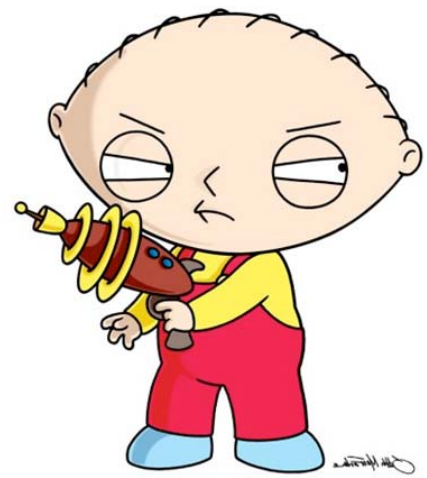
Lecture 13
Point Groups and Character Tables

Symmetry elements/operations can be manipulated by
Group Theory, Representations and Character Tables

So, What IS a group?

And, What is a Character???



A GROUP is a collection of entities or elements which satisfy the following four conditions:

1) The product of any two elements (including the square of each element) must be an element of the group. For symmetry operations, the multiplication rule is to successively perform operations.

2) One element in the group must commute with all others and leave them unchanged. Therefore the "E",

$$EX = XE = X$$

3) The associative law of multiplication must hold

$$A(BC) = (AB)C$$

4) Every element must have a reciprocal which is also an element of the group. i.e.,

$$X(X^{-1}) = (X^{-1})X = E$$

Note: An element may be its own reciprocal.

Groups may be composed of anything: symmetry operations, nuclear particles, etc. Simplest is +1, -1.

All the groups which follow the same multiplication table are called representations of the same group. ➔ ***Character Tables***

Table 6.4 The C_{2v} character table

C_{2v}	E	C_2	σ_v	σ_v'	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	
B_1	1	–1	1	–1	x, R_y	xy
B_2	1	–1	–1	1	y, R_x	zx, yz

Character table for point group C_{3v}

C_{3v}	E	$2C_3$ (z)	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	z	x^2+y^2, z^2	z^3, $x(x^2-3y^2)$, $z(x^2+y^2)$
A_2	+1	+1	-1	R_z	-	$y(3x^2-y^2)$
E	+2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)	(xz^2, yz^2) $[xyz, z(x^2-y^2)]$ $[x(x^2+y^2), y(x^2+y^2)]$

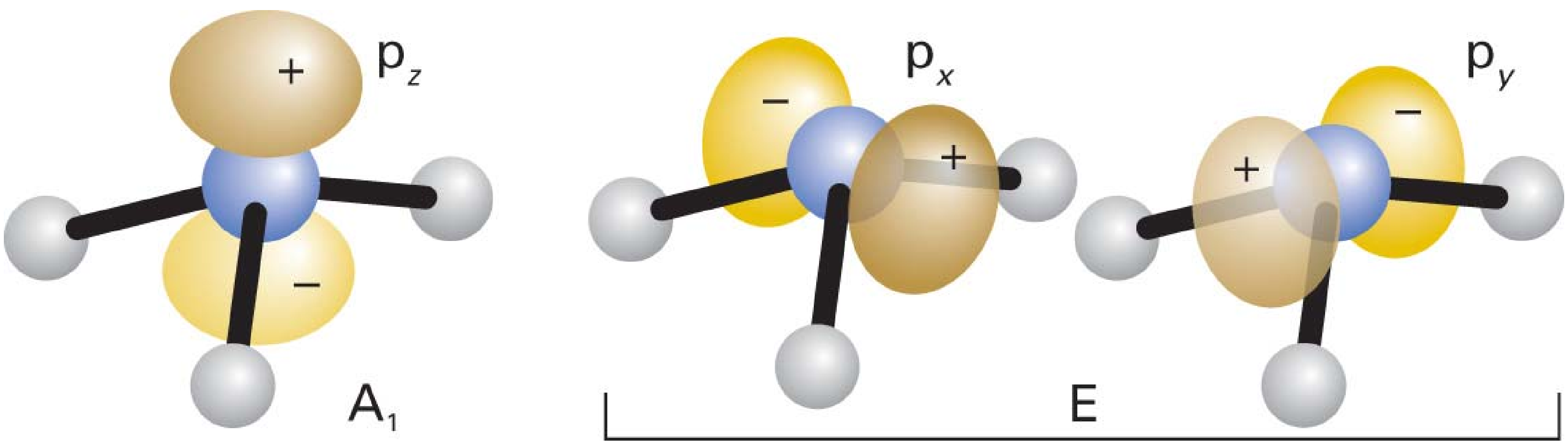


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Table 6.3 The components of a character table

