Chapter 16. Molecular Symmetry

I. Symmetry

Elements	Operations
axis	rotation about an axis
mirror plane	reflection thru a plane
inversion center	inversion thru a center
....	

Five symmetry elements and corresponding operations:

i. Doing nothing, identity E

ii. Rotation about an n-fold axis C_n

A rotation of $360^{o}/n$.

C_3 C_4 C_6

Axis with the largest n is the principal axis.

n symmetry operations:

$n = 3$

$$C_3^1 \qquad C_3^2 \qquad C_3^3 = E$$

$$C_3^1 C_3^1 = C_3^2, \quad C_3^1 C_3^2 = E$$

iii. Inversion through a center of symmetry i

iv. Reflection through a mirror plane σ

Vertical plane σ_v: parallel to principal axis.
Horizontal plane σ_h: perpendicular to principal axis

Dihedral plane σ_d: bisects two C_2 axes perpendicular to the principal axis.

v. Improper rotation about an axis of improper rotation S_n

Rotation + reflection

Symmetry groups

Group: A collection of elements (symmetry operations) that satisfy the following conditions:

a. There is always an identity element.
b. Every element has an inverse.
c. Any products of two elements are also elements of the group.
d. Multiplication of elements is associative A(BC)=(AB)C.

Point group: at least a point unchanged. A molecule belongs to a point group.

Space group: point group + translational symmetries.

$C_1 : E$

$C_i : \quad E, i$

$C_s : \quad E, \sigma$

C_n : E, C_n

C_{nv} : E, C_n , $n\sigma_v$

C_{nh} : E, C_n , σ_h

D_n : E, C_n , nC_2 (2-fold axes perpendicular to C_n)

D_{nh} : E, C_n , nC_2, σ_h

D_{nd} : $E, C_n, nC_2, n\sigma_d$

S_n: E, S_n.

$C_i = S_2$

Tetrahedral groups T , T_h and T_d
Octahedral groups O, O_h *and* O_d
Rotational group R_3.
Group can be determined by flow diagram.

Consequences of symmetry

i. Polarity

A polar molecule (with permanent electric dipole) belongs to one of the groups C_n, C_{nv} and C_s.

CO belongs to $C_{\infty v}$ and is polar.

N_2 belongs to $D_{\infty h}$ and is non-polar.

ii. Chirality

Chiral molecule: cannot be superimposed by its mirror image.

A chiral molecule must not have i or σ.
Chiral molecules can change the polarization of light.

Usefulness:

i. Classify molecules.
ii. Save computational efforts.
iii. Determine selection rules.

II. Character table

Representation and character table

<u>Representation</u>: mathematical elements representing symmetry operations.

Example: H_2O (C_{2v} group, four elements)

E:	$(x\ y\ z) \rightarrow (x\ y\ z)$
C_2^1:	$(x\ y\ z) \rightarrow (-x\ -y\ z)$
σ_v:	$(x\ y\ z) \rightarrow (x\ -y\ z)$
σ_v':	$(x\ y\ z) \rightarrow (-x\ y\ z)$

$x\ y\ z$ as bases

In particular,

$$\sigma_v C_2^1(x\ y\ z) = \sigma_v(-x\ -y\ z) = (-x\ y\ z) = \sigma_v'(x\ y\ z)$$

Multiplication table

	1st operation			
2nd operation	E,	C_2^1,	σ_v,	σ_v'
E	E,	C_2^1,	σ_v,	σ_v'
C_2^1	C_2^1,	E,	σ_v',	σ_v
σ_v	σ_v,	σ_v',	E,	C_2^1
σ_v'	σ_v',	σ_v,	C_2^1,	E

Matrix rep:

E: $$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

C_2^1: $$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

σ_v: $$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

σ_v': $$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

Verification:

$$\sigma_v C_2^1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v'$$

3-D rep $\Gamma^{(3)}$ spanned by $(x\ y\ z)$

Trace of matrix (sum of diagonal elements) is called <u>character</u> χ

	E	C_2^1	σ_v	σ_v'	
χ	3	-1	1	1	($\Gamma^{(3)}$)

$\Gamma^{(3)}$ can be reduced to a direct sum of two matrix reps:

$$\Gamma^{(3)} = \Gamma^{(1)} + \Gamma^{(2)}$$

$\Gamma^{(1)}$ is spanned by z (<u>irreducible representation, irrep</u>).

	E	C_2^1	σ_v	σ_v'	
χ	1	1	1	1	($\Gamma^{(1)}$)

$\Gamma^{(2)}$ can be further reduced to the direct sum of two 1D reps spanned by x and y.

<u>Character table</u>: list of characters of all its irreps.

