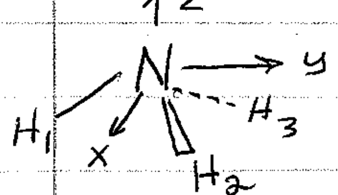
Examples



$NH_3 \rightarrow C_{3v}$

Elements: C_3 about z, $3\sigma_v$ (N–H)

Operations: E; C_3, C_3^2; $\sigma_1, \sigma_2, \sigma_3$

Note: $C_3^{-1} = C_3^2$

$\sigma_i = \sigma_i^{-1}$ self inverse

Group Theory should reflect similarity of σ's, C_3's

Multiplication Table

$h=6$	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

Notes:

1) $\{E, C_3, C_3^2\}$ form a cyclic group SUBGROUP, order $= 3$ is a divisor of $h=6$
2) $\{E, \sigma_i\}$ also SUBGROUP for each σ_i, order $=2$

$X^{-1}AX$: $E\, C_3\, E = C_3$ (self-conjugate)

$$\left.\begin{array}{l} C_3^2\, C_3\, C_3 = C_3 \\ C_3\, C_3\, C_3^2 = C_3 \end{array}\right\} C_3^{-1} = C_3^2$$

Class formed (C_3, C_3^2)

$$\left.\begin{array}{l} \sigma_1\, C_3\, \sigma_1 = \sigma_1 \cdot \sigma_3 = C_3^2 \\ \sigma_2\, C_3\, \sigma_2 = \sigma_2 \cdot \sigma_1 = C_3^2 \\ \sigma_3\, C_3\, \sigma_3 = \sigma_3 \cdot \sigma_2 = C_3^2 \end{array}\right\} \sigma_i = \sigma_i^{-1}$$

same follow for $(\sigma_1, \sigma_2, \sigma_3)$

C_{2v} Representations

	E	C_2	$\sigma_{(yz)}$	$\sigma'_{(xz)}$
Γ_1	1	1	1	1
Γ_2	1	−1	1	−1
Γ_3	1	1	−1	−1
Γ_4	1	−1	−1	1

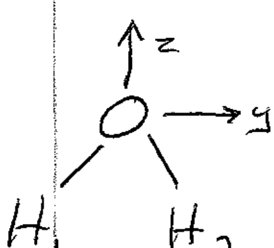
Multiplication Table

	E	C_2	$\sigma_{(yz)}$	$\sigma'_{(xz)}$
E	E	C_2	σ	σ'
C_2	C_2	E	σ'	σ
σ	σ	σ'	E	C_2
σ'	σ'	σ	C_2	E

$$\Gamma_5 = \left[\begin{pmatrix}1&0\\0&1\end{pmatrix}, \begin{pmatrix}1&0\\0&-1\end{pmatrix}, \begin{pmatrix}1&0\\0&-1\end{pmatrix}, \begin{pmatrix}1&0\\0&1\end{pmatrix}\right] = \begin{pmatrix}\Gamma_1&0\\0&\Gamma_4\end{pmatrix}$$

eg. $\begin{pmatrix}1&0\\0&-1\end{pmatrix} \cdot \begin{pmatrix}1&0\\0&-1\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix}$

like: $C_2 \cdot \sigma = \sigma'$



<u>Interchange matrix</u>; operate on $\begin{pmatrix}H_1\\H_2\end{pmatrix}$ vector

$$\underset{E}{\begin{pmatrix}1&0\\0&1\end{pmatrix}} \quad \underset{C_2}{\begin{pmatrix}0&1\\1&0\end{pmatrix}} \quad \underset{\sigma_{xz}}{\begin{pmatrix}0&1\\1&0\end{pmatrix}} \quad \underset{\sigma'_{yz}}{\begin{pmatrix}1&0\\0&1\end{pmatrix}}$$

Rotation matrix; operate on $\begin{pmatrix}x\\y\\z\end{pmatrix}$ vector

$$\underset{E}{\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}} \quad \underset{C_2}{\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}} \quad \underset{\sigma}{\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}} \quad \underset{\sigma'}{\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}}$$

$$\begin{pmatrix}\cos\phi&\sin\phi&0\\-\sin\phi&\cos\phi&0\\0&0&1\end{pmatrix} \quad \phi = 180^\circ$$