Name of point group*	Symmetry operations *R* arranged by class (E, C_n, etc.)	Functions	Further functions	Order of group, *h*
Symmetry species (Γ)	Characters (χ)	Translations and components of dipole moments (x, y, z), of relevance to IR activity; rotations	Quadratic functions such as z^2, xy, etc., of relevance to Raman activity	

* Schoenflies symbol.

Consequences of Symmetry

- Only the molecules which belong to the $\mathbf{C_n}$, $\mathbf{C_{nv}}$, or $\mathbf{C_s}$ **point** group can have a permanent dipole moment.
- A molecule may be chiral only if it does not have an axis of improper rotation **Sn**.
- IR Allowed transitions may be predicted by symmetry operations
- Orbital overlap may be predicted and described by symmetry

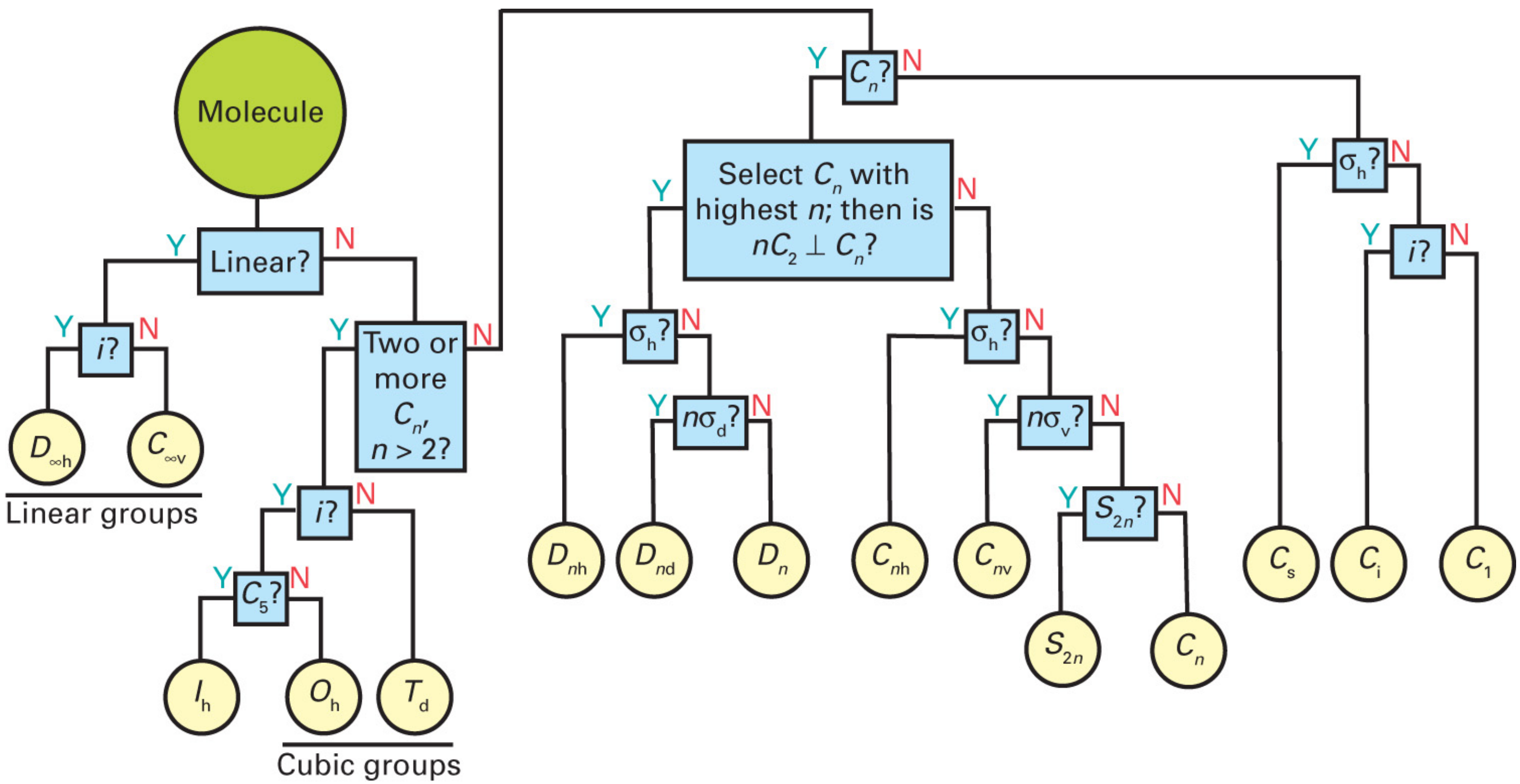
Point Group Assignments and Character Tables

