Assigning irreducible representations the easy way

Schoenflies point group notation is unhelpful in the deduction of irreducible representations and the best way to proceed from the Schoenflies group symbol is as follows

a. find the position of the Schoenflies point group in a table of Laue classes

b. convert this group symbol into a symbol from the table below

c. follow the rules for generation of irreps given

Easy irrep assignment begins with a glance at the table of point groups in Laue classes below

Table 1 - Point groups in Laue classes

Partition	System	G	$\bar{G}$		Gi
[1,1,1]	Triclinic	1			i
(Asymmetric	Monoclinic	2		$\bar{2}$	$2i$
Tops)	Orthogonal	22	$2\bar{2}$		$22i$
[2,1]	Trigonal	3			3i
(Symmetric		32	$3\bar{2}$		$32i$
Tops)	Tetragonal	4		$\bar{4}$	4i
		42	$4\bar{2}$	$\bar{4}2$	$42i$
	Pentagonal	5			52
		52	$5\bar{2}$		$52i$
	Hexagonal	6		$\bar{6}$	$6i$
		62	$6\bar{2}$	$\bar{6}2$	$62i$
	Heptagonal	7			$7i$
		72	$7\bar{2}$		$72i$
	Octagonal	8		$\bar{8}$	$8i$
		82	82	$\bar{8}2$	$82i$
		.....			
	Infinite	∞			∞i
		$\infty 2$	$\infty\bar{2}$		$\infty 2i$
[3]	Tetrahedral	23			$23i$
(Spherical	Octahedral	432		$\bar{4}32$	$432i$
Tops)	Icosahedral	532			$532i$

Notice first that all point groups in the first two Laue partitions are either cyclic n or dihedral $n2$ Laue classes defined by the rotational groups of order n and 2n. All groups in a Laue class have identical irreps except the centred group on the right of the table where the irreps are a direct product of the class irrep with the irrep of space inversion, doubling the number of irreps, adding subscripts g and u. A group $n2$ contains group n as an index-2 subgroup and therefore contains the cyclic group irreps within the dihedral group irreps. Similarly, a

dihedral group exists within a centred dihedral group. It follows that every irrep deduction begins with a cyclic group irrep assignment even when more symmetry is present.

Cyclic groups have the one-dimensional irreps shown in Table 2 below. An n-fold cyclic group has n irreps consisting of two special irreps A and B together with conjugate pair irreps E_{+x} and E_{-x}that make up the collection. Notice that B irreps only occur when n is an even number. (A and B are just E_n and $E_{n/2}$). Cyclic group irreps may be even or odd, depending on whether subscript x in E_n is even or odd. Irrep A is always even and B is even when *n/2* is even and odd otherwise.

Table 2 - Cyclic stem irreps

n	Irrep stems	n	Irrep stems
1	A	2	A, B
3	A, E_{+1}, E_{-1}	4	A, B, E_{+1}, E_{-1}
5	$A, E_{+1}, E_{-1}, E_{+2}, E_{-2}$	6	$A, B, E_{+1}, E_{-1}, E_{+2}, E_{-2}$
7	$A, E_{+1}, E_{-1}, E_{+2}, E_{-2}, E_{+3}, E_{-3}$	8	$A, B, E_{+1}, E_{-1}, E_{+2}, E_{-2}, E_{+3}, E_{-3}$
	.....		
∞	$A, E_{+1}, E_{-1}, E_{+2}, E_{-2}, .., E_{\infty}$		

Dihedral group irreps follow from cyclic stems: A and B irreps are split into separate one-dimensional A_1, A_2, B_1 and B_2 irreps while conjugate pairs of E_{+x} and E_{-x} irreps are merged into two-dimensional irreps E_x. Groups on a row of the Laue class table above have the same irreps because they are distinct physical examples of the same abstract group. Centred groups on the right-hand side of Table 1 have twice as many irreps available as other groups in their row. Groups of this kind are direct products of any other group in the row with central inversion (parity inversion) and their irreps are distinguished with of subscripts g and u.

The first step is to discover sets of equivalent atoms in a molecule within the point group being considered. These are atoms that are exchanged during symmetry operations. Irreps for each set of equivalent atoms are deduced separately then added together to arrive at a result for the whole molecule. The number of equivalent atoms must be a factor of the order of the group so, for example, a group of order 16 can only have 8,4,2 or 1 equivalent atoms and when the number is lower than the order of the group the atoms concerned must be positioned on a symmetry axis or plane. Irreps are first deduced for the cyclic group of the molecule being investigated. These irreps are treated as stems from which centred or dihedral irreps can be deduced where appropriate. Finally, irreps for dihedral centred molecules can be obtained when relevant.

A summary of the rules for deducing symmetry irreps.

1. Cyclic groups n

a. n equivalent atoms contribute 1 of each irrep stem (from table above)

b. single atoms on the axis in group n each contribute an A irrep

2. Cyclic groups $\bar{n}$

a. n equivalent atoms contribute 1 of each irrep stem (from table above)
b. $n/2$ equivalent atoms on a horizontal mirror contribute 1 of each **even** irrep stem
c. pairs of axial atoms in $\bar{n}$ contribute stems $A + B$

3. Centred cyclic groups ni – (derive n irreps first) then
a. $2n$ equivalent atoms inherit two identical sets of irreps from n and one set is given g subscripts the other u subscripts.
b. n equivalent atoms must be on a horizontal mirror plane and subscript g is applied to even stems of group n and u to odd stems.
c. pairs of axial atoms contribute $A_g + A_u$.