	E	C_2^1	σ_v	σ_v'	basis
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

The last column is the basis for different irreps.

$$xy \xrightarrow{E} xy, \quad xy \xrightarrow{C_2^1} xy, \quad xy \xrightarrow{\sigma_v} x(-y), \quad xy \xrightarrow{\sigma_v'} (-x)y$$

Symmetry species (label of irrep)

A: 1-D irreps with +1 under principal rotation.
B: 1-D irreps with -1 .. .. ..
E: 2-D irreps.
T: 3-D irreps.

Subscript determined by χ for σ_v or perpendicular C_2 axis.

Dimension of an irrep (d_j): size of matrix of the irrep.
Order (h): total number of operations.
Class: operations of the same kind.

Properties of characters for irreps

i. Characters are unique, independent of basis.

ii. Characters of elements in the same class are identical.

iii. Order of a group is related to dimensions of irreps by

$$\sum_j d_j^2 = h$$

iv. Characters form a set of mutually orthogonal vectors (Grand Orthogonality Theorem).

$$\sum_O \chi_i(O)\chi_j(O) = h\delta_{ij}$$

where O denotes the symmetry operations.

A_1A_1: $(1\times1+1\times1+1\times1+1\times1) = 4$

A_1A_2: $[1\times1+1\times1+1\times(-1)+1\times(-1)] = 0$

v. Number of irreps = number of classes.

vi. Any rep can be decomposed into irreps:

$$\chi(O) = \sum_i a_i \chi_i(O)$$
$$a_i = \frac{1}{h}\sum_O \chi(O)\chi_i(O)$$

vii. To construct the basis for a particular irrep (i), define projection operator:

$$\hat{P}_i = \frac{d_i}{h}\sum_O \chi_i(O)\hat{O},$$

where d_i is the dimensionality of the irrep.

Example: A matrix rep for C_{2v} group has the following characters: Γ=4, 2, 0, 2. Determine how many times each irrep is contained in it.

$$a_{A_1} = \frac{1}{4}[4\times1+2\times1+0\times1+2\times1] = 2$$
$$a_{A_2} = \frac{1}{4}[4\times1+2\times1+0\times(-1)+2\times(-1)] = 1$$

$$a_{B_1} = \frac{1}{4}\left[4\times 1 + 2\times(-1) + 0\times 1 + 2\times(-1)\right] = 0$$
$$a_{B_2} = \frac{1}{4}\left[4\times 1 + 2\times(-1) + 0\times(-1) + 2\times 1\right] = 1$$

In other words:

$$\Gamma = 2A_1 + A_2 + B_2$$

III. Applications

Classification of MOs (H_2O**):**

$$a_1\text{: } \Psi = c_1(\mathrm{sH}_a + \mathrm{sH}_b) + c_2\mathrm{sO} \ + c_3\mathrm{p_z O}$$

because this MO is invariant under all symmetry operations in C_{2v}. Thus, it is a base for the A_1 irrep.

Similarly,

$$b_2\text{: } \Psi = c_1(\mathrm{sH}_a - \mathrm{sH}_b) + c_2\mathrm{p_y O}$$

Orbital degeneracy is determined by χ under E.

Vanishing integrals and SALC:

<u>Only AOs with the same symmetry species form MOs because otherwise the overlap integral is zero.</u>

Consider an overlap integral

$$I = \int f_1 f_2 d\tau$$

$f_1\ f_2$ must contain the total symmetric irrep A_1 if I is non-zero.

Example: Judge whether I is zero if $f_1 = p_x$ and $f_2 = p_y$ for H_2O.

i. Find the irrep each function belongs to and write its characters.

f_1:	B_1	1	-1	1	-1
f_2:	B_2	1	-1	-1	1

ii. Multiply them together by column

$f_1\ f_2$:		1	1	-1	-1

iii. Find out if it contains A_1. If not, $I = 0$.

The characters belong to the A_2 irrep. So I is zero.

<u>A spectral transition is forbidden if the transition dipole is zero.</u>

Example. Judge whether

$$I = \int f_1\ f_2\ f_3 d\tau$$

is zero if $f_1 = p_x$, $f_2 = p_y$ and $f_3 = xy$ for H_2O.

The characters for the bases are

f_1:	B_1	1	-1	1	-1
f_2:	B_2	1	-1	-1	1
f_3:	A_2	1	1	-1	-1

The product:

$f_1 f_2 f_3$:	1	1	1	1

So, the characters belong to the A_1 irrep. So *I* may be non-zero (but could be very small).

<u>Symmetry-adapted linear combination</u>

LCAO-MO with molecular symmetry is called symmetry-adapted linear combinations (SALC).

