	c^2	\bar{c}^3	E
c^2	c^2	\bar{c}^3	E	\bar{c}
\bar{c}^3	\bar{c}^3	E	\bar{c}	c^2

Non-rotational groups may also be formed as the direct product of a rotational group and the parity inversion group, producing groups that contain the space inversion element (i) itself. Centrosymmetric groups of this kind (Gi) derived from rotational groups G are simple products $G + iG$. Thus the 4-fold cyclic group produces the centrosymmetric group as follows

$$4i = \{E, c, c^2, c^3\} + i\{E, c, c^2, c^3\}$$

A cyclic group n of order n has a direct product centred group ni of order $2n$ while a dihedral group nu of order $2n$ forms a centred group nui of order $4n$. Groups of the [3] partition form centred groups $23i$, $43i$ and $53i$

A given molecule is easily assigned to a point group by first finding its rotational group. Once found this is either the final result or an index-2 subgroup of a very limited number of non-rotational groups. Since there are so few possible larger groups the process is trivial and does not require complex if-then-else tables. Imagine as an example the planar benzene molecule shown in Fig. 1a with the z axis in the centre at right angles to the plane and the y axis cutting through a pair of opposite carbon atoms. Generators 6 and u are visibly present and therefore the molecule belongs to rotational group $6u$. Space inversion is also present so the highest order group for the molecule is $6ui$. Figure 1b shows another molecule with a 3-fold rotation about the z axis and a 2-fold rotation about the y axis so is immediately assigned to the $3u$ rotational point group. This could be an index-2 subgroup of $3ui$ or $\bar{6}u$ but, since some non-rotational symmetry is obvious and it is not centrosymmetric, it must be the latter.

Matrix representations

Matrix representations of groups are constructed to describe transformations of entities such as atoms or vectors during symmetry operations. Matrix representations $D(p)$ and $D(q)$ of group operations p and q multiply out according to the abstract group of the Laue

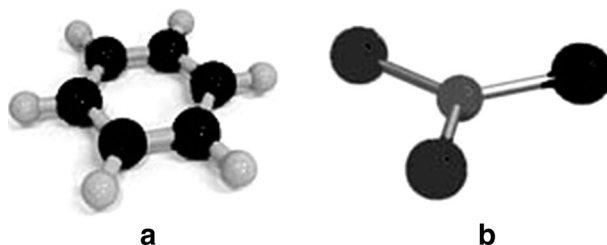
**Fig. 1** Two hexagonal dihedral molecules with symmetries $6ui$ and $\bar{6}u$

Table 5 Hexagonal cyclic irrep table

$\bar{6}$	E	\bar{c}	c^2	\bar{c}^3	c^4	\bar{c}^5			
6	E	c	c^2	c^3	c^4	c^5			
A	1	1	1	1	1	1	z		$R_z, z^2, x^2 + y^2,$
B	1	-1	1	-1	1	-1		z	
E_1	1	ε	ε^2	-1	ε^{2*}	ε^*	(x, y)		$(R_x, R_y)(xz, yz),$
E_{-1}	1	ε^*	ε^{2*}	-1	ε^2	ε		(x, y)	$(x^2 - y^2, xy)$
E_2	1	ε^2	ε^{2*}	1	ε^2	ε^{2*}			
E_{-2}	1	ε^{2*}	ε^2	1	ε^{2*}	ε^2			

class. Only matrices of the generator operations are required to construct all matrices for a given group because, by definition, they generate the group elements. Matrices derived from practical applications are generally reducible in that they may be reduced to a number of irreducible representations (irreps) that are of interest in spectroscopic applications. It is instructive to first look at the hexagonal classes of the [2,1] partition then broaden the treatment to the general case and to the other partitions.

