Course Outline

1. Symmetry, Group Theory, and Electronic Structure

1.1 Fundamentals

1.2 Symmetry and Group Theory

1.3 Vibrational Spectroscopy

2. Ground State Spectroscopic Methods

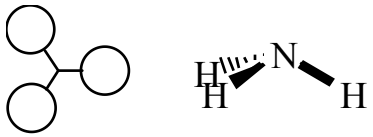
3. Excited State Spectroscopic Methods

4. Other Physical Methods

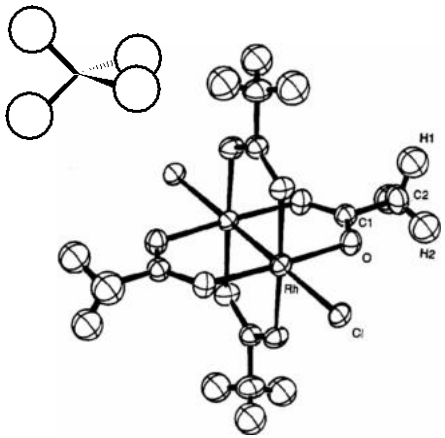
1.2 Symmetry and Group Theory

Some Important Definitions

- **symmetry operation:** movement of an object such that every point of the object is coincident with an equivalent point
- **symmetry element:** geometrical entity with respect to which a symmetry operation is performed



Element	*Symmetry Operation*	*Symbol*
Plane of symmetry	Reflection of all points through the plane	σ_v, σ_h, σ_d
Inversion center	Inversion of all points through the inversion center	i
Proper axis of rotation	Rotation of all points about the axis by an amount m x $(2\pi/n)$ [for C_n^m]	C_2, C_3, C_3^2, C_4, ...
Improper axis of rotation	Coupled rotation about an axis/reflection perpendicular to that axis by m x $(2\pi/n)$	S_2, S_3, S_3^2, S_4, ...
(Identity)	Do nothing	E



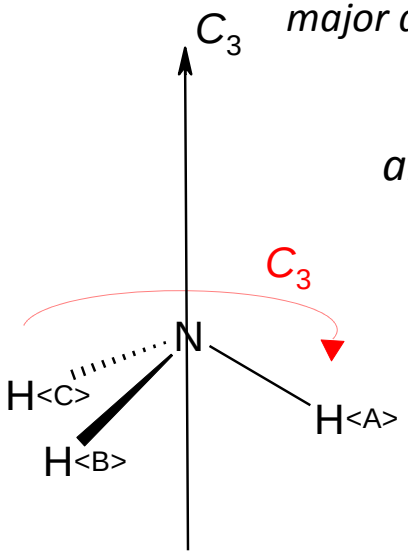
Mathematical Groups

- collection of elements with mathematical four properties:
  - **IDENTITY** → There is an element *e* of the group such that $a \bullet e = e \bullet a = a$ for any element a of the group
  - **CLOSURE** → If *a* and *b* are in the group then the result of $a \bullet b$ is also a member of the group
  - **INVERSE** → For any element *a* of the group there is an a^{-1} such that $a \bullet a^{-1} = a^{-1} \bullet a = e$
  - **ASSOCIATIVITY** → If *a*, *b* and *c* are in the group then $(a \bullet b) \bullet c = a \bullet (b \bullet c)$
  - general definitions for any group of mathematical elements (*a*, *b*, *c*, etc.) under a particular operator (• above)
  - commutativity is not necessary (special groups → **Abelian**)
- **Symmetry Point Groups** are mathematical groups where:
  - the elements are *symmetry operations*
  - the operator simply states that operations should be performed sequentially from right to left... (product of operations)

$C_2 \times C_2 \times \sigma_v = C_2 C_2 \sigma_v \rightarrow$ do σ_v and then 2 C_2 rotations

Do the symmetry operations for NH_3 form a point group?

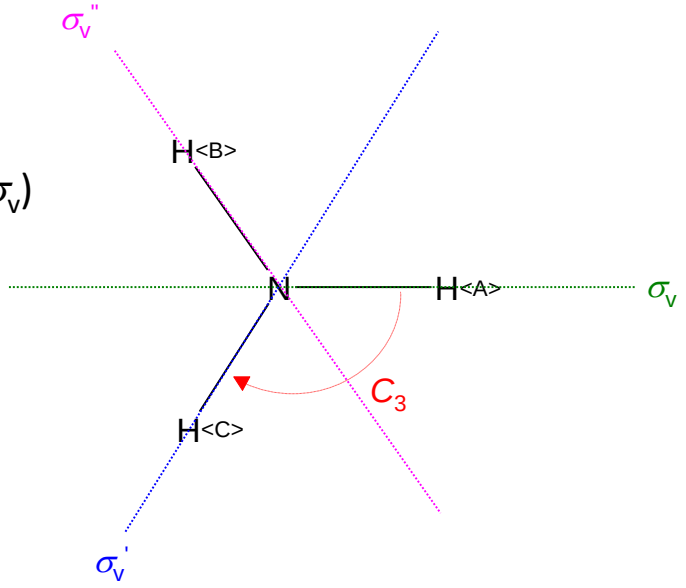
- what are the symmetry operations?



major axis → three-fold axis of symmetry (C_3) leads to $\boldsymbol{C_3^1}$ & $\boldsymbol{C_3^2}$ operations

any other axes of rotation? no… but looking down main axis…

three distinct vertical planes of symmetry (σ_v)



$$\text{symmetry operations} \Rightarrow C_3^1, C_3^2, \sigma_v, \sigma_v', \sigma_v''$$

1.2 Symmetry and Group Theory

- Construct multiplication table $\alpha \times \beta$

$\beta \Downarrow$ \ $\alpha \Rightarrow$	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E

- **Identity →** Yes!
- **Closure →** Yes!
- **Inverse →** Yes!
- **Associativity →** Yes!

$$C_3^1 \times \sigma_v \times C_3^2 = \underbrace{C_3^1 \times \sigma_v}_{\sigma_v''} \times C_3^2 = C_3^1 \times \underbrace{\sigma_v \times C_3^2}_{\sigma_v''}$$
$$= \sigma_v'$$

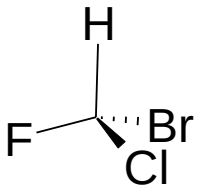
Symmetry Point Groups

- Localized symmetry representations of geometric objects
  - All molecules belong to a "point" group
  - the "point" $\rightarrow$ invariant point where all symmetry elements converge
- Extended structures (crystals) described by **Space Groups**
  - Space groups = point groups + translational symmetry (crystallography)
- Nomenclature $\rightarrow$ two systems in general use

Operation:	Schönflies Notation	International Notation
Identity:	E	1
Proper Rotation:	C_n	n
Mirror Plane $\perp$ Principal Axis:	σ_h	$/m$
Mirror Plane $\parallel$ Principal Axis:	σ_v, σ_d	m
Improper Rotation:	S_n	$\overline{n}$
Inversion:	i	$\overline{1}$

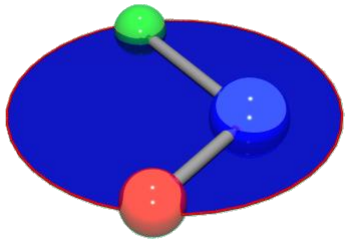
1.2 Symmetry and Group Theory

- Low Symmetry Point Groups
  - contain no rotational symmetry elements
  - symmetry defined for a specific geometry (frozen coordinates)



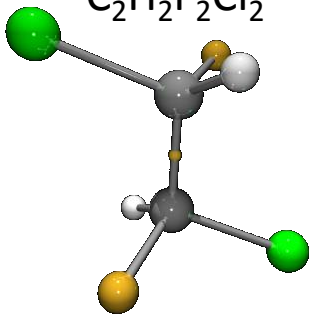
$C_1 \;\; 1 \rightarrow E \;\; \text{only}$

FNO



$C_s \;\; m \rightarrow \sigma_h, E$

$C_2H_2F_2Cl_2$

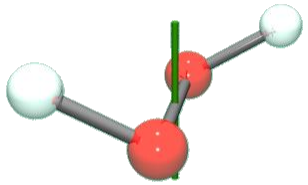


$C_i \;\; \bar{1} \rightarrow i, E$

1.2 Symmetry and Group Theory

- Rotational Point Groups
  - contains only **one** rotational axis
  - other elements possible...