POINT GROUPS

A collection of symmetry operations all of which pass through a single point

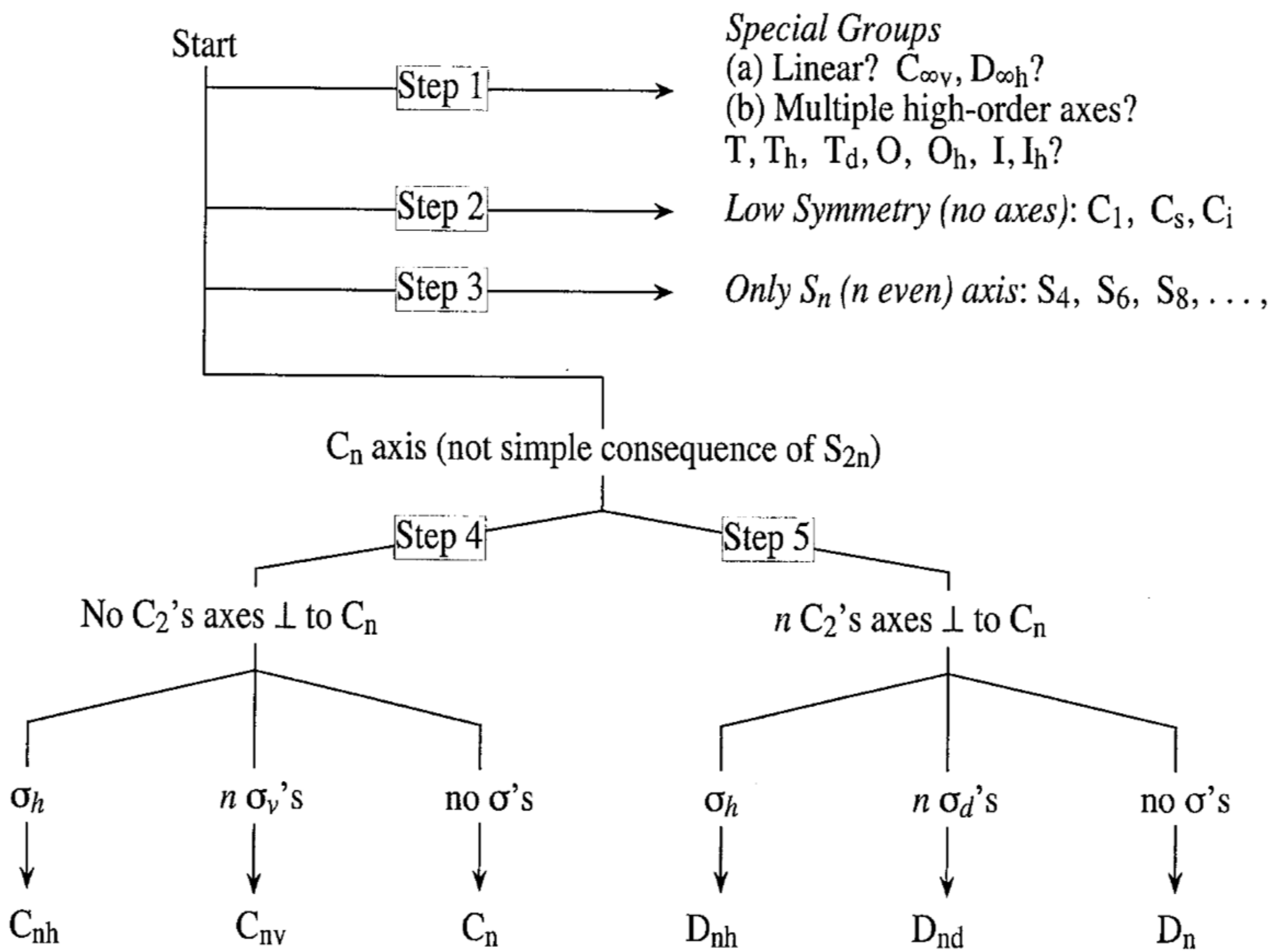
A point group for a molecule is a quantitative measure of the symmetry of that molecule

