Reducing reducible rep → irred. rep.

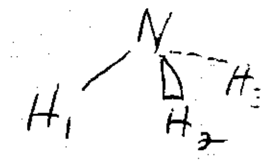
$$\chi_r(R) = \sum_i a_i \chi_i(R)$$

$$a_i = \frac{1}{h} \sum_R \chi_r(R)\chi_i^*(R) \quad \text{or} \quad a_i = \frac{1}{h} \sum_{k}^{\text{over classes}} \chi_r(C_k)\chi_i(C_k) N_k$$

Examples — Consider

C_{3v}	E	C_3	σ
Γ_1	1	1	1
Γ_2	1	1	−1
Γ_3	2	−1	0

Consider interchange matrix of H's in NH_3



$$\begin{array}{cccc} & E & C_3 & \sigma_v \\ \chi_H = & 3 & 0 & 1 \end{array}$$

$$\Gamma_H = \underset{E}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \quad \underset{C_3}{\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}} \quad \underset{\sigma_v}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}}$$

Γ_H is reducible, what is it composed of?

$$a_j^H = \frac{1}{h} \sum_{C_k} N_k \chi_H(C_k) \chi_j(C_k)$$

$$a_1 = \frac{1}{6}\left[\overset{N_k}{1} \cdot \overset{\chi_H}{3} \cdot \overset{\chi_j}{1} + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot 1\right] = 6/6 = 1$$

$$a_2 = \frac{1}{6}\left[1 \cdot 3 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot -1\right] = 0/6 = 0$$

$$a_3 = \frac{1}{6}\left[1 \cdot 3 \cdot 2 + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot 0\right] = 6/6 = 1$$

thus $\Gamma_H = \Gamma_1 + \Gamma_3$ or $\underline{1D + 2D = 3D}$

check

note from $\Gamma(E)$ being identity matrix this always works on in H_2O $\rightarrow$ x y z form bases as does matrices:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1
Γ_2	1	-1	1	-
Γ_3	1	-1	-1	
Γ_4	1	1	-1	-

$$\chi_{xyz} = 3, -1, 1, 1$$

~~so~~ $a^{\Gamma_1} = \frac{1}{4}\left(3\cdot1\cdot1 + (-1)\cdot1\cdot1 + 1\cdot1\cdot1 + 1\cdot1\cdot1\right)$
$= \frac{1}{4}(4) = 1$

each class $l_i = 1$

$a^{\Gamma_2} = \frac{1}{4}\left(3\cdot1 + (-1)(-1) - 1\cdot1 + 1\cdot(-1)\right) = 1$

$a^{\Gamma_3} = \frac{1}{4}\left(3\cdot1 + (-1)(-1) + 1(1) + 1(1)\right) = 1$

$a^{\Gamma_4} = \frac{1}{4}\left(3\cdot1 + (-1)1 + 1(-1) + 1(-1)\right) = 0$

~~so~~ $\Gamma_{xyz} = \Gamma_1 + \Gamma_2 + \Gamma_3$

In general this particular decomposition will prove to be very useful for analyses of normal modes and for A orbitals $\rightarrow$ MO's

Mullikan notation

labling irred rep as Γ_i is ok but gives no clue as to composure –

Mullikan notation designed to denote dimension and symmetry (sym/anti) w/r/t center of

Dimension :	1-D	A or B	
	2 D	E	
	3 D	T	(old/phys - F)
	4 D	U	(old/G)

Principal axis ~~subscript~~ - 1D — A sym
B anti

$C_2 \perp$ Principl subscript 1D 1 - sym
(or vert plane) note ambiguity 2 - anti
if 2 classes σ

σ_h - horiz plane superscript all dim — ′ - sym
″ - anti

inversion center subscript all — g - sym
u - anti

ex C_{2v} - all 1D

Γ_1 1 1 1 1 $\rightarrow A_1$
Γ_2 1 -1 1 -1 $\rightarrow B_1$
Γ_3 1 -1 -1 1 $\rightarrow B_2$
Γ_4 1 1 -1 -1 $\rightarrow A_2$

C_{3v}
Γ_1 - 1 1 1 $\rightarrow A_1$
Γ_2 - 1 1 -1 $\rightarrow A_2$
Γ_3 - 2 -1 0 $\rightarrow E$

~~G~~ not sym
C_{4v}: A_1, A_2, B_1, B_2, E

Note All groups need A_{1g}, total sym

~~4/11/88~~

Mon

quick

Special Case – Abelian Groups

Abelian → operations (el of G) commute

? did I get this wrong earlier?

Now if $AB = BA$ for all el $\subset G$

$X^{-1}AX = X^{-1}XA = A$ " "

therefore every element is in a class by itself

thus given our rules: # classes = # irred rep

h dim abelian grp → h rep

from $\sum l_i^2 = h$

$l_i = 1$ for all irred rep

→ So Abelian has h 1-D irred rep + norm

Example – $\boxed{\text{Cyclic group:}}$ $E, A, A^2 \ldots A^{h-1}$

$E = A^h$

So for 1D $\Gamma(E) = 1$

$\Gamma(A) = \cancel{E}(1)^{1/h}$

$$\begin{array}{lccccccc} & E & A & A^2 & & & & A^{h-1} \\ \Gamma_{A_1} = & 1 & 1 & 1 & 1 & 1 & \cdots & 1 \end{array}$$

Clearly

what of rest?