H_2O_2

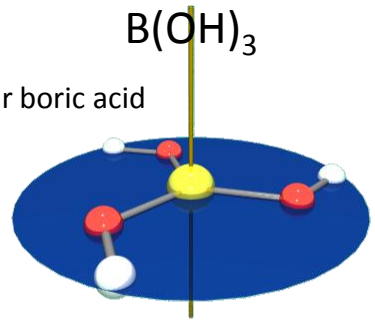


$C_2 \quad 2$

$C_n \quad n \rightarrow C_n, \ldots, C_n^n = E$

$B(OH)_3$

planar boric acid

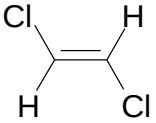


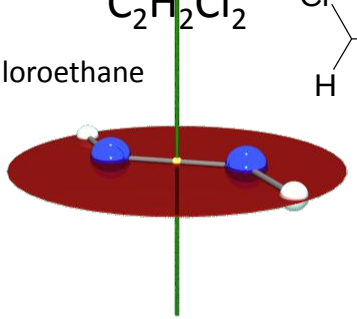
$C_{3h} \quad \overline{6}$

$E, C_3, C_3^2, \sigma_h, S_3, S_3^5$

$C_2H_2Cl_2$

trans-1,2-dichloroethane





$C_{2h} \quad 2/m$

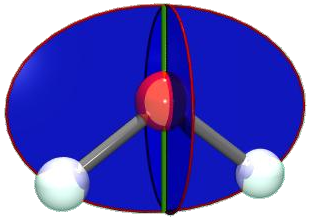
$E, C_2, \sigma_h, i = S_2$

$$C_{nh}\left(n/m, \underset{\text{odd } n}{\overline{(2n)}}\right) \rightarrow C_n, \ldots, C_n^n = E, \sigma_h \quad (n \text{ even})$$

1.2 Symmetry and Group Theory

- Rotational Point Groups (continued)

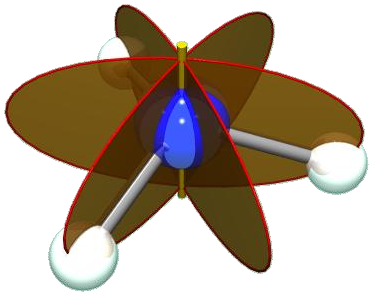
H_2O



$E, C_2, \sigma_v, \sigma_v'$

C_{2v} $2mm$

NH_3



$E, C_3, C_3^2, \sigma_v, \sigma_v', \sigma_v''$

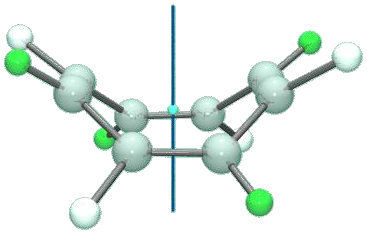
C_{3v} $3m$

HCl

$E, C_\infty, \infty\sigma_v$

$C_{\infty v}$

$C_8H_4F_4$



E, S_4

S_4 $\overline{4}$

$$C_{nv}\left(\underset{\text{even } n}{nmm}, \underset{\text{odd } n}{nm}\right) \rightarrow C_n, \ldots, C_n^n = E, n(\sigma_v)$$

$$S_n \quad \overline{n} \quad \rightarrow S_n, \ldots, S_n^{2n} = E$$

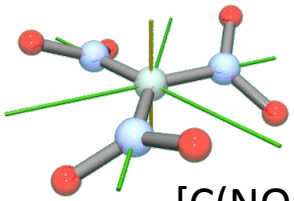
- S_n exists uniquely for even n ≥ 4, since
  - $S_1 \equiv C_s$
  - $S_2 \equiv C_i$
  - $S_n \equiv C_{nh}$ for all odd n ≥ 3

1.2 Symmetry and Group Theory

- Dihedral Point Groups → more than one axis of rotation

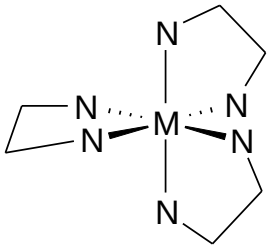
$$D_n \begin{pmatrix} n22\,, & n2 \\ \text{even } n & \text{odd } n \end{pmatrix} \rightarrow C_n, \ldots, C_n^n = E, nC_2$$

perpendicular to C_n

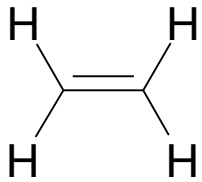


D_3 32

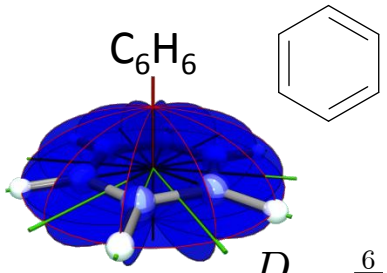
$[C(NO_2)_3]^-$



$$D_{nh} \quad n/m\ 2/m\ 2/m \rightarrow C_n, \ldots, C_n^n = E, nC_2, \sigma_h, n\sigma_v$$



D_{2h} $\frac{2}{m}\frac{2}{m}\frac{2}{m}$



D_{3h} $\frac{6}{m}\frac{2}{m}\frac{2}{m}$

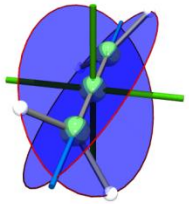
H—C≡C—H

$D_{\infty h}$

$$D_{nd} \quad \text{variable} \rightarrow C_n, \ldots, C_n^n = E, nC_2, n\sigma_v$$

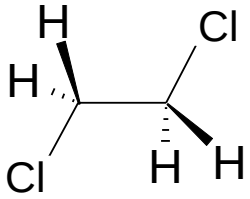
bisecting C_2

allene



D_{2d}

trans-1,2-dichloroethane

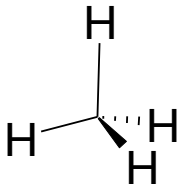


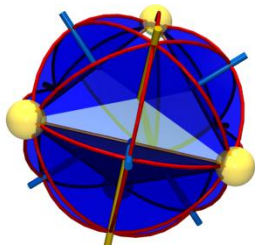
D_{3d} $\bar{3}\,2/m$

1.2 Symmetry and Group Theory

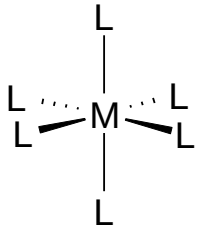
- High Symmetry Point Groups
  - multiple primary axes of rotation

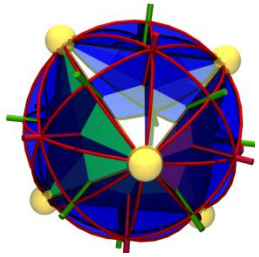
$T_d \rightarrow 4C_3, 4C_3^2$



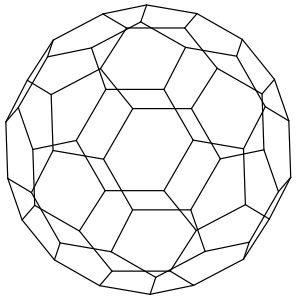


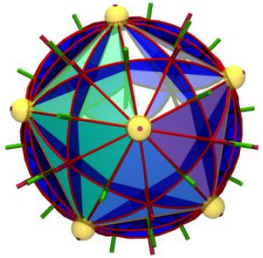
$O_h \rightarrow 3C_4, 3C_2, 3C_4^3, \ldots$





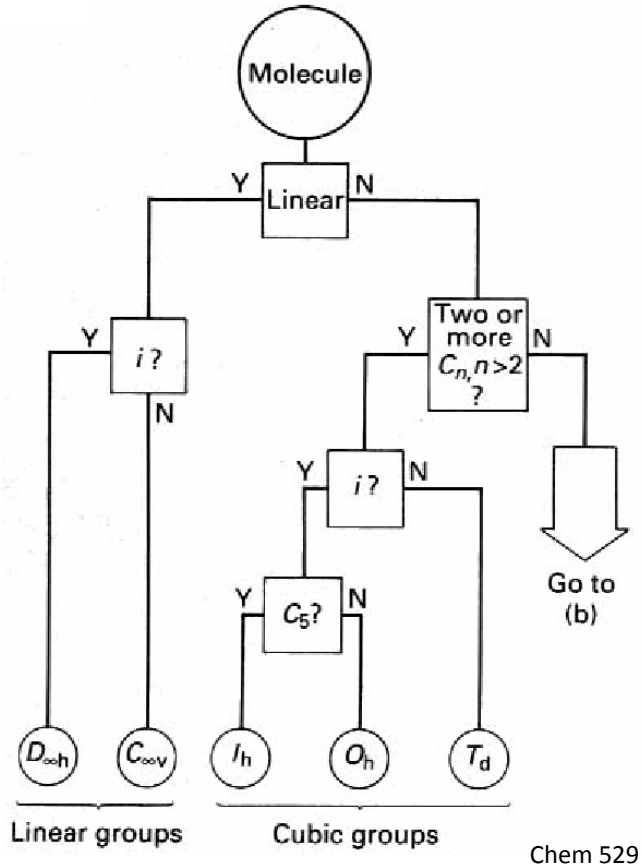
$I_h \rightarrow C_5, C_6, \ldots$

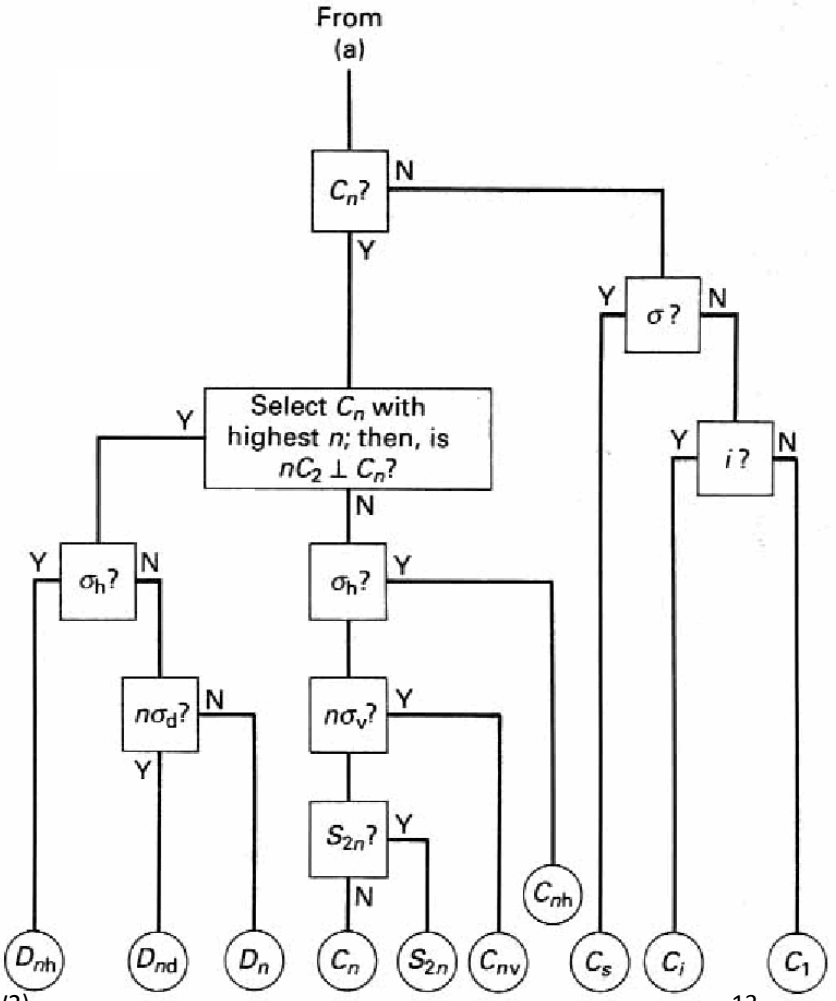




Classification of Molecules into Point Groups

1. Match symmetry elements of molecule with those of the character tables of a point group (more on this later).
2. Use a flow chart:





