CHM 310

Prof. Sanusi's Part

structure, geometry

- Shape & energy of molecule are related

Symmetry → can be sliced into identical 2 parts

& gives fundamental rep.

Mulliken Symbol

+ + +

+ − −

− + −

− − +

i – operation

$\hat{i}$ – element

COM – where weight of object concentrates

08/04/2025

Group theory & Quantum Mechanics of Molecules

There are two(2) parts to the course accomplished in the PTE. II

ⓐ The first part is group theory - we're going to learn symmetry operation/elements and symmetry functions and you will learn about point groups, then you'll learn characters table & representation.

ⓑ Quantum Mechanics of molecules is d 2nd part.

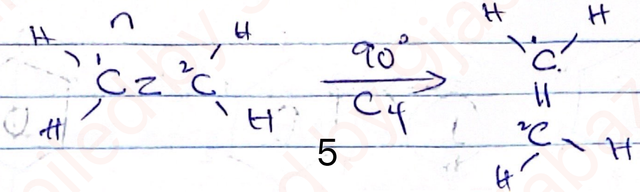
Symmetry Elements / Operations

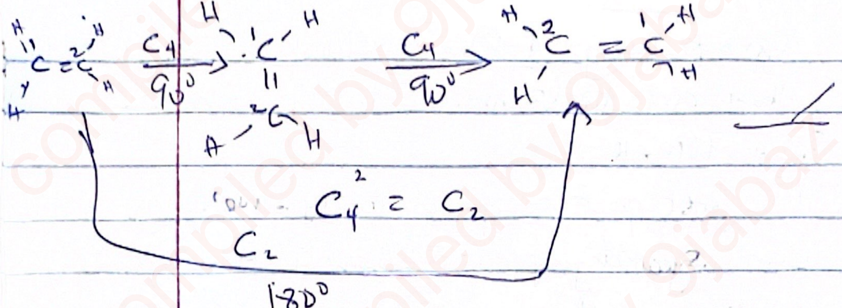
The following symmetry operations may be symmetry elements of molecules. All these operations will leave one point in the molecule, the centre of mass (COM) invariant, i.e unchanged and therefore must pass through that point.

① The element, $\hat{E}$ is called the identity element/operation. This does nothing at all to the object.

② $\hat{C}_n$ → This is called proper rotation operator/element.

$C_n = \frac{2\pi}{n}$





$C_4^2 = C_2$

This operator rotates the object or function about an axis through the Centre of mass by an angle $\frac{2\pi}{n}$. For example $\hat{C}_3$ ~~is a symmetry element~~ rotates by 120° (n = 3)

$\hat{C}_3^2$ rotates by 240° (n = 3 but the operation twice),

C_3^{-1} rotates by -120° (360-120)

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

Note the operator equalities and

$C_3^3 = E$

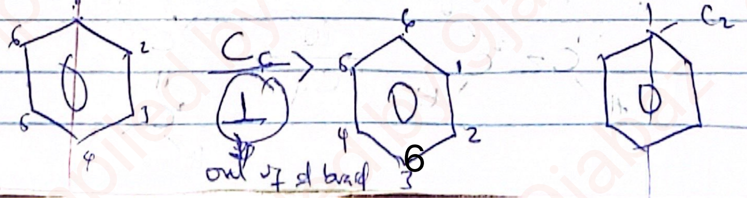
$C_3^{-1} = C_3^2$

$C_4^2 = C_2$

The operator C_4 rotates by 90° and C_2 by 180°, therefore

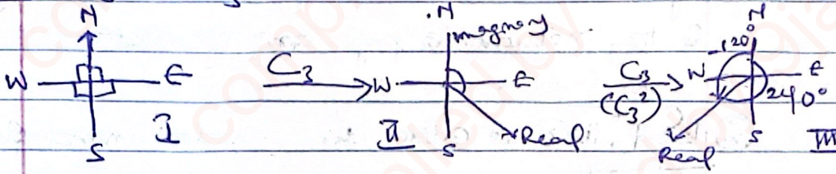
$C_4^2 = C_2$.

* If the object has several rotation axes, that of highest order (largest n value) is called the principal axis.

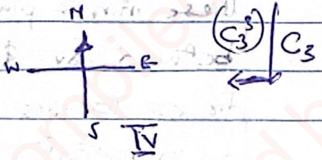


In the case of a tie (several axes of the same order), any of the axes may be considered to be the principal axis.