Cyclic groups of order n have n 1D irreps that are easily produced by repeated applications of generators ε^x where x takes values 1 to n and $\varepsilon = e^{i2\pi/n}$. Table 5 shows the hexagonal case after some simplifications have been made. Irreps generated by $\varepsilon^6 = +1$ and $\varepsilon^3 = -1$ are labeled A and B while conjugate pairs of irreps from generators ε^x and $\varepsilon^{n-x} = \varepsilon^{x*}$ are labeled E_x and E_{-x} . These are stem symbols to which subscripts might be added to represent irreps in dihedral and centrosymmetric groups. It is important to note that value x in E_x and E_{-x} is part of the stem, not an added subscript. Isomorphic cyclic groups 6 and $\bar{6}$ have the same irrep table because they belong to the same abstract group and irrep tables are characteristic to the abstract group. Polar vectors x, y and z are assigned to different irreps in each concrete group because of the effect of space inversion. Notice however that assignments for axial vectors are the same because they are not affected by space inversion and those of products are the same because two inversions cancel out. As shown below, the inclusion of these vector assignments in irrep and character tables of the [2,1] partition is unnecessary because they follow a predictable pattern.

Base vector transformation matrices for generator c in the [2,1] partition describe a clockwise rotation in the xy plane and may be shown in real or complex forms as follows

$$D(c) = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} e^{-i\theta} & 0 & 0 \\ 0 & e^{i\theta} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Powers $D(c^2), D(c^3), \dots$ are easily derived by matrix multiplication. Complex forms of base vector transformational matrices are diagonal and already reduced to their irreducible representations. Clearly, x transforms as $e^{-i\theta} = e^{-i2\pi/n}$ which is E_{-1} , y transforms as $e^{i\theta} = e^{i2\pi/n}$ which is E_1 and z transforms as A . It follows that base vectors in all such groups in the [2,1] partition have transformations $A + E_1 + E_{-1}$.

The negated rotational generator $D(c) \times D(i) = D(\bar{c})$ has real and complex base vector transformations

$$D(\bar{c}) = \begin{pmatrix} -\cos \theta & \sin \theta & 0 \\ -\sin \theta & -\cos \theta & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -e^{-i\theta} & 0 & 0 \\ 0 & -e^{i\theta} & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

In this case x transforms as $-e^{-i\theta} = -e^{-i2\pi/n}$. Translating to irrep symbols allows a simple equation

$$-\epsilon^t = \epsilon^{\left(\frac{n}{2}-t\right)*}$$

Thus irrep E_t is “negated” to produce irrep $E_{-\left(\frac{n}{2}-t\right)}$ and irrep E_{-t} to produce $E_{\left(\frac{n}{2}-t\right)}$. A little arithmetic now shows that the negations of E_{-1} and E_1 are $E_{\left(\frac{n}{2}-1\right)}$ and $E_{-\left(\frac{n}{2}-1\right)}$ which are in turn E_{max} and E_{-max} where max is the largest value possible in a given cyclic group. These results are true for any n -fold cyclic group \bar{n} in the [2,1] partition so the base vector transformation matrices always reduce to $B + E_{max} + E_{-max}$.

Space inversion forms a group $\{E, i\}$ with two irreps A_g and A_u as shown in Table 6. Polar vectors in this table transform as A_u and axial vectors as A_g . Centrosymmetric groups have irrep tables that are simply the products of those for the corresponding rotational group and that shown in Table 6. The number of irreps is doubled, one half taking the g subscript the other half the u subscript. It follows that the base vector assignments for all groups in cyclic Laue classes of the [2,1] partition may be summarized as in Table 7.

Dihedral groups in the [2,1] partition contain pairs of cyclic elements c^x and c^{n-x} that collapse into one dihedral class and corresponding pairs of cyclic irreps E_x and E_{-x} that collapse into a single 2D dihedral irrep E_x . On the other hand, 1D cyclic stems A and B acquire subscripts 1 and 2, denoting u_y generator values of 1 and -1 , to give irreps A_1, A_2, B_1 and B_2 . Once again, this simplified Mulliken notation, based on the abstract group of the Laue class, is used to label the hexagonal dihedral irreps in Table 8

Table 6 Irrep table for group i

	E	i	
A_g	1	1	R_x, R_y, R_z
A_u	1	-1	x, y, z

Table 7 Base vector assignments in [2,1] cyclic groups

n	$A + E_1 + E_{-1}$
\bar{n}	$B + E_{max} + E_{-max}$
$n\bar{i}$	$A_u + E_{1u} + E_{-1u}$