Representations of Groups → Character Tables

- Illustrations can describe effects of symmetry operations , but more convenient to use a representational shorthand notation
  - **Representations** → symbols that contain information associated with the entire set of symmetry operations of a point group
  - **Character Tables** → summary of relationships (characters) btw reps & individual symmetry operations

Point Group — Symmetry operations (grouped by classes of related ops)

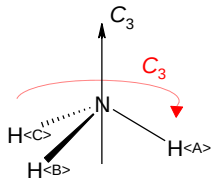
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y), (R_x,R_y)$	$(x^2\text{-}y^2, xy), (xz,yz)$

sum of coefficients gives order of group $\Rightarrow h_{C_{3v}} = 1+2+3 = \boxed{6}$

characters $\Rightarrow \chi$

irreducible representations $\Rightarrow \Gamma_{IR}$

geometrical bases/transformations



1.2 Symmetry and Group Theory

- General Organization of Character Tables

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Mulliken Symbols used to indicate Γ_{IR}

$\chi(\hat{E})$ = 1 then A or B
= 2 then E
= 3 then T

For 1 dimensional irreps:

$\chi(\hat{C}_n^1)$ = +1 then A (*i.e.* symmetric)
= -1 then B (*i.e.* antisymmetric)

$\chi(\perp \hat{C}_n^1)$ *or* $\chi(\hat{\sigma}_v)$ = +1 then Sub1 (*e.g.* A_1)
= -1 then Sub2

Symmetry elements are usually, but not always, organized by the following priority:

$E > C_n > C_n' > i > S > \sigma_h > \sigma_v > \sigma_d$

$\chi(\hat{i})$ = +1 then Subg (*i.e.* gerade)
= -1 then Subu (*i.e.* ungerade)

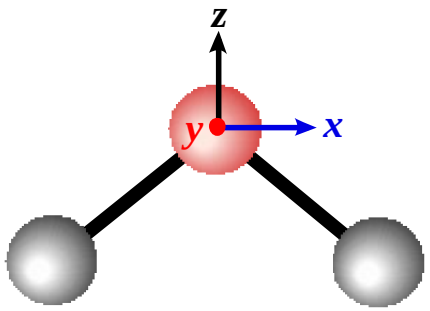
if no $\hat{i}$: $\chi(\hat{\sigma}_h)$ = +1 then Super' (*e.g.* A_2')
= -1 then Super“

1.2 Symmetry and Group Theory

- Building a Simple Character Table
  - Determine the effect of all symmetry operations on a series of geometrical basis vectors and tensors $x, y, z, R_x, R_y, R_z, xy, xz, yz, x^2 - y^2, z^2, etc.$

$$\Rightarrow C_{2v} \equiv E, C_2, \sigma_v, \sigma_v' \quad (\sigma_{xz}\ \sigma_{yz})$$

- e.g. H_2O



$\vec{x}$	$\vec{y}$	$\vec{z}$
$E(\vec{x}) = +\vec{x}$	$E(\vec{y}) = +\vec{y}$	$E(\vec{z}) = +\vec{z}$
$C_2(\vec{x}) = -\vec{x}$	$C_2(\vec{y}) = -\vec{y}$	$C_2(\vec{z}) = +\vec{z}$
$\sigma_{xz}(\vec{x}) = +\vec{x}$	$\sigma_{xz}(\vec{y}) = -\vec{y}$	$\sigma_{xz}(\vec{z}) = +\vec{z}$
$\sigma_{yz}(\vec{x}) = -\vec{x}$	$\sigma_{yz}(\vec{y}) = +\vec{y}$	$\sigma_{yz}(\vec{z}) = +\vec{z}$

$\vec{R}_x$	$\vec{R}_y$	$\vec{R}_z$
$E(\vec{R}_x) = +\vec{R}_x$	$E(\vec{R}_y) = +\vec{R}_y$	$E(\vec{R}_z) = +\vec{R}_z$
$C_2(\vec{R}_x) = -\vec{R}_x$	$C_2(\vec{R}_y) = -\vec{R}_y$	$C_2(\vec{R}_z) = +\vec{R}_z$
$\sigma_{xz}(\vec{R}_x) = -\vec{R}_x$	$\sigma_{xz}(\vec{R}_y) = +\vec{R}_y$	$\sigma_{xz}(\vec{R}_z) = -\vec{R}_z$
$\sigma_{yz}(\vec{R}_x) = +\vec{R}_x$	$\sigma_{yz}(\vec{R}_y) = -\vec{R}_y$	$\sigma_{yz}(\vec{R}_z) = -\vec{R}_z$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_1	+1	+1	+1	+1	z
Γ_2	+1	+1	-1	-1	R_z
Γ_3	+1	-1	+1	-1	x or R_y
Γ_4	+1	-1	-1	+1	y or R_x

double-check accuracy of character table by ensuring that products of two operations still work...

1.2 Symmetry and Group Theory

- label irreps using rules defined previously...

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
$A_1 \Rightarrow \Gamma_1$	+1	+1	+1	+1	z
$A_2 \Rightarrow \Gamma_2$	+1	+1	-1	-1	R_z
$B_1 \Rightarrow \Gamma_3$	+1	-1	+1	-1	x or R_y
$B_2 \Rightarrow \Gamma_4$	+1	-1	-1	+1	y or R_x

← symmetric with respect to all symmetry operations
= ***totally symmetric representation***

- ***totally symmetric representation*** is very special...
  - always exists – defines the actual symmetry of the point group
  - mathematically, only functions that are totally symmetric will have non-zero integrals when integrated over all space:

$$\int_{-\infty}^{\infty} f(\tau)d\tau \neq 0 \quad \rightarrow \text{if} \quad f(\tau) \mapsto A_1$$

← in C_{2v} symmetry

$$\int_{-\infty}^{\infty} f(\tau)d\tau = 0 \quad \rightarrow \text{if} \quad f(\tau) \mapsto \text{any other } \Gamma_i$$

Five Theorems for Complete Set of Irreps in a Point Group

- Sum of squares of the dimensions of Γ_i of a group = the order of the group (*h*)

$$\sum_i \left[\chi_i(\hat{E})\right]^2 = h$$

- Sum of squares of the characters in Γ_i = the order of the group

$$\sum_{\hat{R}} \left[\chi_i(\hat{R})\right]^2 = h$$

- Γ_i are mutually orthogonal (i.e. they define a minimal basis set)

$$\sum_{\hat{R}} \chi_i(\hat{R})\chi_j(\hat{R}) = 0 \text{ for } i \neq j$$

- For a given Γ_i, the characters of all operations belonging to the same class are identical
  - ops can be turned into one another by changing reference frame
- Number of Γ_i equals the number of classes

$\mathbf{C_{3v}}$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

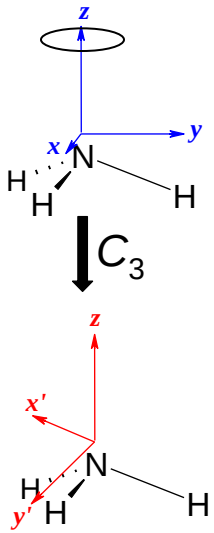
1.2 Symmetry and Group Theory

- not all point groups can constructed in this way
  - can be completed by using theorems + other mathematical approaches
  - luckily, you generally don't have to build character tables from scratch
  - what about representations that don't give +1 and/or -1 as characters?

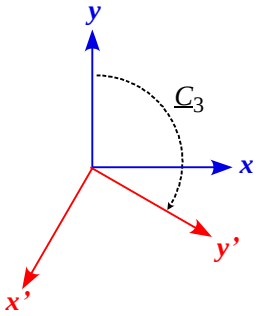
$\mathbf{D_{4h}}$	E	$2C_4(z)$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+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	-	z^3, $z(x^2+y^2)$
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-	xyz
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	$z(x^2-y^2)$
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-	(xz^2, yz^2) (xy^2, x^2y), (x^3, y^3)

Degenerate Irreducible Representations

- So far, operations have all transformed into ± themselves
  - characters represent simple transformations (1x1 matrices)
- in some point groups → transformation gives LC of vectors
  - results in degenerate representations…
- e.g. let's look at the effect of a C_3 rotation in NH_3 (C_{3v}) on (x,y,z)



looking from above, we see that the *x,y* axes transform into linear combinations of each other…



$$x' = \cos\ \tfrac{2\pi}{3}\ x - \sin\ \tfrac{2\pi}{3}\ y = -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y$$

$$y' = \sin\ \tfrac{2\pi}{3}\ x + \cos\ \tfrac{2\pi}{3}\ y = +\tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y$$

$$or\ldots(\text{in matrix form})$$

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

in this case, the (*x*,*y*) pair must be considered as inseparable since they require each other to be properly defined within C_{3v}.

