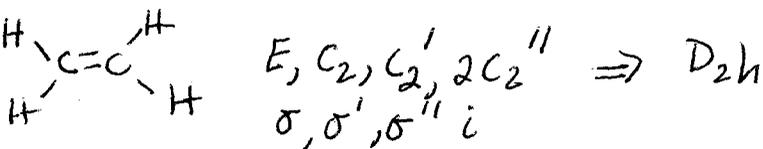
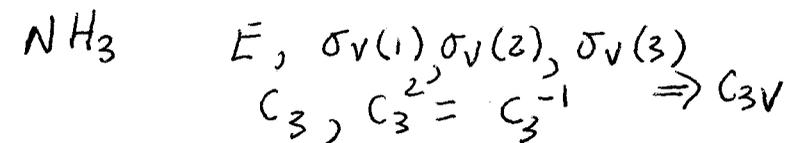
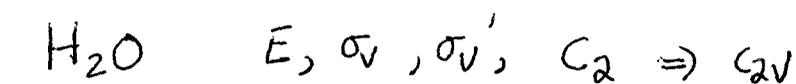


Symmetry elements

- $E$  - identity
- $C_n$  n-fold rotation
- $\sigma$  mirror plane
- $i$  inversion
- $S_n$  n-fold rotation-reflection



.....

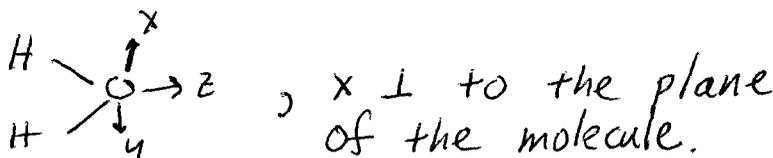
↑  
group

$\sigma_v \Rightarrow$  mirror plane contains princ. rotational axis

$\sigma_h \Rightarrow$  mirror plane  $\perp$  to the princ. axis.

Symmetry operators can be represented by matrices

Example



$$\begin{aligned} \hat{E} &: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \hat{C}_2 &: \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \hat{\sigma}_V &: \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \hat{\sigma}_V' &: \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned}$$

$$\begin{aligned} \hat{C}_2 \cdot \hat{C}_2 &= \hat{E} \\ \hat{C}_2 \cdot \hat{\sigma}_V &= \hat{\sigma}_V' \\ &\text{etc} \end{aligned}$$

form a representation for the  $C_{2v}$  group

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_V$	$\hat{\sigma}_V'$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_V$	$\hat{\sigma}_V'$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}_V'$	$\hat{\sigma}_V$
$\hat{\sigma}_V$	$\hat{\sigma}_V$	$\hat{\sigma}_V'$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}_V'$	$\hat{\sigma}_V'$	$\hat{\sigma}_V$	$\hat{C}_2$	$\hat{E}$

group multiplication table

In this case there are simpler representations

$C_{2v}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_V$	$\hat{\sigma}_V'$	
$A_1$	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	$x, R_x, xz$
$B_2$	1	-1	-1	1	$y, R_y, yz$

Character table

↑ irreducible representations

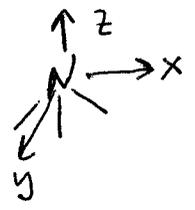
$A_1$  = totally symmetric representation

- $p_z \rightarrow a_1$
- $p_x \rightarrow b_1$
- $p_y \rightarrow b_2$

for  $C_{2v}$  all irreducible representations are 1-dimensional  
 $\Rightarrow$  No degeneracies

$C_{3v}$  is an example of a group with a degenerate representation

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



rotate  $120^\circ$ , "mixes" x and y

E is a 2-fold degenerate representation

The different representations are orthogonal

$$A_1 \times A_2 = 1 \cdot 1 + 2 \cdot 1 \cdot 1 + 3 \cdot 1 \cdot (-1) = 0$$

$$A_2 \times E = 1 \cdot 2 + 2 \cdot (1) \cdot (-1) + 0 = 0$$

Electronic structure

- $C_{2v}$  group
- $a_2^2 \rightarrow A_1$
  - $b_1 b_2 \rightarrow A_2$
  - $a_2 b_2 \rightarrow A_1$
  - $b_1 a_2 \rightarrow B_2$

$\int \psi_1 \hat{H} \psi_2 d\tau = 0$   
if  $\psi_1, \psi_2$  not the same symmetry.

---

$\int \psi_1 \hat{A} \psi_2 d\tau = 0$  if  $\psi_1 \hat{A} \psi_2$  does not contain totally symm. repr.

Selection rules

$$\int a_1 z a_1 d\tau \neq 0 \quad a_1 \rightarrow a_1$$

$$\int a_1 z b_2 d\tau = 0 \quad a_1 \rightarrow b_1$$

$$\int a_1 x b_1 d\tau \neq 0 \quad \text{etc}$$

allowed transitions