Assignment of Symmetry Elements to Point Group: At first Looks Daunting.



Daunting? However almost all we will be concerned with belong to just a few symmetry point groups

A Simpler Approach



POINT GROUPS

A collection of symmetry operations all of which pass through a single point

A point group for a molecule is a quantitative measure of the symmetry of that molecule

ASSIGNMENT OF MOLECULES TO POINT GROUPS

STEP 1 : LOOK FOR AN AXIS OF SYMMETRY

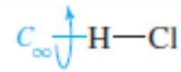
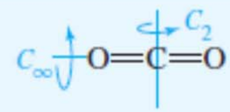
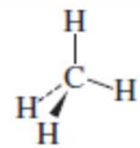
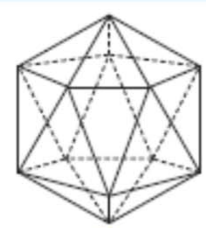
If one is found - go to STEP 2

If not: look for

(a) plane of symmetry - if one is found, molecule belongs to point group C_s

Point Group Assignments: MFT Ch. 4

TABLE 4.3 Groups of High Symmetry

Group	Description	Examples
$C_{\infty v}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.	
$D_{\infty h}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.	
T_d	Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.	
O_h	These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.	
I_h	Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations—120 in all.	 $B_{12}H_{12}^{2-}$ with BH at each vertex of an icosahedron

In addition, there are four other groups, T, T_h, O, and I, which are rarely seen in nature. These groups are discussed at the end of this section.

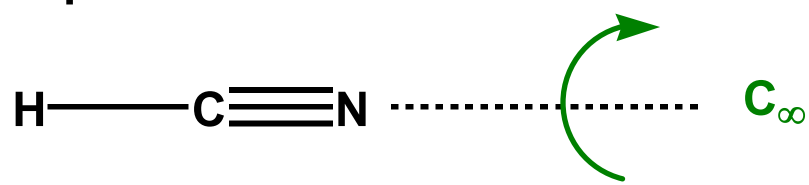
LINEAR MOLECULES

Do in fact fit into scheme - but they have an infinite number of symmetry operations.

Molecular axis is C_∞ - rotation by any arbitrary angle $(360/\infty)^o$, so infinite number of rotations. Also any plane containing axis is symmetry plane, so infinite number of planes of symmetry.