1.2 Symmetry and Group Theory

- how do we build the character table for C_{3v}?
  - remember – (x,y) must now be considered together...
  - symmetry operations are E, $2C_3$, $3\sigma_v$

$$\hat{E}\ \vec{z} = +1\ \vec{z}$$

$$\hat{E}\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix} = \begin{pmatrix}+1 & 0\\ 0 & +1\end{pmatrix}\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix}$$

$$+2$$

$$\hat{C}_3\ \vec{z} = +1\ \vec{z}$$

$$\hat{C}_3\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix} = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ +\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix}$$

$$\hat{C}_3^2\ \vec{z} = +1\ \vec{z}$$

$$\hat{C}_3^2\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix} = \begin{pmatrix}-\frac{1}{2} & +\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix}$$

$$-1$$

$$\hat{\sigma}_v\ \vec{z} = +1\ \vec{z}$$

$$\hat{\sigma}_v\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix} = \begin{pmatrix}+1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\vec{x}\\ \vec{y}\end{pmatrix}$$

$$0$$

- **characters** of 2×2 transformation matrices are the traces of those matrices

$$\mathrm{Tr}\begin{pmatrix}a & b\\ c & d\end{pmatrix} = a + d$$

- within a class of operations
  - matrices are not necessarily the same
  - trace of the matrices must be identical

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	$\Leftarrow z$
A_2	1	1	-1	
E	2	-1	0	$\Leftarrow x, y$

Uses of Character Tables – Direct Products

- often important to know the symmetry of a function that results from the product of two or more other functions, i.e. $f = f_1 \cdot f_2$
- symmetry of product function = direct product of components

$$\text{if } f = f_1 \cdot f_2 \text{ , and } \begin{matrix} f_1 \mapsto \Gamma_1 \\ f_2 \mapsto \Gamma_2 \end{matrix} \text{ then } f \mapsto \Gamma_{DP} = \Gamma_1 \times \Gamma_2$$

direct product

- DP obtained by multiplying the characters of each component Γ_i
  - e.g. in C_{3v} symmetry with $f_1 \mapsto A_1$ and $f_2 \mapsto A_2$

from C_{3v} char table $\Rightarrow$

	E	$2C_3$	$3\sigma_v$
A_1	+1	+1	+1
A_2	+1	+1	-1
$A_1 \times A_2 =$	(1)(1)	(1)(1)	(1)(-1)
=	1	1	-1 = A_2

a direct product involving the totally symmetric representation simply results in getting the same function back...

$$\Gamma_{symm} \times \Gamma_i = \Gamma_i$$

$$A_1 \times \Gamma_i = \Gamma_i$$

1.2 Symmetry and Group Theory

- e.g. in C_{3v} symmetry with $f_1 \mapsto E \text{ and } f_2 \mapsto E$

from C_{3v} char table $\Rightarrow$

	E	$2C_3$	$3\sigma_v$
E	+2	-1	0
E	+2	-1	0
E x E =	(2)(2)	(-1)(-1)	(0)(0)
=	(4)	1	0 = ***?????***

dimension of $E \times E$ is 4... but the greatest dimensionality Γ_i in C_{3v} is E (with 2)
→ **product is *reducible***

- DP may result in a complex solution:
  - product must be linear combination of irreps $\Rightarrow \Gamma_{red} = \Gamma_1 + \Gamma_2 + \ldots$
    - any function can be broken down into a linear comb. of basis functions
  - reducible reps can therefore be reduced into its component irreps
    - can use a multiplication table to find that

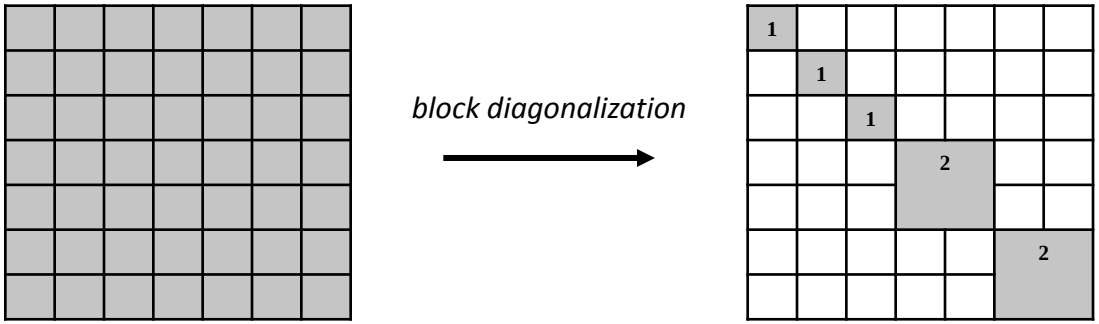
$$E \times E = A_1 + A_2 + E$$

    - we say that $E \times E$ **contains** A_1, A_2, and E

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

Uses of Character Tables – Reducible & Irreducible Reps

- character table contains complete set of irreps for a group
  - everything in the group can be reduced into LC of these irreps
- properties of a set of N operations represented by N×N matrix
  - usually a reducible representation
  - always possible to rearrange them to produce LC of irreps
  - N×N matrix representing symmetry operations reduces to smaller 1×1, 2×2, and 3×3 matrices, which are the irreps → i.e. block diagonalization



1.2 Symmetry and Group Theory

- reduction formula to generate component irreps
  - All reducible reps can be reduced to a linear combination of irreps:

$$\chi_{red}(\hat{R}) = \sum_i \mathrm{a}_i \chi_i(\hat{R})$$

  - coefficients for component irreps is calculated using reduction formula:

$$\mathrm{a}_i = \frac{1}{h}\sum_R n_R \chi_{red}(\hat{R})\chi_i(\hat{R})$$

    - $\chi_{red}(R)$ = character of the reducible representation, Γ_{red}, for operation R
    - $\chi_i(R)$ = character of the irreducible representation, Γ_i, for operation R
    - a_i = number of times a particular irrep, Γ_i, occurs in the reducible rep

- e.g. E×E in C_{3v}

$\boldsymbol{C_{3v}}$	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	(x,y), (R_x,R_y)
$E \times E$	(2)(2)	(-1)(-1)	(0)(0)	
Γ_{DP}	4	1	0	

1.2 Symmetry and Group Theory

$\boldsymbol{C_{3v}}$	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	(x,y), (R_x,R_y)
$E \times E$	(2)(2)	(-1)(-1)	(0)(0)	
Γ_{DP}	4	1	0	

$$a_{A_1} = \frac{1}{h}\sum_R \left[n_R\right]\left[\chi_{red}(\hat{R})\right]\left[\chi_{A_1}(\hat{R})\right]$$

$$= \frac{1}{6}\left(\overset{1}{n_{\hat{E}}}\overbrace{\chi_{red}(\hat{E})}^{4}\overbrace{\chi_{A_1}(\hat{E})}^{1} + \overset{2}{n_{\hat{C}_3}}\overbrace{\chi_{red}(\hat{C}_3)}^{1}\overbrace{\chi_{A_1}(\hat{C}_3)}^{1} + \overset{3}{n_{\hat{\sigma}_v}}\overbrace{\chi_{red}(\hat{\sigma}_v)}^{0}\overbrace{\chi_{A_1}(\hat{\sigma}_v)}^{1} \right)$$

$$= \frac{1}{6}\ 1\cdot 4\cdot 1 + 2\cdot 1\cdot 1 + 3\cdot 0\cdot 1\ = \boxed{1}$$

1.2 Symmetry and Group Theory

$$a_{A_2} = \frac{1}{6}\left(\overset{1}{n_{\hat{E}}} \overbrace{\chi_{red}(\hat{E})}^{4} \overbrace{\chi_{A_2}(\hat{E})}^{1} + \overset{2}{n_{\hat{C}_3}} \overbrace{\chi_{red}(\hat{C}_3)}^{1} \overbrace{\chi_{A_2}(\hat{C}_3)}^{1} + \overset{3}{n_{\hat{\sigma}_v}} \overbrace{\chi_{red}(\hat{\sigma}_v)}^{0} \overbrace{\chi_{A_2}(\hat{\sigma}_v)}^{-1} \right)$$

$$= \frac{1}{6}\ 1\cdot 4\cdot 1 + 2\cdot 1\cdot 1 + 3\cdot 0\cdot -1\ = \boxed{1}$$

$$a_E = \frac{1}{6}\left(\overset{1}{n_{\hat{E}}} \overbrace{\chi_{red}(\hat{E})}^{4} \overbrace{\chi_{E}(\hat{E})}^{2} + \overset{2}{n_{\hat{C}_3}} \overbrace{\chi_{red}(\hat{C}_3)}^{1} \overbrace{\chi_{E}(\hat{C}_3)}^{-1} + \overset{3}{n_{\hat{\sigma}_v}} \overbrace{\chi_{red}(\hat{\sigma}_v)}^{0} \overbrace{\chi_{E}(\hat{\sigma}_v)}^{0} \right)$$

$$= \frac{1}{6}\ 1\cdot 4\cdot 2 + 2\cdot 1\cdot -1 + 3\cdot 0\cdot 0\ = \boxed{1}$$

$$\Gamma_{E\times E} = 1\cdot A_1 + 1\cdot A_2 + 1\cdot E$$

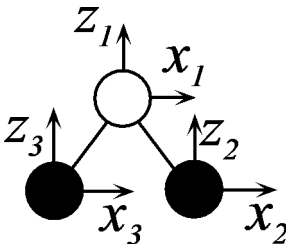
$$= \boxed{A_1 + A_2 + E}$$

Using Reducible Representations → Molecular Vibrations

- symmetry of molecular motions determined by generating appropriate reducible representations!
  - use local cartesian coordinates for all *N* atoms in the molecule
  - these describe all 3*N* nuclear motions that are possible
  - break down into: translations, vibrations, and rotations
- e.g. determine symmetry of all vibrational modes for H_2O:

there are three sets of cartesian coordinates – *i.e.* 9 basis vectors

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	+1	+1	+1	+1
A_2	+1	+1	-1	-1
B_1	+1	-1	+1	-1
B_2	+1	-1	-1	+1