10/04/2025 $C_3^2 \equiv C_3^{-1}$

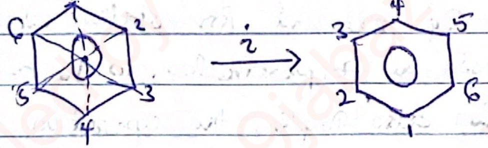


$C_3^3 = E$



Notice the similarity/semblance in object I & IV
The identity, E, of I is retained in IV after performing the operation C_3^3. Therefore, C_3^3 is equal to E.

③ Inversion, i - also called a centre of symmetry

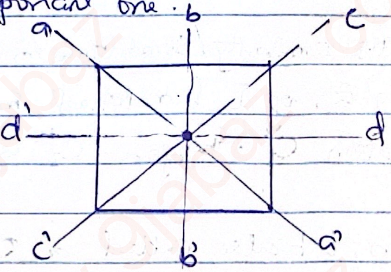


④ The horizontal mirror plane reflection, σ_h :- It is a mirror plane that is perpendicular to a

principal axis

⑤ The vertical mirror plane reflection, σ_v + If we picture the object with its proper axis of rotation up-down, these mirror planes are also up-down, that is, they include a proper axis of rotation.

⑥ σ_d; this is called the dihedral mirror plane reflection. These mirror planes are also vertical. The distinction between σ_v & σ_d is often somewhat arbitrary; for as far as we will get into ~~the~~ subject, it is not an important one.



① There's a C_4 element for rotation about the z-axis (the z-axis is perpendicular to the centre of the square. This also implies the operation C_4^2 is equivalent to C_2. The C_4 is the principal axis.

ii) There are four (4) C_2 axes that are perpendicular to C_4; aa', bb', cc' and dd'.

iii) The plane of the board/paper is a mirror plane; Since it is perpendicular to C_4 (the principal axis. This element is called σ_h

iv) There are 2 types of vertical mirror image plane — the plane aa'z and the plane cc'z which pass through the corners of the square and bb'z & dd'z which pass through the sides. Two of these are called σ_v and two are called σ_d. The choice are to which pair is called 'vertical' and which is 'diagonal' is a matter of convention.

v) There is a centre of symmetry, $\hat{i}$.

vi) There's another element of a type we've not yet discussed — the improper rotation, S_n.

$$S_n = C_n \cdot \sigma_h$$

7) S_n, The improper rotation Operator + the operation. S_n is defined as a rotation about an axis by an angle $\frac{2\pi}{n}$ followed by a reflection in a mirror plane that is perpendicular to that axis.

$$S_n = C_n \cdot \sigma_h$$

If C_n & S_h are symmetry element already, then their product, S_n, must also be such. But it's possible for S_n to be a symmetry element without necessarily requiring that C_n (proper rotation) or σ_h be such.

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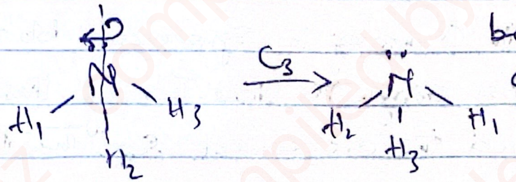


belongs to C_{3v} point group.

Group

If two symmetry operations (A_1 & A_2) are symmetry element of an object, then their product, A_3 is

$\hat{A}_3 = \hat{A}_1 \times \hat{A}_2$, is also a symmetry element.

E.g improper rotation, S_n. Any set of operations for which any product of member of that set is a member of d set. Called a group.

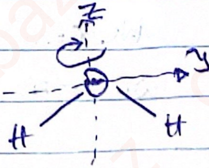
All the symmetry operations of a molecule form such group. The study of the mathematical properties of such a collection of symmetry element is called Group Theory.

Groups containing only symmetry element that leave one point for the molecule invariant - those described above (i.e, 1-7). - are called point groups. Group theory is useful in the study of crystal. c

~~A~~ Crystal which is made up of an infinite lattice of atoms/molecules, has, in addition to point symmetry, symmetry element like translations that move a molecule into an adjacent lattice position. Groups that contain such element/operations are called space group. Only point groups will be focused on here. Each o

Each distinct group of symmetry element has a name. There are two systems for naming point groups, the Hermann-Mauguin system favoured by crystallographers and the Schoenflies system favoured by molecular spectroscopist.

Here, we shall discuss only the latter (i.e Schoenflies). In the Schoenflies system, the names of the groups, the names of the group & the names of the operation are very similar, for example: C_2 is an operation, while C_2 is a group name - ~~So~~ So, be careful not to mix up these two concepts



The symmetry element of H_2O

x-axis is ⊥ to the board/paper.

(a) $C_2(z)$ [C_2 about z), rotation about the z axis by 180°.