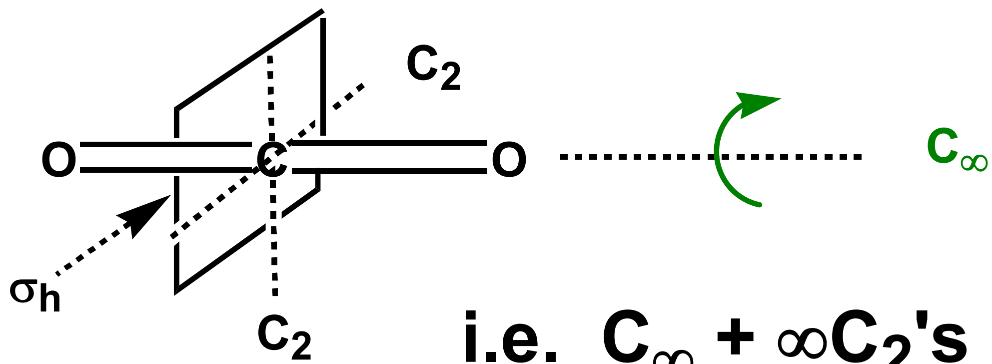
Divide linear molecules into two groups:

(i) No centre of symmetry, e.g.:



No C_2's perp. to main axis, but ∞ σ_v's containing main axis: point group $C_{\infty v}$

(ii) Centre of symmetry, e.g.:



i.e. $C_\infty + \infty C_2\text{'s} + \sigma_h$

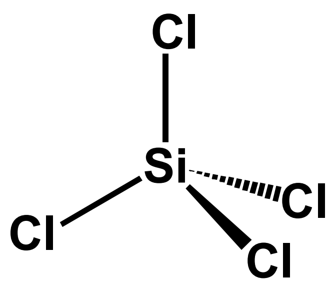
Point group $D_{\infty h}$

Highly symmetrical molecules

A few geometries have several, equivalent, highest order axes. Two geometries most important:

Regular tetrahedron

e.g.

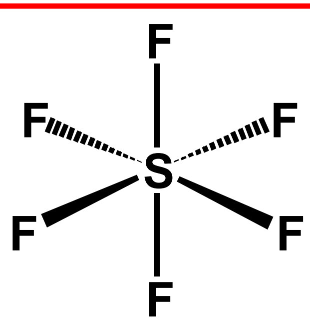


4 C_3 axes (one along each bond)
3 C_2 axes (bisecting pairs of bonds)
3 S_4 axes (coincident with C_2's)
6 σ_d's (each containing Si and 2 Cl's)

Point group: T_d

Regular octahedron

e.g.



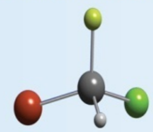
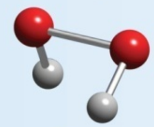
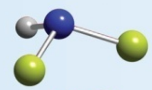
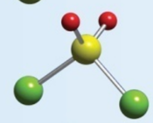
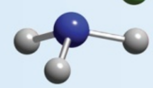
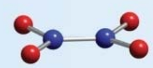
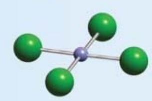
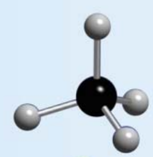
3C_4's (along F-S-F axes)
also 4 C_3's. 6 C_2's, several planes, S_4, S_6 axes, and a centre of symmetry (at S atom)

Point group O_h

These molecules can be identified without going through the usual steps.

Note: many of the more symmetrical molecules possess many more symmetry operations than are needed to assign the point group.

Table 6.2 The composition of some common groups

Point group	Symmetry elements	Shape	Examples
C_1	E		SiHClBrF
C_2	E, C_2		H_2O_2
C_s	E, σ		NHF_2
C_{2v}	$E, C_2, \sigma_v, \sigma_v'$		SO_2Cl_2, H_2O
C_{3v}	$E, 2C_3, 3\sigma_v$		NH_3, PCl_3, $POCl_3$
$C_{\infty v}$	$E, C_2, 2C_\varphi, \infty\sigma_v$		OCS, CO, HCl
D_{2h}	$E, 3C_2, i, 3\sigma$		N_2O_4, B_2H_6
D_{3h}	$E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v$		BF_3, PCl_5
D_{4h}	$E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d$		XeF_4, *trans*-$[MA_4B_2]$
$D_{\infty h}$	$E, \infty C_2', 2C_\varphi, i, \infty\sigma_v, 2S_\varphi$		CO_2, H_2, C_2H_2
T_d	$E, 8C_3, 3C_2, 6S_4, 6\sigma_d$		CH_4, $SiCl_4$
O_h	$E, 8C_3, 6C_2, 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$		SF_6