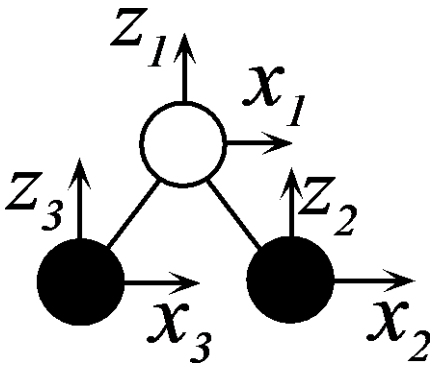


perform all operations on every basis vector: three possible outcomes:

+1 → no change
-1 → reversed
0 → change in position

1.2 Symmetry and Group Theory

- determine the symmetry of all vibrational modes for H_2O



C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	+1	+1	+1	+1
A_2	+1	+1	-1	-1
B_1	+1	-1	+1	-1
B_2	+1	-1	-1	+1

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
x_1				
y_1				
z_1				
x_2				
y_2				
z_2				
x_3				
y_3				
z_3				
Γ_{red}				

1.2 Symmetry and Group Theory

- this 3*N* representation can be reduced into its component irreducible representations:

$$\Gamma_{3N}^{(C_{2v})} = \mathrm{a}_{A_1} A_1 + \mathrm{a}_{A_2} A_2 + \mathrm{a}_{B_1} B_1 + \mathrm{a}_{B_2} B_2 = 3\ A_1 + 1\ A_2 + 3\ B_1 + 2\ B_2$$

- represents symmetry of all nuclear motions:

$$\Gamma_{3N} = \Gamma_{trans} + \Gamma_{vib} + \Gamma_{rot}$$

  - only want vibrational degrees of freedom
  - must remove translations & rotations

- character table gives answer
  - translations along *x*, *y*, *z* transform as *x*, *y*, *z*
  - rotations around *x*, *y*, *z* transform as R_x, R_y, R_z

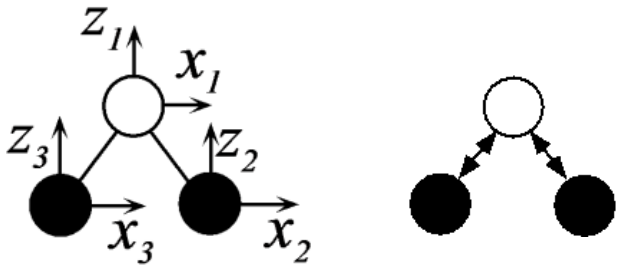
C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	+1	+1	+1	+1	z
A_2	+1	+1	-1	-1	R_z
B_1	+1	-1	+1	-1	x, R_y
B_2	+1	-1	-1	+1	y, R_x

- remove these and the remainder must be the vibrations!

$$\begin{aligned}\Gamma_{vib} &= \Gamma_{3N} - \Gamma_{trans} - \Gamma_{rot} \\ &= \left[3A_1 + A_2 + 3B_1 + 2B_2\right] - \left[A_1 + B_1 + B_2\right] - \left[A_2 + B_1 + B_2\right] \\ &= \boxed{2A_1 + 1B_1}\end{aligned}$$

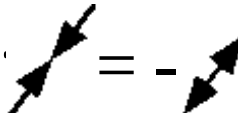
Visualizing Molecular Vibrations: Using Internal Coordinates

- just determined that H_2O has
  - three fundamental vibrational modes (*a.k.a.* normal modes)
  - with the following symmetry: A_1, A_1, and B_1
- but... what do these look like?
  - this can be done by group theory...
  - much easier if we modify our basis vectors → use internal coordinates
- int coord are chemically more relevant (correspond to largest forces)
  - distances (r) ≡ bond distances
  - angles (θ) ≡ bond angles
  - dihedral angles (ϕ) ≡ bond torsion angles
  - intrinsically exclude translations & rotations



1.2 Symmetry and Group Theory

- use OH bond distances in H_2O as a basis vectors..



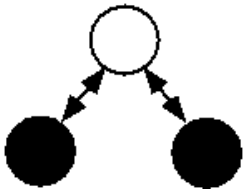
  - the opposite of a stretch is a compression such that

- what happens to these two vectors when we operate on them…

	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	2	0	2	0

$$\Gamma_{OH} = A_1 + B_1$$

- reducible representation is for both OH stretches!
  - used Δr_1 and $\Delta r_2 \rightarrow A_1$ & B_1 stretches therefore involve BOTH Δr_1 and Δr_2
  - must build SALCs of the component vectors
    - SALC = symmetry-adapted linear combination



Constructing Symmetry Adapted Linear Combinations

- transform set of localized functions that do NOT transform within a point group into an analogous set of delocalized functions that do!
  - used in many areas of chemistry → MO theory, vibrational analysis, etc.
  - anywhere where symmetry is useful – SALCs must be invoked
  - **projection** of localized functions onto correct symmetry irreps

projection operator for Γ_i → $\hat{P}^i(\phi) = \frac{l_i}{h}\sum_R \chi_i(R)\hat{R}(\phi)$

dimension of ***i***th *irrep*

apply operation on a basis vector

  - important things to remember:
    - each operation must be done independently (can't do just one per class!)
    - procedure yields *unnormalized* SALCs (must be normalized)

1.2 Symmetry and Group Theory

$$S_i \equiv \hat{P}_i(\Delta r_1) \propto \sum_R \chi_i(R)\hat{R}(\Delta r_1)$$

- *e.g.* H_2O (again!)
  - construct the functions (S_i) from the internal coordinates (Δr)
  - look at Δr_1 first... and how it transforms in A_1

$$\begin{aligned} S_{A_1} &\propto (1)\left[\hat{E}(\Delta r_1)\right] + (1)\left[\hat{C}_2(\Delta r_1)\right] + (1)\left[\hat{\sigma}_{xz}(\Delta r_1)\right] + (1)\left[\hat{\sigma}_{yz}(\Delta r_1)\right] \\ &\propto (1)\left[\Delta r_1\right] + (1)\left[\Delta r_2\right] + (1)\left[\Delta r_1\right] + (1)\left[\Delta r_2\right] \\ &\propto \boxed{\Delta r_1 + \Delta r_2} \end{aligned}$$

this only works if component functions are orthogonal!

- this must be normalized $\rightarrow$ $N = \dfrac{1}{\sqrt{\sum_j c_j^2}}$

$$\boxed{S_{A_1} = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)}$$

- for B_1 symmetry:

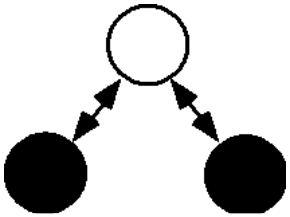
$$\begin{aligned} S_{B_1} &\propto (1)\left[\hat{E}(\Delta r_1)\right] + (-1)\left[\hat{C}_2(\Delta r_1)\right] + (1)\left[\hat{\sigma}_{xz}(\Delta r_1)\right] + (-1)\left[\hat{\sigma}_{yz}(\Delta r_1)\right] \\ &\propto (1)\left[\Delta r_1\right] + (-1)\left[\Delta r_2\right] + (1)\left[\Delta r_1\right] + (-1)\left[\Delta r_2\right] \\ &\propto \boxed{\Delta r_1 - \Delta r_2} \end{aligned}$$

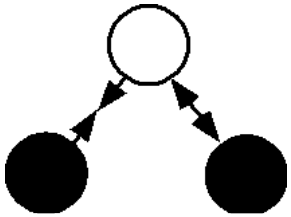
$$\boxed{S_{B_1} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)}$$

1.2 Symmetry and Group Theory

- The stretching vibrational modes are therefore
  - $A_1 \rightarrow$ symmetric linear combination of Δr_1 and Δr_2
  - $B_1 \rightarrow$ antisymmetric linear combination of Δr_1 and Δr_2
  - vibrational spectroscopy $\rightarrow$ SALCs are referred to as symmetry coordinates

$$S_{A_1} = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2) \qquad S_{B_1} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

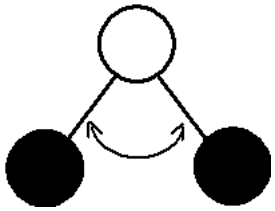




1.2 Symmetry and Group Theory

- we still have one vibrational mode left... (the other A_1 mode)
  - we have one internal coordinate left... the H-O-H bending mode
  - performing symmetry operations on this coordinate gives...