ⓑ $\sigma_v(xz)$ which is a reflection in the xz plane, i.e ⊥ to the paper.

ⓒ $\sigma_v'(yz)$ is a reflection in the plane of the board/paper, yz.

ⓓ E', identity element.

22/04/2025 That this is

$$C_2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$$\underset{xz}{\sigma_v} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}, \quad \sigma_v' \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

$$\sigma_v C_2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \sigma_v \begin{bmatrix} -x \\ -y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

This is the same result obtained for σ_v', therefore, we get the operator equality which means that we can write that

$$\sigma_v C_v = \sigma_v'$$

We can from this information construct ~~the~~ what we refer to as multiplication table.

Multiplication table for water molecule

	E	C_2	$\sigma_v(xz)$	$\sigma_v'[\sigma_v(yz)]$
E	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
C_2	C_2	E	$\sigma_v(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	E	C_2
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	C_2	E

The above table contains no new operations. These four operations (E inclusive) form a group and the name of the group is C_{2v}.

Naming a point groups

It's not generally necessary to recognize all symmetry element of a group in order to find the name of the group. Some elements are implied; for example, C_4 implies C_4 twice and C_4 thrice, and C_n together with σ_h implies S_n. Therefore, we need in only identify certain essential element in order to identify the point group

How do we identify Point Group

- Groups with no proper rotation axis

ⓐ C_1 :- Contains only E, i.e, no symmetry at all, for example; CHFBrCl, &

Ⓑ C_s :- This has a mirror plane together with identity E. i.e E & σ

Ⓒ C_i :- Contains E and i

* Ⓓ S_n :- Contains, E and S_n. Note that $S_1 \equiv \sigma$, $S_2 \equiv i$, so therefore, these groups would be called C_s & C_i respectively.

23/04/2025

- Groups with one proper rotation axis

Ⓐ C_n :- contains E, and C_n only - no mirror planes or other symmetry element

Ⓑ C_{nv} : Contains E, C_n and n-vertical mirror plane called σ_v. Examples H_2O is C_{2v} and it contains 2-vertical mirror plane, NH_3 is not planar has a C_3 axis and therefore it's 3 σ_v it belongs to the point group C_{3v}.

Ⓒ C_{nh} :- Contains E, C_n, and horizontal mirror plane σ_h.

- The Dihedral groups

Ⓐ D_n :- Contains E, C_n, and n-C_2 axes that are perpendicular to C_n (where C_n is the principal axis). The case, $n = 2$ is rather special, since it has 3 mutually perpendicular C_2 axes; this group is sometimes called V

b) D_{nh} :- Contains E, C_n, nC_2 axes, and a mirror plane that is perpendicular to the principal axis, σ_h.

{ a principal axis
{ any other rotation that is ⊥ to the principal axis - you have a D.

24/4/2025

It also has n-vertical mirror planes & i if n is an even number. If n=2, this group is called V_h and is equivalent to D_{2h}

c) D_{nd} :- Contains E, C_n, nC_2, and n-vertical mirror plane called σ_d. It also contains an improper axis of rotation of double order, i.e S_{2n} parallel to C_n. It'll also contain i, when n is odd. It's possible for n = 2. If n = 2, this grp is called $V_d = D_{2d}$

- Linear Groups

These are special cases of the above for $n = \infty$. That is, rotation about the axis by any angle is a symmetry element. There are 2 cases:

$C_{\infty v}$:- linear unsymmetrical. e.g HCl, HCN, etc

$D_{\infty h}$:- linear symmetrical. e.g H_2, CO_2, etc.

- Cubic Groups

These are groups with more than one principal axis C_n, where $n \geq 3$. Those of chemical interest include the tetrahedral.

D - 1 principal axis
Cubic - >1 principal axis

a) T_d : The symmetry of a regular tetrahedral, e.g CH_4.

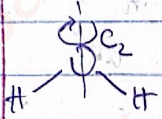
b) O_h : The symmetry of a regular octahedral, e.g SF_6