→ easy soln: $\Gamma_p(\cancel{A}) = e^{2\pi i\, p/h}$, $p = 1, 2, \ldots, h$ $\Gamma_p(E) = \left[e^{2\pi i p/h}\right]^h = e^{\cdot}$

in this sense $\Gamma_{A_1} = \Gamma_h$ $p = h$ all rep $e^{2\pi i} = 1$

handout

example

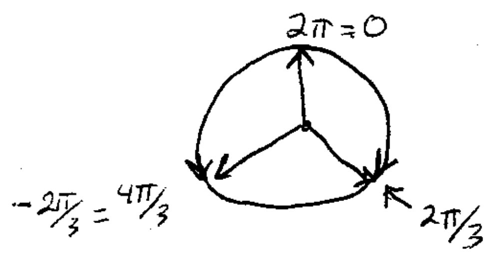
C_3 :	$\cancel{E}$ C_3	C_3^2	$C_3^3 = E$
Γ_1	$e^{2\pi i/3}$	$e^{4\pi i/3}$	$e^{6\pi i/3} = 1$
Γ_2	$e^{4\pi i/3}$	$e^{8\pi i/3}$	$e^{12\pi i/3} = 1$
Γ_3	$e^{2\pi i} = 1$	$(e^{2\pi i})^2 = 1$	$(e^{2\pi i})^2 = 1$

* ~~So~~ then $\Gamma_3 = A_1 = \quad 1 \quad 1 \quad 1$

rearrange

	E	C_3	C_3^2	
A_1	1	1	1	
	1	$e^{2\pi i/3}$	$e^{4\pi i/3}$	→ clockw
	1	$e^{4\pi i/3}$	$e^{2\pi i/3}(e^{2\pi i}=1)$	→ counte

Note: $e^{4\pi i/3} = e^{-2\pi i/3} = \left(e^{2\pi i/3}\right)^*$



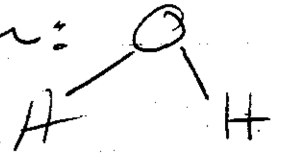
rewrite

	E	C_3	C_3^2
A_1	1	1	1
E	1	ε	ε^*
	1	ε^*	ε

The second two representations are
basically the same thing but
correspond to rotations clockwise
and counter clockwise — energetically
they will behave alike → in QM
→ give the symbol E — degen
but separable if have sense of clo/count-
[illegible]

Handout / ex *

What do all of these things have to do with **molecules**?

Consider:  to describe bonding we will need to discuss

orbitals

O : $2s$, $2p_z$, $2p_x$, $2p_y$

H : $1s_1$ $1s_2$

	E	C_2	σ_v	σ_v'	
Γ_{2s} :	1	1	1	1	A_1 i.e. no effect
Γ_{2p_z} :	1	1	1	1	A_1
Γ_{2p_x} :	1	−1	−1	1	— B_1
Γ_{2p_y} try					
Γ_H					— doesn't work $H_1 \rightarrow H_2$
$\Gamma_{H_1+H_2}$:	1	1	1	1	A
$\Gamma_{H_1-H_2}$:	1	−1	−1	1	— B_1

* or $\Gamma_{2p} = \Gamma_{2p_x} + \Gamma_{2p_y} + \Gamma_{2p_z} = \Gamma_{xyz} = 3 \;\; -1 \;\; 1 \;\; 1 = A_1 + B_1 + B_2$

$$\begin{cases} a_{A_1} = \tfrac{1}{4}(3\cdot 1 + -1\cdot 1 + 1\cdot 1 + 1 \\ \quad = 4/4 \\ a_{A_2} = \tfrac{1}{4}(3\cdot 1 + -1\cdot 1 + 1\cdot -1 + 1\cdot \\ \quad \tfrac{1}{4}(3-3) = 0 \\ a_{B_1} = \tfrac{1}{4}(3\cdot 1 + (-1)(1) + 1\cdot -1 + 1 \\ \quad = 4/4 = 1 \\ a_{B_2} = \tfrac{1}{4}(3\cdot 1 + (-1)(-1) \text{ same} \end{cases}$$

or consider vibration of H_2O
bond stretches, angle bends

Γ_α =	1	1	1	1	A_1
Γ_{OH} −					doesn't wo
Γ_{OH+OH} =	1	1	1	1	A_1
Γ_{OH-OH} =	1	−1	−1	1	B_1

* or $\Gamma_{2OH} = 2 \;\; 0 \;\; 0 \;\; 2$ $\begin{cases} a_{A_1} = \tfrac{1}{4}(2\cdot 1 + 2\cdot 1) = 1 \\ a_{B_1} = \tfrac{1}{4}(2\cdot 1 + 2\cdot 1) = 1 \end{cases}$