	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	1	1	1	1



$$\Gamma_{\mathrm{HOH}} = A_1$$

  - 1st order approximation of the normal modes for H_2O are...

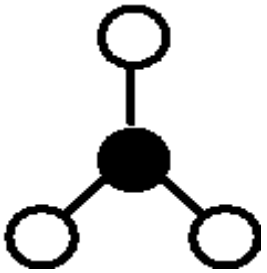
$$S_{A_1} = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$$
$$S_{A_1} = \Delta\theta$$
$$S_{B_1} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

these two modes have the same symmetry and therefore can mix to form linear combinations...

normal coordinate analysis *allows for such mixing and uses experimental data to determine extent of mixing in TRUE normal modes.*

1.2 Symmetry and Group Theory

- e.g. vibrational modes of $[NO_3]^-$
  - find the point group of the molecule → D_{3h}
  - operate using Cartesian axes of each atom



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{3N}	12	0	-2	4	-2	2

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

- reduce the representation…

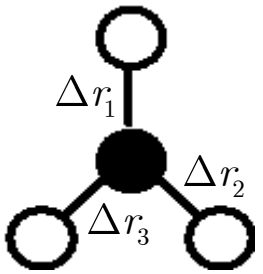
$$\Gamma_{3N} = A_1' + A_2' + 3E' + 2A_2'' + E''$$

- remove translations & rotations

$$\begin{aligned}\Gamma_{vib} &= \Gamma_{3N} - \Gamma_{trans} - \Gamma_{rot} = \Gamma_{3N} - \Gamma_{x,y,z} - \Gamma_{R_x,R_y,R_z} \\ &= \left[A_1' + A_2' + 3E' + 2A_2'' + E''\right] - \left[E' + A_2''\right] - \left[A_2' + E_2''\right] \\ &= \boxed{A_1' + 2E' + A_2''}\end{aligned}$$

1.2 Symmetry and Group Theory

- determine contributions from stretching vibrations
  - use bond distances are basis vectors
  - generate a reducible representation



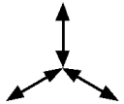
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\Delta r}$	3	0	1	3	0	1

$$\Gamma_{\Delta r} = A_1' + E'$$

  - find the projections of the basis vector to generate appropriate SALCs

$$\begin{aligned} S_{A_1'} &\propto (1)\left[\hat{E}(\Delta r_1)\right] + (1)\left[\hat{C}_3^1(\Delta r_1) + \hat{C}_3^2(\Delta r_1)\right] + (1)\left[\hat{C}_2(\Delta r_1) + \hat{C}_2'(\Delta r_1) + \hat{C}_2''(\Delta r_1)\right] \\ &\quad + (1)\left[\hat{\sigma}_h(\Delta r_1)\right] + (1)\left[\hat{S}_3^1(\Delta r_1) + \hat{S}_3^2(\Delta r_1)\right] + (1)\left[\hat{\sigma}_v(\Delta r_1) + \hat{\sigma}_v'(\Delta r_1) + \hat{\sigma}_v''(\Delta r_1)\right] \\ &\propto (1)\left[\Delta r_1\right] + (1)\left[\Delta r_2 + \Delta r_3\right] + (1)\left[\Delta r_1 + \Delta r_2 + \Delta r_3\right] + (1)\left[\Delta r_1\right] + (1)\left[\Delta r_2 + \Delta r_3\right] + (1)\left[\Delta r_1 + \Delta r_2 + \Delta r_3\right] \\ &\propto \Delta r_1 + \Delta r_2 + \Delta r_3 \end{aligned}$$

$$S_{A_1'} = \boxed{\tfrac{1}{\sqrt{3}}\left(\Delta r_1 + \Delta r_2 + \Delta r_3\right)}$$

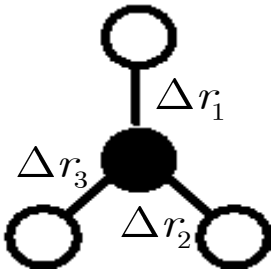


$$\begin{aligned} S_{E'} &\propto (2)\ \Delta r_1 + (-1)\ \Delta r_2 + \Delta r_3 + (0)\ \Delta r_1 + \Delta r_2 + \Delta r_3 + (2)\ \Delta r_1 + (-1)\ \Delta r_2 + \Delta r_3 + (0)\ \Delta r_1 + \Delta r_2 + \Delta r_3 \\ &\propto 2\Delta r_1 - \Delta r_2 - \Delta r_3 \end{aligned}$$

$$S_{E'} = \boxed{\tfrac{1}{\sqrt{6}}\ 2\Delta r_1 - \Delta r_2 - \Delta r_3}$$

1.2 Symmetry and Group Theory

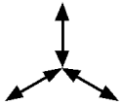
- applying S_{A_1} on $\Delta r_{2,3}$ in D_{3h}



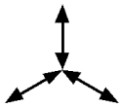
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\Delta r}$	3	0	1	3	0	1

$$\Gamma_{\Delta r} = A_1' + E'$$

$$S_{A_1'} \propto (1)\left[\hat{E}(\Delta\vec{r}_2)\right] + (1)\left[\hat{C}_3^1(\Delta\vec{r}_2) + \hat{C}_3^2(\Delta\vec{r}_2)\right] + (1)\left[\hat{C}_2(\Delta\vec{r}_2) + \hat{C}_2'(\Delta\vec{r}_2) + \hat{C}_2''(\Delta\vec{r}_2)\right]$$
$$+ (1)\ \hat{\sigma}_h(\Delta\vec{r}_2) + (1)\left[\hat{S}_3^1(\Delta\vec{r}_2) + \hat{S}_3^2(\Delta\vec{r}_2)\right] + (1)\left[\hat{\sigma}_v(\Delta\vec{r}_2) + \hat{\sigma}_v'(\Delta\vec{r}_2) + \hat{\sigma}_v''(\Delta\vec{r}_2)\right]$$
$$\propto (1)\ \Delta\vec{r}_2 + (1)\ \Delta\vec{r}_3 + \Delta\vec{r}_1 + (1)\ [\Delta\vec{r}_3 + \Delta\vec{r}_1 + \Delta\vec{r}_2] + (1)\ [\Delta\vec{r}_2] + (1)\ [\Delta\vec{r}_3 + \Delta\vec{r}_1] + (1)\ [\Delta\vec{r}_3 + \Delta\vec{r}_1 + \Delta\vec{r}_2]$$
$$\propto \Delta\vec{r}_1 + \Delta\vec{r}_2 + \Delta\vec{r}_3$$
$$S_{A_1'} = \boxed{\tfrac{1}{\sqrt{3}}(\Delta\vec{r}_1 + \Delta\vec{r}_2 + \Delta\vec{r}_3)}$$



$$S_{A_1'} \propto (1)\left[\hat{E}(\Delta\vec{r}_3)\right] + (1)\left[\hat{C}_3^1(\Delta\vec{r}_3) + \hat{C}_3^2(\Delta\vec{r}_3)\right] + (1)\left[\hat{C}_2(\Delta\vec{r}_3) + \hat{C}_2'(\Delta\vec{r}_3) + \hat{C}_2''(\Delta\vec{r}_3)\right]$$
$$+ (1)\ \hat{\sigma}_h(\Delta\vec{r}_3) + (1)\left[\hat{S}_3^1(\Delta\vec{r}_3) + \hat{S}_3^2(\Delta\vec{r}_3)\right] + (1)\left[\hat{\sigma}_v(\Delta\vec{r}_3) + \hat{\sigma}_v'(\Delta\vec{r}_3) + \hat{\sigma}_v''(\Delta\vec{r}_3)\right]$$
$$\propto (1)\ \Delta\vec{r}_3 + (1)\ \Delta\vec{r}_2 + \Delta\vec{r}_1 + (1)\ [\Delta\vec{r}_2 + \Delta\vec{r}_3 + \Delta\vec{r}_1] + (1)\ [\Delta\vec{r}_3] + (1)\ [\Delta\vec{r}_2 + \Delta\vec{r}_1] + (1)\ [\Delta\vec{r}_2 + \Delta\vec{r}_3 + \Delta\vec{r}_1]$$
$$\propto \Delta\vec{r}_1 + \Delta\vec{r}_2 + \Delta\vec{r}_3$$
$$S_{A_1'} = \boxed{\tfrac{1}{\sqrt{3}}(\Delta\vec{r}_1 + \Delta\vec{r}_2 + \Delta\vec{r}_3)}$$



1.2 Symmetry and Group Theory

- for *E'* symmetry, there must be two vibrations that transform together
  - we have found one of them: $S^{(1)}_{E'} = \boxed{\frac{1}{\sqrt{6}}\ 2\Delta\vec{r}_1 - \Delta\vec{r}_2 - \Delta\vec{r}_3}$
  - finding the second vibrational mode – use rules of mathematical groups
    - applying any operation of the group on the above function must lead to:
      - ± itself
      - ± another degenerate function (in this case, its only partner)
      - a linear combination of these degenerate functions
- apply C_3 to existing *E'* vibrational mode $f \propto \hat{C}_3(S_{E'}(1)) = -\Delta\vec{r}_1 + 2\Delta\vec{r}_2 - \Delta\vec{r}_3$
  - same thing as doing the projection of Δr_2 onto *E'*
  - is this new function orthogonal to the first?