Grand Orthogonality Examples

C_{2v}	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1
Γ_2	1	−1	1	−1
Γ_3	1	1	−1	−1
Γ_4	1	−1	−1	1

eg. $\sum_R \Gamma_i \Gamma_i = 4/1$

~~try~~ $\Gamma_2\Gamma_2 = [1\cdot1 + (-1)(-1) + 1\cdot1 + (-1)(-1)]$
$= 4$

$\sum_R \Gamma_i \Gamma_j = 0$ if $i \neq j$

try $\Gamma_2\Gamma_3 = [1\cdot1 \cancel{(-1)} 1 + 1\cdot(-1) + (-1)(-1)] = 0$

Note: the Γ_5, Γ_6 rep's are not irreducible

$\sum_{i=1}^{n} l_i^2 = h$ $\quad C_{2v}$: $h = 4$ could have $l_i = 1$, $n = 4$
or $l_i = 2$, $n = 1$
but must have one $l_i = 1$ for simple rep: 1, 1, 1, 1
i.e. $l_i = 1$, only 4 irred rep

C_{3v} : $h = 6$ can do: $l_i = 1$, $n = 6$
? are there 6 indep 6-vectors?
$n = 5, 4$ will not work
ex $n = 5$: $\sum l_i^2 = \cancel{5 \text{ for } l_i = 1}$
$\sum l_i = 8$ for $l_i = 1$, $l_5 = 2$
$n = 3$: $l_1 = l_2 = 1$, $l_3 = 2$
$\sum l_i^2 = 1 + 1 + 4 = 6$

C_{4v} : $h = 8$ $\quad n = 8$ − $l_i = 1$ trivial
$n = 5$ − $l_i = 1$, $l_5 = 2$: $\sum l^2 = 8$

Character Table generation

\# irred. rep. = # classes

C_{2v} $h=4$, $n=4$

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

all in class by self

	E	C_2	σ_v	σ_v'	
Γ_1	1	1	1	1	← set up tot. sym
Γ_2	1	-1	1	-1	← orthog to Γ_1
Γ_3	1	1	-1	-1	← orthog to $\Gamma_{1,2}$
Γ_4	1	-1	1	-1	← orthog to all

analogy:

get set of 4 orthogonal (linearly independent) 4-vectors ~~over~~ 4-D vector-space

C_{3v} $h=6$, $n=3$

E – class by self

C_3, C_3^2 – same class

$\sigma_1, \sigma_2, \sigma_3$ – " "

	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	← totally sym.
Γ_2	1	1	-1	← σ_v opp sign (3-3)
Γ_3	2	-1	0	

needed for (2-2) orthog to $\Gamma_{1,2}$

dimension of 2 means ref: $\begin{pmatrix}1&0\\0&1\end{pmatrix} \Rightarrow \chi = 2$ $\Big\}$ $\underline{\chi_i(E) = l_i}$

C_{4v} $h=8$, $n=5$

E – self

$C_4, C_4^3 (=C_4^{-1})$ – class

C_2 – class

σ_1, σ_3 – class $= \sigma_v$

σ_2, σ_4 – class $= \sigma_d$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	$h=8$
Γ_1	1	1	1	1	1	← total sym
Γ_2	1	1	1	-1	-1	← orthog
Γ_3	1	-1	1	-1	1	– "
Γ_4	1	-1	1	1	-1	– "
(must be 2d) → Γ_5	2	0	-2	0	0	← check

Problem Session
4342 SES - Mon 1-2 pm

Chem 406 - 4/5/89

We have seen that a set of matrices of dimension n can form a representation of the group if it has the same mult table

Note: if $n=1$ have set of integers, these will only work if each ~~[illegible]~~ $|\Gamma_i| = 1$

In general can convert this set of matrices to another with similarity transform

i.e.

$$(E, A, B \ldots) \longrightarrow (E', A', B' \ldots)$$

where $A' = Z^{-1} A Z$

and Z is a unitary matrix

$ZZ^{+} = E$ (identity matrix)

or $Z^{-1} = Z^{+}$, $+ \rightarrow$ conjugate transpose or adjunct

aside Hermitian: $H = H^{+}$,

When Z is chosen so that $(E, A, B \ldots)$ become "most block diagonal" then the blocks are irreducible Representation and original matrices

i.e. $A' = \begin{pmatrix} \Gamma_I^{A} & & \\ & \Gamma_J^{A} & \\ & & \Gamma_K^{A} \end{pmatrix}$, etc.

