

OLLSCOIL NA hÉIREANN, GAILLIMH  
NATIONAL UNIVERSITY OF IRELAND, GALWAY

SUMMER EXAMINATIONS 2004

Second Year Mathematics

**MA207 - Mathematics for Molecular Science**

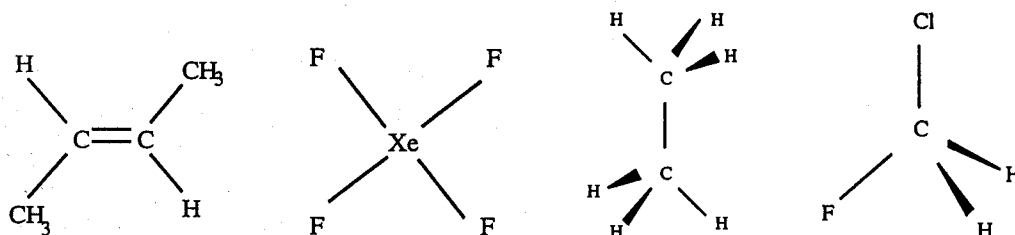
Dr Dave Johnson  
Professor T. Hurley  
Dr J. Burns  
Dr G. Ellis

Time allowed: *two* hours  
Attempt *three* questions

1. (a) Find the  $3 \times 3$  matrix representing rotation through  $45^\circ$  about the  $z$ -axis followed by reflection in the  $xy$ -plane.
- (b) Decide which one of the following two matrices represents a symmetry, and then decide whether this symmetry is a rotation or an improper rotation.

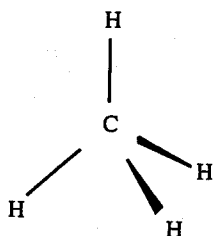
$$A = \begin{pmatrix} \frac{1}{3} & \frac{2}{3} & \frac{2}{3} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{4}{3\sqrt{2}} & -\frac{1}{3\sqrt{2}} & \frac{1}{3\sqrt{2}} \end{pmatrix}, B = \begin{pmatrix} \frac{1}{3} & \frac{2}{3} & \frac{2}{3} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{4}{3\sqrt{2}} & -\frac{1}{3\sqrt{2}} & -\frac{1}{3\sqrt{2}} \end{pmatrix}.$$

- (c) The ammonia molecule  $NH_3$  has six symmetries:  $E$  = identity,  $C_3$  = rotation through  $120^\circ$  about the  $z$ -axis,  $C_3^2$  = rotation through  $240^\circ$  about the  $z$ -axis, and, for  $1 \leq i \leq 3$ ,  $\sigma_i$  = reflection in the plane containing the  $z$ -axis and  $i$ th  $N-H$  bond. Determine the multiplication table of ammonia's symmetry group.
2. (a) Use the algorithm in the Appendix to determine the point groups of the following four molecules. Give full details of how you arrive at your answers.



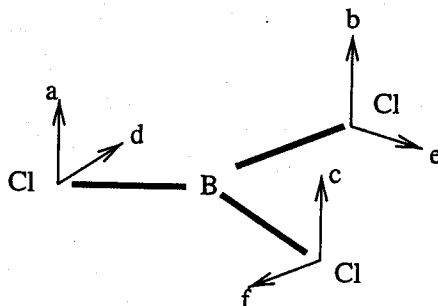
- (b) Find a 1-dimensional representation of the group  $C_{3v} = \{E, C_3, C_3^2, \sigma_1, \sigma_2, \sigma_3\}$  to which a  $p_z$  orbital belongs. Also find a 1-dimensional representation of  $C_{3v}$  to which  $R_z$  belongs (where  $R_z$  is continuous rotation about the  $z$ -axis).

3. (a) The methane molecule



has point group  $T_d$  whose character table is given in the Appendix. Determine the character  $\chi$  of  $T_d$  generated by the four  $C-H$  bonds. Then express  $\chi$  as a sum of irreducible characters. What atomic orbitals might be used to construct a set of four  $\sigma$ -orbitals with lobes directed towards the hydrogen atoms in  $CH_4$ ?