4. The C_{nv} Groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	R_z	
E_1	2	2 cos 72°	2 cos 144°	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	2 cos 144°	2 cos 72°	0		$(x^2 - y^2, xy)$

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1		
B_2	1	−1	1	−1	−1	1		
E_1	2	1	−1	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	−1	−1	2	0	0		$(x^2 - y^2, xy)$

6. The D_{nh} Groups

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

9. The Cubic Groups (Continued).

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^5$	$3\sigma_h$		$\varepsilon = \exp(2\pi i/3)$
A_g	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_u	1	1	1	1	-1	-1	-1	-1		
E_g	1	ε	ε^*	1	1	ε	ε^*	1		$(2z^2-x^2-y^2,$
	1	ε^*	ε	1	1	ε^*	ε	1		$x^2-y^2)$
E_u	1	ε	ε^*	1	-1	$-\varepsilon$	$-\varepsilon^*$	-1		
	1	ε^*	ε	1	-1	$-\varepsilon^*$	$-\varepsilon$	-1		
T_g	3	0	0	-1	3	0	0	-1	(R_x, R_y, R_z)	(xz, yz, xy)
T_u	3	0	0	-1	-3	0	0	1	(x, y, z)	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O	E	$6C_4$	$3C_2(=C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	-1	1	1	-1		
E	2	0	2	-1	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	1	-1	0	-1	(R_x, R_y, R_z); (x, y, z)	
T_2	3	-1	-1	0	1		(xy, xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Table 6.4 The C_{2v} character table

C_{2v}	E	C_2	σ_v	σ_v'	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	
B_1	1	–1	1	–1	x, R_y	xy
B_2	1	–1	–1	1	y, R_x	zx, yz

Table 6.5 The C_{3v} character table

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	z^2
A_2	1	1	–1	R_z	
E	2	–1	0	(x, y) (R_x, R_y)	(zx, yz) $(x^2 - y^2, xy)$

Character table for $C_{\infty v}$ point group

	E	**$2C_\infty$**	**...**	**∞ &sigma$_v$**	**linear, rotations**	**quadratic**
A_1=Σ^+	1	1	...	1	z	x^2+y^2, z^2
A_2=Σ^-	1	1	...	-1	R_z	
E_1=Π	2	2cos(Φ)	...	0	(x, y) (R_x, R_y)	(xz, yz)
E_2=Δ	2	2cos(2ϕ)	...	0		(x^2-y^2, xy)
E_3=Φ	2	2cos(3ϕ)	...	0		
...	...	...	...	...		

Character table for $D_{\infty h}$ point group

	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C'_2$	linear functions, rotations	quadratic
$A_{1g}=\Sigma^+_g$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g}=\Sigma^-_g$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g}=\Pi_g$	2	2cos(ϕ)	...	0	2	-2cos(ϕ)	...	0	(R_x, R_y)	(xz, yz)
$E_{2g}=\Delta_g$	2	2cos(2ϕ)	...	0	2	2cos(2ϕ)	...	0		(x^2-y^2, xy)
$E_{3g}=\Phi_g$	2	2cos(3ϕ)	...	0	2	-2cos(3ϕ)	...	0		
...	...	...	...	...	...	...	...	...		
$A_{1u}=\Sigma^+_u$	1	1	...	1	-1	-1	...	-1	z	
$A_{2u}=\Sigma^-_u$	1	1	...	-1	-1	-1	...	1		
$E_{1u}=\Pi_u$	2	2cos(ϕ)	...	0	-2	2cos(ϕ)	...	0	(x, y)	
$E_{2u}=\Delta_u$	2	2cos(2ϕ)	...	0	-2	-2cos(2ϕ)	...	0		
$E_{3u}=\Phi_u$	2	2cos(3ϕ)	...	0	-2	2cos(3ϕ)	...	0		
...	...	...	...	...	...	...	...	...		