Chem 406 4/7/89

Grand Orthogonality on Representations (Γ_i)

$$\sum_R [\Gamma_i(R)_{nm}][\Gamma_j(R)_{n'm'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij}\delta_{nn'}\delta_{mm'}$$

Great restriction on form of irreducible representation
also on number: $\sum_{i=1}^{n} l_i^2 = h$ $n = \#$ irred rep

Easier with Characters

$$\sum_R \chi_i(R)\chi_j^*(R) = \begin{cases} h \text{ for } i=j \\ 0 \text{ for } i \neq j \end{cases}$$

all elements of a class, same χ

$$\sum_C N_c \chi_i(C)\chi_j(C) = h\delta_{ij} \qquad N_C = \# \text{ in class}$$

Now: Characters of each irred. rep form a vector orthog. to other irred rep. These are h-dimensional vectors but have only n independent elements thus these vectors can define an n-dimensional space. That then is the # of irred, rep,

or # Classes = # irred. rep.

Problemsets

Chem 406 - 4/14/89

We're finishing up "technique" development before going on to applications

Last time talked about Products of representations to learn how to evaluate $\int f_i f_j \cdots d\tau$

general: a) if $\Gamma_A \otimes \Gamma_B = \Gamma_{AB}$ $\quad \Gamma_{AB} \ni \Gamma_{A_1}$ (totally sym) iff $A = B$, only once

b) Nature of Γ_{AB} from reducing it to $\Gamma_{AB} = \sum_{i=1}^{n} a_i \Gamma_i$ lin. comb. irred rep by using characters

Now if know what symmetries is some combined representation want to know form as applied to case of interest

Projection operators used to give linear combination of (in our case, functions) that give a representation "Symmetry Adapted Linear Comb."

$\{f_i\}$ forms function space if all g in space: $g = \sum_i c_i f_i$

n-dim: $\{f_i\}$ $i = 1-n$, f_i indep

scalar prod: $\langle f|g\rangle = \int f^* g \, d\tau$

for f_i basis fcts: $\langle f_i|f_j\rangle = \delta_{ij}$ orthonormal; $c_i = \langle g|f_i\rangle$

Chem 406 4/17/89

The end of formal G.T. + IRS all in one!

Projection operator: $P_{st}^{j} = \frac{l_j}{h}\sum_R [\Gamma^j(R)_{st}]^* \hat{R}$

note: a) operator linear comb weight by matrix elem of representation

b) to use: need - effect of operator on fct
- form of representation

derivation on orthonormal basis

$$\underline{P_{s't'}^{j}\,\phi_t^{k} = \delta_{kj}\,\delta_{tt'}\,\phi_{s'}^{k}}$$

if general fct $\psi^k = \sum c_i \phi_i^k$

easiest to choose $s' = t' = t$

$$\underline{P_{tt}^{j}\,\psi^{j} = c_{tj}\,\phi_t^{j}}$$

project out the ϕ_t^j component of ψ

(note used $\delta_{kj}\,\delta_{tt'}$)

$\underline{C_{3v}}$ Examples: $\underline{P_{11}^{A_1}(z)} = \frac{1}{6}\{\underset{\Gamma_{11}^{A_1}}{1}\cdot \underset{E\cdot z}{z} + 1\cdot z \cdots 1\cdot z\} = \frac{6z}{6} = z$

on z is a rep of A_1

$\underline{P_{11}^{A_1}(x)} = \frac{1}{6}\{1\cdot x + 1\cdot(-x+\sqrt{3}y)/2 \cdots\} = \frac{0x}{6} = 0$

$C_3 \cdot x$ rotates into l.c x, y

$\underline{P_{11}^{E}(x)} = \frac{1}{6}\{\underset{\Gamma_{11}^{E}}{1}\cdot x + (-\frac{1}{2})(-x+\sqrt{3}y)/2 + \cdots\} = \frac{6x}{6} = x$

similarly $P_{22}^{E}(y) = y$, $P_{22}^{E}(x) = 0 = P_{11}^{E}(y) = P_{11}^{E}(z)$

$\underline{x, y}$ - rep of E in C_{3v} x, y orthog $E_1 = x$, $E_2 = y$