<u>Projection operator method:</u>

The projection operator for a particular irrep (i) is defined as follows:

$$\hat{P}_i = \frac{d_i}{h} \sum_O \chi_i(O)\hat{O}$$

For the A_1 irrep in C_{2v} for H_2O, we have

$$\hat{P}_{A_1} = \frac{1}{4}\left(E + C_2^1 + \sigma_v + \sigma_v'\right)$$

and

$$\hat{P}_{A_1}\mathrm{sH}_a = \frac{1}{4}\left(E + C_2^1 + \sigma_v + \sigma_v'\right)\mathrm{sH}_a$$

$$= \frac{1}{4}\left(\mathrm{sH}_a + \mathrm{sH}_b + \mathrm{sH}_b + \mathrm{sH}_a\right) = \frac{1}{2}\left(\mathrm{sH}_a + \mathrm{sH}_b\right)$$

$$\hat{P}_{A_1}\mathrm{sH}_b = \frac{1}{2}\left(\mathrm{sH}_a + \mathrm{sH}_b\right)$$

$$\hat{P}_{A_1}\mathrm{sO} = \frac{1}{4}\left(E + C_2^1 + \sigma_v + \sigma_v'\right)\mathrm{sO}$$

$$= \frac{1}{4}\left(\mathrm{sO} + \mathrm{sO} + \mathrm{sO} + \mathrm{sO}\right) = \mathrm{sO}$$

$$\hat{P}_{A_1}\mathrm{p_xO}=0$$

$$\hat{P}_{A_1}\mathrm{p_yO}=0$$

$$\hat{P}_{A_1}\mathrm{p_zO}=\mathrm{p_zO}$$

So

$$a_1\text{: } \Psi = c_1(\mathrm{sH}_a + \mathrm{sH}_b) + c_2\mathrm{sO} + c_3\mathrm{p_zO}$$

For the B_2 irrep, we have

$$\hat{P}_{B_2} = \frac{1}{4}\left(E - C_2^1 - \sigma_v + \sigma_v'\right)$$

and

$$\hat{P}_{B_2}\mathrm{sH}_a = \frac{1}{4}\left(E - C_2^1 - \sigma_v + \sigma_v'\right)\mathrm{sH}_a$$

$$= \frac{1}{4}\left(\mathrm{sH}_a - \mathrm{sH}_b - \mathrm{sH}_b + \mathrm{sH}_a\right) = \frac{1}{2}\left(\mathrm{sH}_a - \mathrm{sH}_b\right)$$

$$\hat{P}_{B_2}\mathrm{sO} = 0$$

$$\hat{P}_{B_2}\mathrm{p_x O} = 0$$

$$\hat{P}_{B_2}\mathrm{p_y O} = \mathrm{p_y O}$$

$$\hat{P}_{B_2}\mathrm{p_z O} = 0$$

So

$$b_2\text{: } \Psi = c_1(\mathrm{sH}_a - \mathrm{sH}_b) + c_2\mathrm{p_y O}$$

<u>Tabulation method:</u>

i. Tabulate results of all operation on AOs,

ii. Multiply the characters to each column,

iii. Add together all the results.

	sH_a	sH_b	sO	$\mathrm{p}_x\mathrm{O}$	$\mathrm{p}_y\mathrm{O}$	$\mathrm{p}_z\mathrm{O}$
E	sH_a	sH_b	sO	$\mathrm{p}_x\mathrm{O}$	$\mathrm{p}_y\mathrm{O}$	$\mathrm{p}_z\mathrm{O}$

C_2^1	sH_b	sH_a	sO	$-p_xO$	$-p_yO$	p_zO
σ_v	sH_b	sH_a	sO	p_xO	$-p_yO$	p_zO
σ_v'	sH_a	sH_b	sO	$-p_xO$	p_yO	p_zO

For A_1 species, multiply (1 1 1 1) to the first column:

$$\Phi = (sH_a + sH_b + sH_b + sH_a)/4 = (sH_a + sH_b)/2$$

second column:

$$\Phi = (sH_b + sH_a + sH_a + sH_b)/4 = (sH_a + sH_b)/2$$

third column:

$$\Phi = sO$$

fourth and fifth columns:

$$\Phi = 0$$

and the sixth column:

$$\Phi = p_zO$$

So, the SALC-MO with A_1 symmetry (the a_1 orbital) is the sum of all the above:

$$a_1\text{: } \Psi = c_1(sH_a + sH_b) + c_2 sO + c_3 p_zO$$

For the B_2 irrep, we have for 1st (and 2nd) column

$$\Phi = (sH_a - sH_b - sH_b + sH_a)/4 = (sH_a - sH_b)/2$$

3rd and 4th columns

$$\Phi = 0$$

5th column

$$\Phi = p_yO$$

6th column

$$\Phi = 0$$

So

$$b_2\text{: } \Psi = c_1(sH_a - sH_b) + c_2 p_y O$$