Table 8 Hexagonal dihedral character table

$\bar{6}u$	E	\bar{c}	c^2	\bar{c}^3	u_y	\bar{u}_d			
$6\bar{u}$	E	c	c^2	c^3	\bar{u}_y	\bar{u}_d			
$6u$	E	c	c^2	c^3	u_y	u_d			
A_1	1	1	1	1	1	1		z	$z^2, x^2 + y^2$
A_2	1	1	1	1	-1	-1	z		R_z
B_1	1	-1	1	-1	1	-1			
B_2	1	-1	1	-1	-1	1		z	
E_1	2	1	-1	-2	0	0	(x, y)	(x, y)	$(R_x, R_y), (xz, yz)$
E_2	2	-1	-1	2	0	0		(x, y)	$(x^2 - y^2, xy)$

There is a clear correlation between base vector assignments for E_x/E_{-x} pairs in the cyclic table and 2D E_x assignments in the dihedral character table. Stem symbol irreps A and B in the cyclic table also correlate to those of the dihedral table but subscripts have to be added to represent values for the u_y rotation. Notice that subscripts in E_x are part of the stem because they arise from the main generator while those of A and B are additions to the stem symbol. Base vectors x, y and z are transformed by the matrix

$$D(u_y) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

In which the character of the combined x and y transformations is clearly $-1 + 1 = 0$ as it must be because E_x irreps depend only on the stem. However, the factor for the z vector is -1 and so the 1D irrep carries subscript 2. Dihedral group $n\bar{u}$ has the negated generator

$$D(\bar{u}_y) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \times \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and the z vector irrep carries subscript 1. It follows that base vector transformations in groups of dihedral Laue classes of the [2,1] partition always have the values shown in Table 9. A simple relationship exists between the assignments contained in this table. Irreps for $n\bar{u}$ are obtained from those of nu by negating the 1D subscripts i.e. switching between 1 and 2. Those of $n\bar{u}$ are obtained by negating the stem symbol i.e. switching between A and B or between E_x and $E_{(n/2)-x}$ where n is the cyclic order.

As already noted, space inversion has no effect on axial transformations or polar vector products and it is possible to summarise these assignments as in Table 10. However, point groups with main rotational axes of order 3 or 4 do not have E_2 irreps and in these cases the substitutions at the bottom of this table are necessary.

Table 9 Base vector assignments in [2,1] dihedral groups

$nu : A_2 + E_1$
$n\bar{u} : A_1 + E_1$
$\bar{n}u : B_2 + E_{max}$
$nui : A_{2u} + E_{1u}$

Table 10 Axial and product base vector assignments for [2,1] dihedral groups

	Vector prod	Irrep
	$z^2, x^2 + y^2$	A_1
	R_z	A_2
	$(R_x, R_y), (xz, yz)$	E_1
	$(x^2 - y^2, xy)$	E_2
$3u$	$(x^2 - y^2, xy)$	E_1
$4u$	$x^2 - y^2$	B_1
$4u$	xy	B_2

Table 11 Orthorhombic irrep table

$2\bar{u}$	E	c	\bar{u}_y	\bar{u}_x		
$2u$	E	c	u_y	u_x		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	z	xy, R_z
B_1	1	-1	1	-1	y	xz, R_y
B_2	1	-1	-1	1	x	yz, R_x

Irreducible representations in the [1,1,1] and [3] partitions

Groups of the [1,1,1] partition only have 1D irreps labeled by simple binary stems A and B and subscripts 1,2, g and u . Triclinic group irreps are trivial while those of the 2-fold cyclic and dihedral groups, called monoclinic and orthorhombic for historical reasons, are easily derived from the orthorhombic form in Table 11. Irrep tables for the [1,1,1] partition group include base vectors and their simple products x^2, y^2, z^2, xy, xz and yz . Irreps and base vector assignments for cyclic group 2 can be found by ignoring the dihedral subscripts. Irreps and base vector assignments for centrosymmetric groups are found as in the [2,1] partition. Simply add subscript u for polar vectors and g for rotational and polar product vectors.