$$\left.\begin{aligned} S^{(1)}_{E'} &\propto +2\Delta\vec{r}_1 - 1\Delta\vec{r}_2 - 1\Delta\vec{r}_3 \\ \hat{C}_3\ S^{(1)}_{E'} &\propto -1\Delta\vec{r}_1 + 2\Delta\vec{r}_2 - 1\Delta\vec{r}_3 \end{aligned}\right\} \quad \begin{aligned} &+2\ \ -1\ +\ -1\ \ +2\ +\ -1\ \ -1 \\ &= -2\ +\ -2\ +\ +1\ = \boxed{-3} \Leftarrow no! \end{aligned}$$

- *f* is not a complementary basis function but → $f = c_1 S^{(1)}_{E'} + c_2 S^{(2)}_{E'}$
  - modify *f* by adding in some amount of first basis vector →

$$f' = f + \alpha S^{(1)}_{E'} = f + \frac{1}{2} S^{(1)}_{E'}$$

1.2 Symmetry and Group Theory

$$f' = f + \frac{1}{2} S^{(1)}_{E'}$$

$$\propto \; -1\Delta\vec{r} + 2\Delta\vec{r}_2 - 1\Delta\vec{r}_3 \; + \tfrac{1}{2} \; +2\Delta\vec{r}_1 - 1\Delta\vec{r}_2 - 1\Delta\vec{r}_3$$

$$\propto \; 0 \; \Delta\vec{r}_1 + \tfrac{3}{2}\Delta\vec{r}_2 - \tfrac{3}{2}\Delta\vec{r}_3$$

$$\propto \boxed{\Delta\vec{r}_2 - \Delta\vec{r}_3}$$

- is this new function (*f'*) orthogonal?
  - we have now generated a partner that is orthogonal to the initial basis function
- what do these look like?

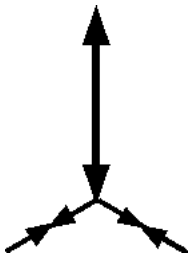
$$S^{(1)}_{E'} \propto +2\Delta\vec{r}_1 - 1\Delta\vec{r}_2 - 1\Delta\vec{r}_3$$

$$f' \propto +0\Delta\vec{r}_1 + 1\Delta\vec{r}_2 - 1\Delta\vec{r}_3$$

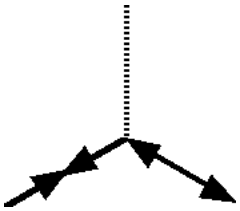
$$+2 \;\; 0 \;+\; -1 \;\; +1 \;+\; -1 \;\; -1$$

$$= \; 0 \;+\; -1 \;+\; +1 \;= \boxed{0} \Leftarrow yes!$$

$$S^{(1)}_{E'} = \boxed{\tfrac{1}{\sqrt{6}} \; 2\Delta\vec{r}_1 - \Delta\vec{r}_2 - \Delta\vec{r}_3}$$



$$S^{(2)}_{E'} = \boxed{\tfrac{1}{\sqrt{2}} \; \Delta\vec{r}_2 - \Delta\vec{r}_3}$$



1.2 Symmetry and Group Theory

- let's consider what we have just determined…
  - formed pair of vibrational modes whom together transform as *E'* in D_{3h}
  - but these basis functions are not unique!
  - other linear combinations of these basis functions will also meet the criteria that we have set out:
    - together they "span the space" of *E'*
    - they are orthogonal to each other

$$S^{(1)}_{E'} = \frac{1}{\sqrt{6}}\ 2\Delta\vec{r}_1 - \Delta\vec{r}_2 - \Delta\vec{r}_3$$

$$S^{(2)}_{E'} = \frac{1}{\sqrt{2}}\ \Delta\vec{r}_2 - \Delta\vec{r}_3$$

  - *e.g.* what if we do a combination of our existing functions?

$$\begin{aligned} S^{(1')}_{E'} &\propto S^{(1)}_{E'} + S^{(2)}_{E'} \\ &\propto\ 2\Delta\vec{r}_1 - \Delta\vec{r}_2 - \Delta\vec{r}_3\ +\ \Delta\vec{r}_2 - \Delta\vec{r}_3 \\ &\propto \boxed{\Delta\vec{r}_1 - \Delta\vec{r}_3} \Rightarrow\Rightarrow\Rightarrow S^{(2')}_{E'} \propto \boxed{2\Delta\vec{r}_2 - \Delta\vec{r}_1 - \Delta\vec{r}_3} \end{aligned}$$

  - chosen description is only one of the possible representations of E'

1.2 Symmetry and Group Theory

- thus far, we have evaluated only two of the components…

$$\Gamma_{vib} = \underbrace{A_1' + E'}_{\downarrow} + E' + A_2''$$

from bond stretches

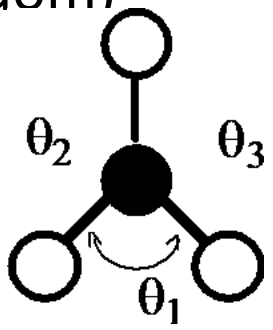
$$S^{\Delta r}_{A_1'} \rightarrow \tfrac{1}{\sqrt{3}}\ \Delta r_1 + \Delta r_2 + \Delta r_3$$

$$S^{\Delta r}_{E'} \rightarrow \tfrac{1}{\sqrt{6}}\ 2\Delta \vec{r}_1 - \Delta \vec{r}_2 - \Delta \vec{r}_3 \quad \& \quad \tfrac{1}{\sqrt{2}}\ \Delta \vec{r}_2 - \Delta \vec{r}_3$$

- now look at bond bending (angular degrees of freedom)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\Delta\theta}$	3	0	1	3	0	1

$$\Gamma_{\Delta\theta} = A_1' + E'$$



- project out the A_1' solution
  - this solution doesn't make any sense – throw it out

$$S^{\Delta\theta}_{A_1'} \rightarrow \tfrac{1}{\sqrt{3}}\ \Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3$$

- what about the E' solution?

$$S^{\Delta\theta}_{E'}(1) \rightarrow \tfrac{1}{\sqrt{6}}\ 2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3$$

$$\& \quad S^{\Delta\theta}_{E'}(1) \rightarrow \tfrac{1}{\sqrt{2}}\ \Delta\theta_2 - \Delta\theta_3$$

1.2 Symmetry and Group Theory

- we are now down to one vibrational mode that is unassigned (and one failure)

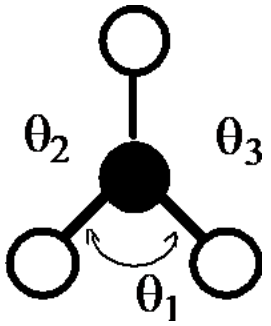
$$\Gamma_{vib} = \underbrace{A_1' + E'}_{\text{from bond stretches}} + \underbrace{E'}_{\text{from bending modes}} + A_2''$$

$$S^{\Delta r}_{A_1'} \rightarrow \tfrac{1}{\sqrt{3}}\ \Delta r_1 + \Delta r_2 + \Delta r_3$$

$$S^{\Delta r}_{E'} \rightarrow \tfrac{1}{\sqrt{6}}\ 2\Delta \vec{r}_1 - \Delta \vec{r}_2 - \Delta \vec{r}_3 \quad \& \quad \tfrac{1}{\sqrt{2}}\ \Delta \vec{r}_2 - \Delta \vec{r}_3$$

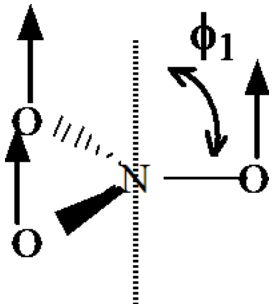
$$S^{\Delta\theta}_{E'} \rightarrow \tfrac{1}{\sqrt{6}}\ 2\Delta \vec{\theta}_1 - \Delta \vec{\theta}_2 - \Delta \vec{\theta}_3 \quad \& \quad \tfrac{1}{\sqrt{2}}\ \Delta \vec{\theta}_2 - \Delta \vec{\theta}_3$$

- let us consider the molecule again, however…
  - θ is defined in the plane – only need two coordinates describe this plane since $\theta_1 + \theta_2 + \theta_3 = 2\pi$
  - the additional coordinate that describes the geometry of this molecule is NOT a simple bond angle… it must be related to a dihedral angle → out of plane distortion!



$$S^{\Delta\phi}_{\Gamma_{\Delta\phi}} \rightarrow \tfrac{1}{\sqrt{3}}\ \Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3$$

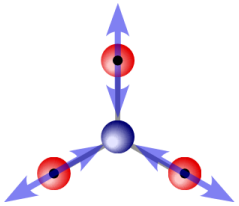
- the rejected mode can exist if we allow for distortion out of the plane
- by inspection, this out-of-plane distortion has A_2" symmetry!



1.2 Symmetry and Group Theory

- the symmetry coordinates for NO_3^- are therefore:

$$A_1' \mapsto \quad S_{A_1'}^{\Delta r} = \frac{1}{\sqrt{3}}\ \Delta r_1 + \Delta r_2 + \Delta r_3$$



–

these modes can mix!