Handout

Cotton Ch 5

2nd tract

Product of two symmetry species transforms as the direct product of their representation

$\boxed{1\text{-D}}$ – this is easy because rep = character = #

hence $\Gamma_1 \otimes \Gamma_2 = \chi_1(R_1)\chi_2(R_1), \chi_1(R_2)\chi_2(R_2), \ldots, \chi_1(R_h)\chi_2(R_h)$

Examples – use C_{2v}

	E	C_2	σ_v^{xz}	σ_v^{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

$$A_2 \otimes B_1 = 1\cdot 1,\ 1\cdot -1,\ -1\cdot 1,\ -1\cdot -1 = 1, -1, -1, 1 = B_2$$

rules

Since all 1-D can use shortcut tricks:

$$A_2 \otimes B_2 = B_1 \qquad B_1 \otimes B_2 = A_2 \quad \text{etc}$$

$A \cdot A = B \cdot B = A$ $\qquad$ $1 \cdot 1 = 2 \cdot 2 = 1$

$A \cdot B = B \cdot A = B$ $\qquad$ $2 \cdot 1 = 1 \cdot 2 = 2$

similarly

$I \cdot I = II \cdot II = I$ $\qquad$ $g \cdot g = u \cdot u = g$

$I \cdot II = II \cdot I = II$ $\qquad$ $u \cdot g = g \cdot u = u$

Handout

Degenerate representations not so trivial

Direct product matrix

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & \ddots & & \\ \vdots & & & \\ a_{n1} & & & a_{nn} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} & \cdots & b_{1m} \\ b_{21} & \ddots & & \\ \vdots & & & \\ b_{m1} & & & b_{mm} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & \cdots & a_{12}b_{11} & \cdots & a_{1n}b \\ a_{11}b_{21} & \ddots & & & & \\ \vdots & & & & & \\ a_{21}b_{11} & a_{21}b_{12} & & \ddots & & \\ \vdots & & & & & \\ a_{n1}b_{m1} & & & & & a_{nn}b_{mm} \end{pmatrix}$$

$n \times n$ $\quad$ $m \times m$ $\quad$ $m \times m$

$mn \times mn$

new rep is much bigger and
consists of series of $m \times n$ matrices $n \times n$ times
– can see this will block out

In our notation $\Gamma_A(R) \otimes \Gamma_B(R) = \Gamma_{AB}(R)$
in general Γ_{AB} will be a reducible rep

$\boxed{ex}$ in C_{3v} $\Gamma_E \sim \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \cdots, \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \cdots$

$E \qquad C_3 \qquad \sigma_1^{xz}$

$$\Gamma_{E \cdot E} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1/4 & -\frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} & 3/4 \\ -\frac{\sqrt{3}}{4} & 1/4 & \frac{3}{4} & -\frac{\sqrt{3}}{4} \\ -\sqrt{3}/4 & 3/4 & 1/4 & -\sqrt{3}/4 \\ 3/4 & -\frac{\sqrt{3}}{4} & -\sqrt{3}/4 & 1/4 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$0 \cdot E \qquad 1 \cdot E$

$\chi_{EE} = \quad 4 \qquad 1 \qquad 0$

(Ex) - Cotton Ch. 5

(1) Two most commonly used integrals for QM calc:

$$\int \phi_i^* \hat{\mathcal{H}} \phi_j \, d\tau = \mathcal{H}_{ij} \quad \text{and} \quad \int \phi_i^* \phi_j \, d\tau = S_{ij}$$

Rules alone say <u>2nd one</u> $S_{ij} = 0$ unless $i = j$

true <u>also</u> <u>1st one</u>, $\mathcal{H}_{ij}$

because $\mathcal{H}$ transforms as A_1

so $\Gamma_{(\mathcal{H}\phi_j)} = \Gamma_{(\phi_j)}$

<u>since</u> $\chi_{\mathcal{H}}(R)\,\chi_{\phi_j}(R) = \chi_{\phi_j}(R)$

i.e. character product of rep = prod char

and character $A_1 = 1$ for all R

<u>or</u> $\underline{\mathcal{H}_{ij} = H_{ii}\delta_{ij}}$

(2) Dipole selection rules — <u>from Time dep Pert Th/Semi Cla</u>

you learned $\boxed{\int \phi_i^* \hat{\mu} \phi_j \, d\tau \neq 0}$

for electric dipole allowed transition

$\mu = \sum_{i=1}^{n} q_i \hat{r}_i$ sum over charges in system, q's constant

μ transforms in same way as

$\hat{r} = (x, y, z)$

For non-zero integral need: $\Gamma_{\phi_i} \otimes \Gamma_{xyz} \otimes \Gamma_{\phi_j} \overset{\supset ?}{\not\subset} \Gamma_{A_1}$

<u>or</u> if $\Gamma_{\phi_i} = A_1$, common for ground state

then $\Gamma_{\phi_j} \in \Gamma_{x,y,z}$ (reducible, in general