Tetrahedral and octahedral classes in the [3] partition behave in many ways like cyclic and dihedral groups in the [2,1] partition. The tetrahedral group has one dimensional irreps A, E_1 and E_{-1} together with a three dimensional T irrep but in the octahedral super-group the E_1/E_{-1} pairs collapse into a 2D irrep while the A and T irreps acquire subscripts 1 and 2. In practice only octahedral groups 43, $\bar{4}3$ and $43i$ are of much importance in this partition and base vector assignments for these groups are equally well attached to the octahedral table. Again the centrosymmetric group irreps and base vector assignments are found as in the [2,1] partition.

The simplified Mulliken notation used above described above uses stem symbols A, B, E_x and T with subscripts 1, 2, g and u . It is very useful to distinguish between even and odd values for each of these symbols. Irrep A is always even while irrep B is even or odd when $n/2$ is even or odd. Irrep symbols E_x are even or odd, depending on whether x is an even or odd number. Subscripts 1 and g are even while 2 and u are odd.

Direct products of representations

Direct products of one-dimensional irreps are simple: products of two even or two odd symbols are even while other products are odd. Direct products of 1D and 2D irreps depend only on stems A and B as follows

$$A \times E_x = E_x \quad B \times E_x = E_{(n/2)-x}$$

On other words a product with A reproduces a stem while one with B negates it. Direct products of two 2D irreps are found by adding and subtracting stem numbers as follows

$$E_x \times E_y = E_{y-x} + E_{y+x}$$

Table 12 Interpretation of dihedral E subscripts

Subscript s	0	$<n/2$	$n/2$	$>n/2$
Result	$A_1 + A_2$	E_s	$B_1 + B_2$	E_{n-s}

Since the position is unimportant in direct products it is always possible to set $x \leq y$ so that the result contains only positive subscripts that can be interpreted according to Table 12

Direct products of 1 and 2D irreps in the [3] partition follow these same rules but higher order irreps also occur. In practice only octahedral groups are of importance and only the 3D irreps of this group need to be considered.

Permutation matrix reduction

When a symmetry operation is applied to a molecule containing m atoms an $m \times m$ permutation matrix traces the exchanges of equivalent atoms during the transformation. These matrices, containing only integers 0 and 1, are images of group operations and so a maximum number of 3 generator matrices is sufficient to produce all group operation matrices. Such matrices are generally reducible and chemists use the “great orthogonality theorem” to apply reductions. Unfortunately, the complex nature of the Schoenflies system means that the theorem is applied to isolated groups with no recognition of their subgroups, providing very little insight into the construction of irreps. Two examples now show how a generator approach improves this situation

Consider first the six symmetrically equivalent carbon (or hydrogen) atoms of a planar benzene molecule in Fig. 1a. Instead of attempting to find irreps for these atoms immediately in the highest order point group of the molecule ($6ui$) a stepwise approach is adopted, first finding the irreps in 6, then $6u$ and finally $6ui$. A few simple rules help. Firstly, n equivalent atoms in a cyclic group of order n always yield one irrep of each kind in that group so an hexagonal set produces the 6 irreps shown in the first line of Table 13. When these cyclic group irreps are correlated to those of the dihedral group $6u$ the stem values of the second line are obtained by inspection and only the 1D subscripts have to be added. There are six carbon atoms but group $6u$ is of order 12 and in such cases only the *even* subscript 1 appears, producing the 1D entries in the second line of Table 13. Finally, atoms in the plane of a centrosymmetric molecule have subscript g on irreps with even stems and u on irreps with odd stems. A stepwise approach of this kind is important because there is no advantage in using a higher order point group than is necessary in a computation.