4. Dihedral groups $n2$ and $\bar{n}2$ (derive n or $\bar{n}$ irreps first) then
a. $2n$ equivalent atoms split and merge cyclic symbols as described above.
b. n equivalent atoms again split and merge but only subscript 1is added to stems A and B if there are 1 or 2 atoms on the horizontal axis. One of each subscript is added if not.
c. Axial pairs of atoms contribute $A_1 + A_2$ in $n2$ and $A_1 + B_2$ in $\bar{n}2$.

5. Dihedral groups $n\bar{2}$ (derive n irreps first) then
a. $2n$ equivalent atoms split and merge cyclic symbols as described above.
b. n equivalent atoms split and merge cyclic symbols as above adding only subscripts 1 if there are 1 or 2 atoms on the $m_y$vertical mirror plane or one of each subscript if not.
c. axial atoms contribute A_1

6. Centred dihedral groups $n2i$ (derive $n2$ irreps first) then
a. $4n$ equivalent atoms yield irreps that are just the two sets of irreps in $n2$ merged into a single set with g and u subscripts.
b. when n is an odd number there is again a simple division between g and u subscripts.
c. when n is an even number $2n$ equivalent atoms must be partly positioned on a vertical mirror plane. If those atoms are on the m_y plane and subscript g is added to the B_1 irrep otherwise u is added to this irrep.
d. n equivalent atoms must be positioned on the horizontal mirror plane so that even and odd stems have g and u subscripts
e. axial pairs always contribute $A_{1g} + A_{2u}$

Cubic groups in the [3] partition
Tetrahedral and octahedral Laue classes are related in a similar way to the cyclic and dihedral group of the [1,1,1] and [2,1] partitions.. Irrep stems are deduced for the tetrahedral form then, if appropriate, extended to the octahedral state. Irreps for molecules of chemical interest are easily derived because they are generally very simple

Benzene

Taking the benzene molecule as an example, we have six equivalent carbon atoms and six equivalent hydrogen atoms. Only the carbon irreps need to be derived because the hydrogen irreps will be identical and the carbon result can simply be doubled. Firstly, the irreps of the cyclic group 6 are derived then the irreps of 62 and finally those of $62i$. The n atoms in cyclic group n always results in one of each possible irrep and for group 6 Table 2 above shows this to be

$$A + B + E_{+1} + E_{-1} + E_{+2} + E_{-2}$$

In point group 62 these become

$$A_1 + B_1 + E_1 + E_2$$

Subscripts for the A and B irreps might have been 1 or 2. Irreps for every set of equivalent atoms must contain the most symmetrical irrep once and only once so A_1 must be in the set. Also, A and B irreps must have as many 1 subscripts as there are atoms on the 2-fold axis passing through the molecule so both must be 1. Finally, the molecule lies on a horizontal plane so g subscripts are added to even irreps and u subscripts to odd irreps.

$$A_{1g} + B_{1u} + E_{1u} + E_{2g}$$

This is only for the carbon atoms so when the hydrogen atoms are added we get

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

Boron trifluoride

This apparently trigonal molecule has point group symmetry $\bar{6}2$ and, taking first the cyclic group symmetry $\bar{6}$, we have only three atoms in representing a 6-fold group. In this case only the three even irreps are chosen from the six possibilities so we are left with

$$A + E_{+2} + E_{-2}$$

.

When this is extended to the dihedral group $\bar{6}2$ this becomes

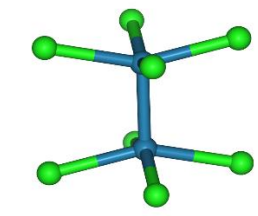
$$A_1 + E_2$$

Again, A_1must be included because it's the most symmetrical irrep. The central boron atom must contribute irrep $A_1$to the total so the irrep total is $2A_1 + E_2$

Inverted cyclic groups $\bar{n}$ might also have pairs of atoms on the main axis that contribute irreps A + B while the central atom contributes irrep A

Rhenium Chloride

A $[Re_2Cl_8]^{2-}$fragment has the 4-fold symmetry $42i$ shown in the image below



It has 8 chlorine atoms attached to two Rhenium atoms and its irreps are deduced first as a cyclic group 4 then as a dihedral group 42 and finally as a centred group $42i$. As a cyclic group it contains two sets of 4 equivalent Cl atoms with two sets containing just one Re atom so there are four sets of equivalent atoms and four sets of irreps.

Point group	Re atoms	Cl atoms

4	$2A$	$2(A + B + E_{+1} + E_{-1})$
42	$A_1 + A_2$	$A_1 + A_2 + B_1 + B_2 + 2E_1$
42*i*	$A_{1g} + A_{2u}$	$A_{1g} + A_{2u} + B_{1g} + B_{2u} + E_{1g} + E_{1u}$