c) Icosahedron, I_h : E.g $B_{12}H_{12}^{2-}$ ion

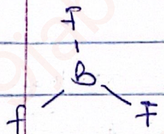
START

LINEAR ? $C_{\infty v}$ or $D_{\infty h}$

H_2O

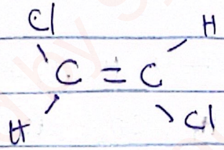


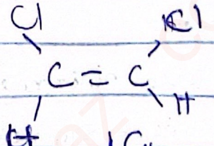
C_{2v}

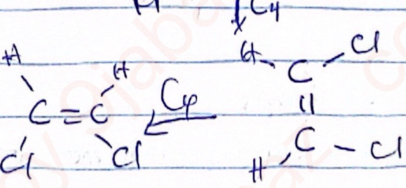


$3C_2$, $3\sigma_v$, C_3

D_{3h}







R K Prasad
Physical Chemistry
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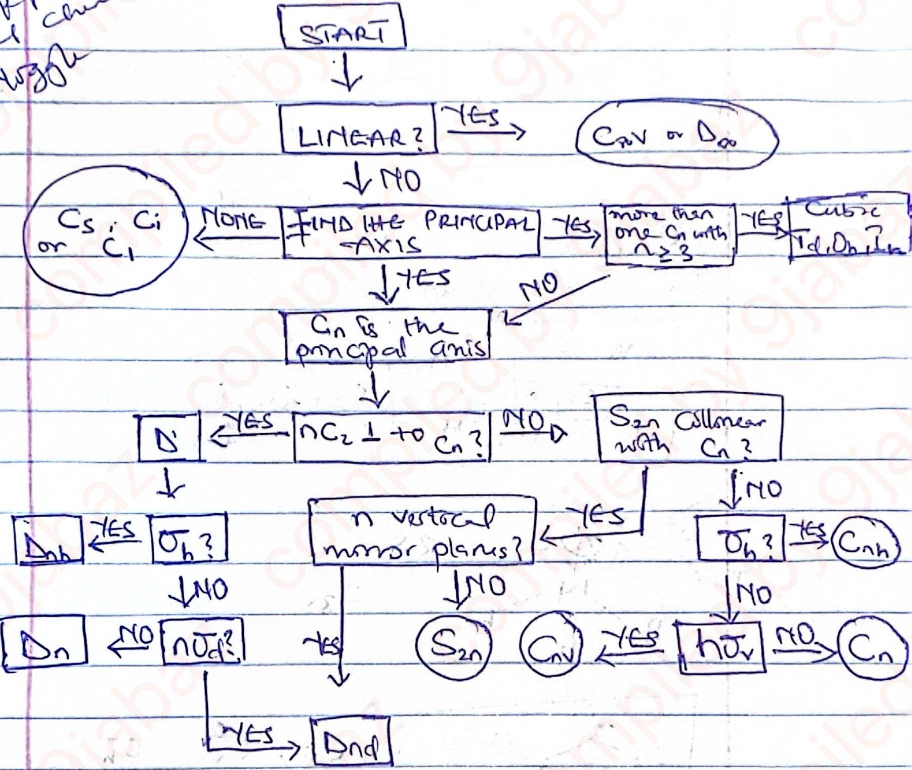

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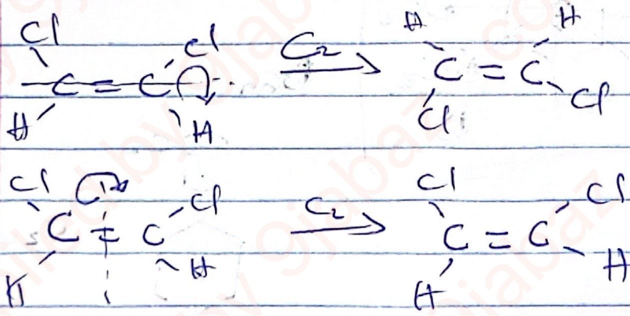
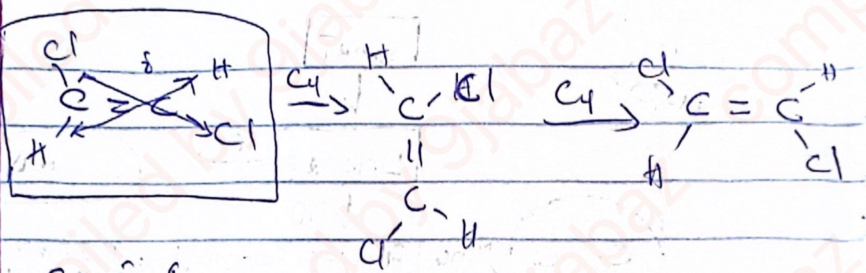
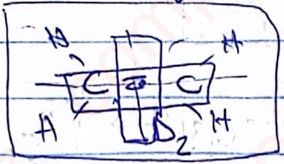


The point group is a C_{2v} σ_v, σ_v'