Transformations for x , y and z vectors placed on each of the six carbon atoms are direct products of the permutation irreps of the molecule and the base vector transformation irreps of $6ui$ as follows

Table 13 Irreps for benzene carbon atoms

Point group	Carbon atoms
6	$A + B + E_1 + E_{-1} + E_2 + E_{-2}$
$6u$	$A_1 + B_1 + E_1 + E_2$
$6ui$	$A_{1g} + B_{1u} + E_{1u} + E_{2g}$

Table 14 Irreps for AB_3 molecule

Point group	A atom	B atoms
$\bar{6}$	A	$A + E_2 + E_{-2}$
$\bar{6}u$	A_1	$A_1 + E_2$

$$(A_{1g} + B_{1u} + E_{1u} + E_{2g}) \times (A_{2u} + E_{1u})$$

When this product is multiplied out according to the simplified rules above the result is that which would have been obtained through applications the “great orthogonality theorem” acting on 18 dimensional matrices.

A second example is provided by the AB_3 molecule of Fig. 1b that chemists describe as “trigonal planar” although in fact it belongs to the hexagonal group $\bar{6}u$ of order 12. Again a stepwise approach is adopted, first finding irreps in the cyclic group $\bar{6}$ then correlating these results up to the higher order group. A central atom in any molecule has the highest level symmetry possible and in this particular case the results shown in the first column of Table 14 are obtained. Permutation matrices for the 3 pendent atoms reduce to just the *even* cyclic irreps because only half of the hexagonal positions are populated. Again when the permutation is correlated to the dihedral group a subscript 1 is added to the 1D irrep.

Permutation matrices for the whole AB_3 molecule reduce to irreps $2A_1 + E_2$. Base vector transformations for this molecule may be found from the direct product as follows

$$(2A_1 + E_2) \times (B_2 + E_2)$$

Correlations of irreducible representations

Point group irreps can be correlated to subgroup irreps through a few simple rules. In the [1,1,1] and [2,1] partitions the following rules apply

- Irreps of the main rotational axis n may be correlated to irreps of index- k subgroups with main rotational axis order of n/k and in this case the stems of the irrep labels are changed as follows

$$A \rightarrow A$$

$$B \rightarrow A(k = \text{even}), B \rightarrow B(k = \text{odd})$$

$$E_x \rightarrow E_{x \bmod n/k}$$

In the 2D case only the target subscript ($x \bmod n/k$) is used in this calculation so it could be applied to any 2D irrep from a higher order group. 2D irreps obtained from such a correlation have to be interpreted according to Table 12 above. Dihedral subscripts remain unchanged during stem correlations.

- Correlations from the irreps of dihedral groups ($nu, n\bar{u}$ and $\bar{n}u$) to those of their index-2 cyclic subgroups (n or \bar{n}) involve no more than removing subscripts from 1D irreps.
- Correlations from centrosymmetric group irreps to index-2 rotational or non-rotational subgroups in the same Laue class are straightforward. Irreps with g subscripts simply drop the subscript. An irrep with u subscripts being correlated to

a rotational group also just drops the u subscript. Correlations to non-rotational isomorphs drop the u subscript and change as follows

$$ni \rightarrow \bar{n} \text{ or } nui \rightarrow \bar{n}u \quad \text{negate irrep stem}$$

$$nui \rightarrow n\bar{u} \quad \text{negate dihedral subscript}$$

In the [3] partition again only the octahedral groups 43 and $\bar{4}3$ are of great interest and a separate table correlating irreps with those of the [2,1] partition is required.

Function space vectors in symmetric environments

One-electron orbitals with quantum number l form a $2l + 1$ dimensional function space that transforms similarly to the base vectors already described. For example, when $l = 2$ there are five d orbital functions of form $e^{im\phi}$ where $m = 2, 1, 0, -1, -2$ and if these functions are rotated through α radians about the z axis the set of wave functions is transformed as follows

$$\begin{pmatrix} e^{2i(\phi+\alpha)} \\ e^{i(\phi+\alpha)} \\ e^0 \\ e^{-i(\phi+\alpha)} \\ e^{-2i(\phi+\alpha)} \end{pmatrix} = \begin{pmatrix} e^{2i\alpha} & 0 & 0 & 0 & 0 \\ 0 & e^{i\alpha} & 0 & 0 & 0 \\ 0 & 0 & e^0 & 0 & 0 \\ 0 & 0 & 0 & e^{-i\alpha} & 0 \\ 0 & 0 & 0 & 0 & e^{-2i\alpha} \end{pmatrix} \begin{pmatrix} e^{2i\phi} \\ e^{i\phi} \\ e^0 \\ e^{-i\phi} \\ e^{-2i\phi} \end{pmatrix}$$