- (b) Boron trichloride  $BCl_3$  has point group  $D_{3h}$  whose character table is given in the Appendix. Determine the character of  $D_{3h}$  generated by the six unit vectors  $a, \dots, f$  indicated below. (Vectors  $a$  and  $d$  are mutually perpendicular, and are also perpendicular to the B-Cl bond. The same is true for the pair  $b, e$  and the pair  $c, f$ .)



4. (a) State Euler's Theorem and use it to classify the *Platonic solids*.  
 (b) Explain why the  $C_{60}$  carbon molecule (the buckyball) has the icosahedral group  $I$  as its group of rotational symmetries.  
 (c) By considering the set of double bonds of the buckyball find a five element set on which  $I$  acts.

# APPENDIX

## Systematic classification of molecules into point groups

$C_n$  = rotation axis

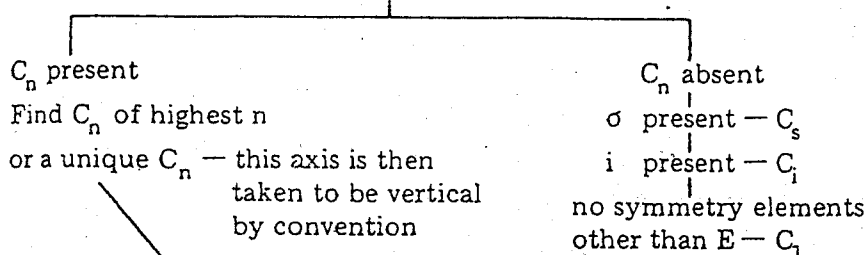
$i$  = inversion centre

$S_n$  = improper axis (alternating axis)  $\sigma$  = plane of symmetry

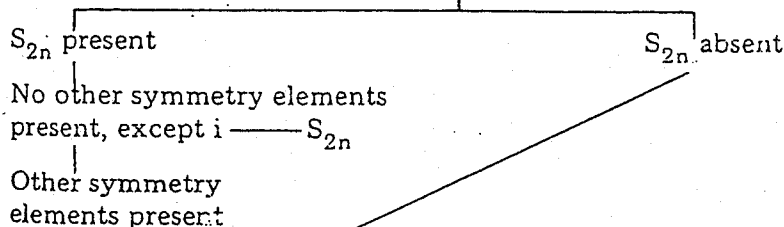
### 1. Examine for special groups

- Linear, no  $\sigma$  perpendicular to molecular axis —  $C_{\infty v}$
- Linear,  $\sigma$  perpendicular to molecular axis —  $D_{\infty h}$
- Tetrahedral —  $T_d$
- Octahedral —  $O_h$
- Dodecahedral or icosahedral —  $I_h$

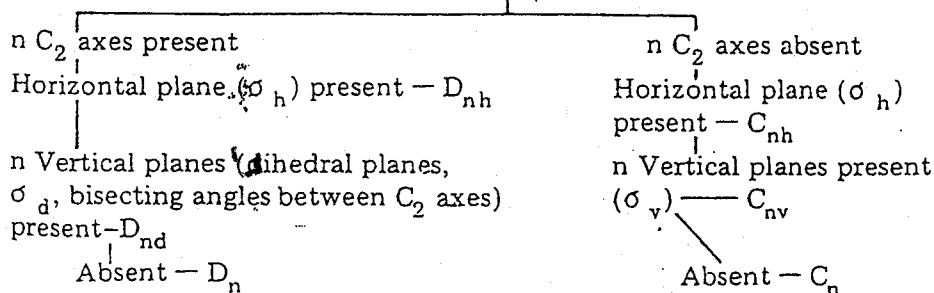
### 2. Examine for a $C_n$ axis



### 3. Examine for $S_{2n}$ colinear with $C_n$



### 4. Examine for n horizontal $C_2$ axes



$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$		
$A_1'$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_2'$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	$(x, y)$	$(x^2 - y^2, xy)$
$A_1''$	1	1	1	-1	-1	-1		
$A_2''$	1	1	-1	-1	-1	1	$z$	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
$A_1$	1	1	1	1	1		$x^2 + y^2 + z^2$
$A_2$	1	1	1	-1	-1		
$E$	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$	
$T_2$	3	0	-1	-1	1	$(x, y, z)$	$(xy, xz, yz)$