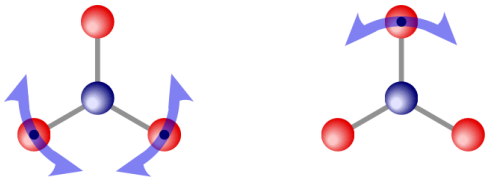
$$E' \mapsto \quad S_{E'}^{\Delta \vec{r}}(1) = \frac{1}{\sqrt{6}}\ 2\Delta\vec{r}_1 - \Delta\vec{r}_2 - \Delta\vec{r}_3$$

$$S_{E'}^{\Delta \vec{r}}(2) = \frac{1}{\sqrt{2}}\ \Delta\vec{r}_2 - \Delta\vec{r}_3$$

–

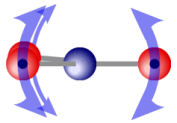
$$E' \mapsto \quad S_{E'}^{\Delta \vec{\theta}}(1) = \frac{1}{\sqrt{6}}\ 2\Delta\vec{\theta}_1 - \Delta\vec{\theta}_2 - \Delta\vec{\theta}_3$$

$$S_{E'}^{\Delta r}(2) = \frac{1}{\sqrt{2}}\ \Delta\vec{\theta}_2 - \Delta\vec{\theta}_3$$



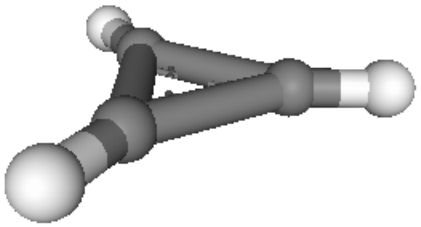
–

$$A_2'' \mapsto \quad S_{A_2''}^{\Delta \vec{\phi}} = \frac{1}{\sqrt{3}}\ \Delta\vec{\phi}_1 + \Delta\vec{\phi}_2 + \Delta\vec{\phi}_3$$

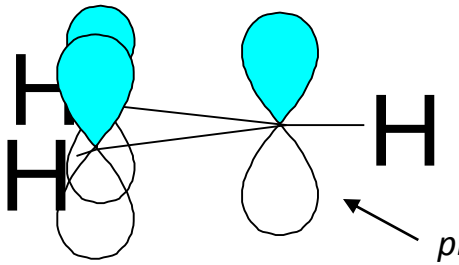


Symmetry in MO theory → Making SALCS from AOs

- same approach used to create delocalized fragment molecular orbitals (FMOs) from localized atomic orbitals (or MOs)…
  - use symmetry to build orbitals that transform properly in the point group
- *e.g.*, the orbitals of the cyclopropenyl cation
  - point group → D_{3h} (same as NO_3^-)
  - use the $2p_z$ orbitals and see how they transform



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	-1	-3	0	1

1.2 Symmetry and Group Theory

- reduce the representation →

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	-1	-3	0	1

$$\Gamma_{red} = A_2'' + E''$$

- Use the projection method to determine appropriate SALCs

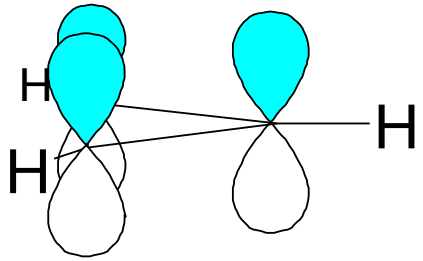
$$\psi_i \equiv \hat{P}_i(p_z(1)) \propto \sum_R \chi_i(R)\hat{R}(p_z(1))$$

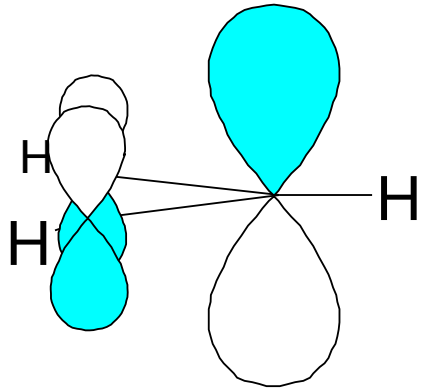
$$\begin{aligned}\psi_{A_2''} \propto\ & (1)\left[\hat{E}(p_z^{(1)})\right]+(1)\left[\hat{C}_3^1(p_z^{(1)})\right]+(1)\left[\hat{C}_3^2(p_z^{(1)})\right]+(-1)\left[\hat{C}_2(p_z^{(1)})\right] \\ & +(-1)\left[\hat{C}_2'(p_z^{(1)})\right]+(-1)\left[\hat{C}_2''(p_z^{(1)})\right]+(-1)\left[\hat{\sigma}_h(p_z^{(1)})\right]+(-1)\left[\hat{S}_3^1(p_z^{(1)})\right] \\ & +(-1)\left[\hat{S}_3^2(p_z^{(1)})\right]+(1)\left[\hat{\sigma}_v(p_z^{(1)})\right]+(1)\left[\hat{\sigma}_v'(p_z^{(1)})\right]+(1)\left[\hat{\sigma}_v''(p_z^{(1)})\right] \\ \propto\ & p_z^{(1)}+p_z^{(2)}+p_z^{(3)} \quad \Rightarrow \quad \psi_{A_2''} = \boxed{\tfrac{1}{\sqrt{3}}\left(p_z^{(1)}+p_z^{(2)}+p_z^{(3)}\right)}\end{aligned}$$

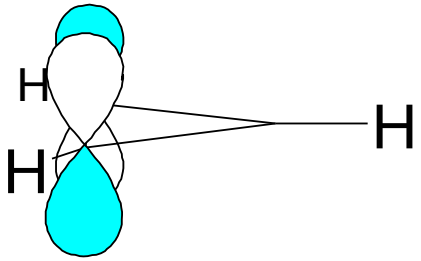
$$\begin{aligned}\psi_{E''} \propto\ & (2)\left[\hat{E}(p_z^{(1)})\right]+(-1)\left[\hat{C}_3^1(p_z^{(1)})\right]+(-1)\left[\hat{C}_3^2(p_z^{(1)})\right]+(0)\left[\hat{C}_2(p_z^{(1)})\right] \\ & +(0)\left[\hat{C}_2'(p_z^{(1)})\right]+(0)\left[\hat{C}_2''(p_z^{(1)})\right]+(-2)\left[\hat{\sigma}_h(p_z^{(1)})\right]+(1)\left[\hat{S}_3^1(p_z^{(1)})\right] \\ & +(1)\left[\hat{S}_3^2(p_z^{(1)})\right]+(0)\left[\hat{\sigma}_v(p_z^{(1)})\right]+(0)\left[\hat{\sigma}_v'(p_z^{(1)})\right]+(0)\left[\hat{\sigma}_v''(p_z^{(1)})\right] \\ \propto\ & 2p_z^{(1)}-p_z^{(2)}-p_z^{(3)} \quad \Rightarrow \quad \psi_{E''} = \boxed{\tfrac{1}{\sqrt{6}}\left(2p_z^{(1)}-p_z^{(2)}-p_z^{(3)}\right)}\end{aligned}$$

1.2 Symmetry and Group Theory

- SALCs generated from the $2p_z$ orbitals in the cyclopropenyl radical are therefore







$$\psi_{A_2''} = \boxed{\frac{1}{\sqrt{3}}\left(p_z^{(1)} + p_z^{(2)} + p_z^{(3)}\right)} \qquad \psi_{E''}^{(1)} = \boxed{\frac{1}{\sqrt{6}}\left(2p_z^{(1)} - p_z^{(2)} - p_z^{(3)}\right)} \qquad \psi_{E''}^{(2)} = \boxed{\frac{1}{\sqrt{2}}\left(p_z^{(2)} - p_z^{(3)}\right)}$$

through orthogonality requirement

Determining Symmetry of Transition Integrals

- use symmetry to evaluate transition integrals for spectroscopy
  - Need to know symmetry of
    - atomic/molecular wavefunctions
    - Transition moment operator ($\hat{M}$)

$$f \propto \left\langle \Psi_g \left| \hat{M} \right| \Psi_e \right\rangle^2$$

  - use direct products to get symmetry of integral $\rightarrow$ $\Gamma_f \mapsto \Gamma_{\Psi_g} \times \Gamma_{\hat{M}} \times \Gamma_{\Psi_e}$

- If AOs centred at point of point group $\rightarrow$ easy to get symmetry

remember, these labels are symmetry labels for spherical symmetry…

$s \mapsto$ totally symmetric
$x^2 + y^2 + z^2$

determining symmetry is really a question of lowering the symmetry

$p \mapsto$ transforms as linear basis vectors
x, y, z

$d \mapsto$ transform as quadratic basis vectors
$xy, xz, yz, x^2 - y^2, 2z^2 - x^2 - y^2$

etc.

1.2 Symmetry and Group Theory

- *e.g.* in octahedral symmetry

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3s_h$	$6s_d$		
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	$x^2+y^2+z^2$	$\mapsto s$
A_{2g}	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1		
E_g	+2	-1	0	0	+2	+2	0	-1	+2	0	$(2z^2\text{-}x^2\text{-}y^2,\ x^2\text{-}y^2)$	$\mapsto d_{x^2-y^2,z^2}$
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	(xy, xz, yz)	$\mapsto d_{xy,xz,yz}$
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1		
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1		
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)	$\mapsto p_{x,y,z}$
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1		

the symmetry of the transition operator will also transform as cartesian functions:

$$\hat{M} = \underset{linear}{\hat{\mu}_1} + \underset{rotation}{\hat{m}_1} + \underset{quadratic}{\hat{\mu}_2} + \hat{m}_2 + \ldots$$

Assignment #2

Submit a manuscript related to your field of study that uses group theory to assist in solving a specific issue...

e.g. explaining the electronic structure of C_{60}...

1. Symmetry, Group Theory, and Electronic Structure

1.1 Fundamentals

1.2 Symmetry and Group Theory

1.3 Vibrational Spectroscopy

2. Ground State Spectroscopic Methods

3. Excited State Spectroscopic Methods

4. Other Physical Methods