Cyclic group irreps E_2, E_1, A, E_{-1} and E_{-2} are obvious in this diagonal transformation matrix and these cyclic irreps correlate upwards to dihedral group irreps E_1, E_2 and A_1 because, for d orbitals, the rotation about the y axis is symmetric. Table 15 shows similar results for l values from 0 to 6 in a ∞u group environment (where the irrep pattern could be expanded infinitely). Orbitals with even l quantum numbers are said to be even functions and have 1D dihedral subscripts of 1 while odd functions have subscript 2. Subscripts of 1D irreps in a $\infty \bar{u}$ environment have to be negated for odd functions but not for even ones because space inversion has no effect in this case. In the centred case ∞ui even orbitals have g irreps and odd ones have u irreps.

Obviously, these irreps only occur when the orbitals are placed in a symmetric environment that permits them and, in the [2,1] partition, the main axial rotation has to be sufficiently large. Finite group irreps may be found by correlation from the infinite order results in Table 15. For example, hexagonal group $6u$ in the [2,1] partition has irreps obtained by correlating the general scheme above to the irreps available in that group,

Table 15 Atomic Orbital irreps in ∞u

l	symbol	irreps
0	s	A_1
1	p	$A_2 + E_1$
2	d	$A_1 + E_1 + E_2$
3	f	$A_2 + E_1 + E_2 + E_3$
4	g	$A_1 + E_1 + E_2 + E_3 + E_4$
5	h	$A_2 + E_1 + E_2 + E_3 + E_4 + E_5$
6	i	$A_1 + E_1 + E_2 + E_3 + E_4 + E_5 + E_6$

Table 16 Atomic orbital irreps in hexagonal environments

	$6u$	$6\bar{u}$	$\bar{6}u$
s	A_1		
p	$A_2 + E_1$	$A_1 + E_1$	$B_2 + E_2$
d	$A_1 + E_1 + E_2$		
f	$A_2 + B_1 + B_2 + E_1 + E_2$	$A_1 + B_1 + B_2 + E_1 + E_2$	$B_2 + A_1 + A_2 + E_1 + E_2$
g	$A_1 + B_1 + B_2 + E_1 + 2E_2$		
h	$A_2 + B_1 + B_2 + 2E_1 + 2E_2$	$A_1 + B_1 + B_2 + 2E_1 + 2E_2$	$B_2 + A_1 + A_2 + 2E_1 + 2E_2$
i	$2A_1 + B_1 + B_2 + 2E_1 + 2E_2$		

producing the results shown in Table 16. Irreps for other point groups in the same Laue class are fairly simply related to the rotational group of the class. Even orbital functions are the same for all groups of a Laue class while those of odd orbital functions are obtained by simple modifications of the rotational values. Representations for the $6\bar{u}$ symmetry environment simply negate 1D subscripts of the rotational representations while those for $\bar{6}u$ just negate the stems. Irreps for $6ui$ simply add g and u subscripts for even and odd orbitals. A similar table might be produced for all Laue classes including the octahedral groups 43, $4\bar{3}$ and $43i$ of the [3] partition.

In summary, it should be clear that the generator and abstract group approach above is much more easily learned and applied than the traditional Schoenflies–Mulliken approach. It can be seen as providing an insight into the subject or as an alternative method. Pages of work in modern text books such as Willock produce simple results obscured by an archaic notation. (Willock 2009). It would be much quicker and easier to work them out in the simplified notation and convert the results back to the traditional notation. Cotton's classic 1960s text describing the chemical applications of group theory adopts a similarly ponderous approach in which simple truths are hidden by a Byzantine methodology (Cotton 1990). All of these problems become more acute on moving to double groups and the fermion irreps required by the Dirac equation. (Dyall and Faegri 2007). However, double groups can also be organized in Laue classes in which double rotational group generators are used to form isomorphs and centrosymmetric groups as above. Since these groups are much larger, the saving in description and computation is even greater.

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