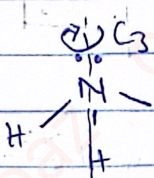
C_2, i, S_h

The point group is a C_{2h}



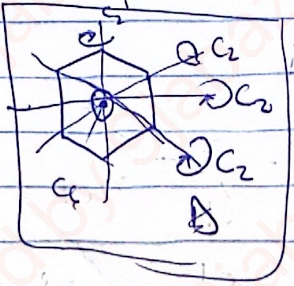
C_2, S_h, S_v, S_v',

D_{2h}



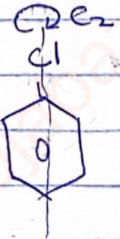
$3S_v$

C_{3v}

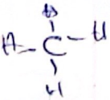


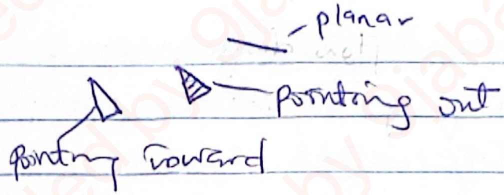
C_6, σ_v, σ_h

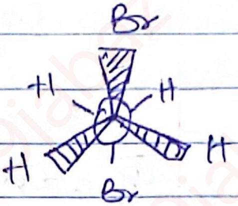
D_{6h}

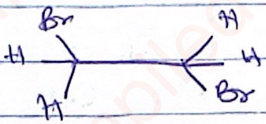


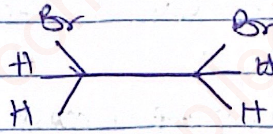
C_{2v}



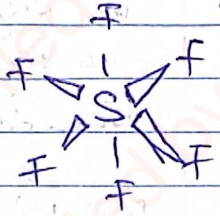








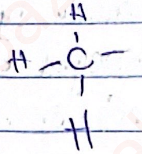
SF_6



O_h

O=C=S

$C_{\infty v}$



T_d

The above flow diagram can be used to determine the point group. The inversion operation is found in the group C_i.

$\hat{i} \equiv S_2$; $\hat{i} \equiv \sigma_h C_2$, if n = even

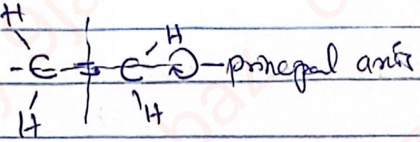
If n = even, you can've C_{nh} & D_{nh}

If n = odd, you can've D_{nd}

$D_{\infty h}$ for linear

The only cubic group of much importance to chemistry are the tetrahedral, octahedral & icosahedron.

N.B: If there are 3 mutually perpendicular C_2 axis, choose the principal axis to the one that passes through the most (or nearest) atoms.



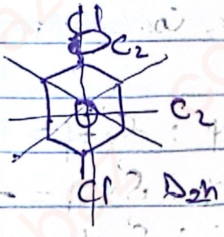
In such a case, there will be $n \perp C_2$ axis.

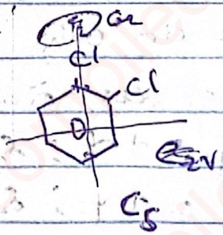
The identification of molecular symmetry element & its point group are usually the first step to identifying understanding the app. of symmetry to chemistry.

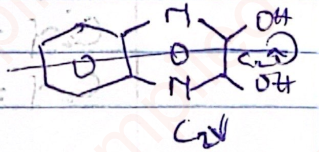
There are several of application of symmetry in chemistry but 2 will be mentioned here briefly.

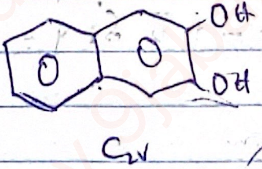
The presence or absence of a permanent dipole moment in molecules depends on symmetry. In particular, permanent dipole moment are permitted only to the group C_n, C_s & C_{nv}.

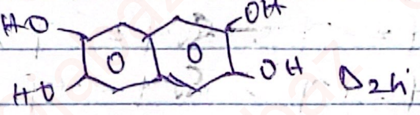
Also, the optical activity, the ability of molecules to twist the plane of polarized light











Symmetry of Functions

In the absence of degeneracy, the wavelengths of a molecule must be either symmetric or anti symmetric with respect to all symmetry operation of the molecule - for example, the wavefuns of molecular orbital of water (C_{2v} symmetry) must be such that

$$C_2\psi = \pm\psi \; ; \; \sigma_v\psi = \pm\psi \; ; \; \sigma_v'\psi = \pm\psi$$

There are only 4 possible combination which are named as follows:

- $C_2\psi = +\psi$; $\sigma_v\psi = +\psi$; $\sigma_v'\psi = +\psi$; A_1-type
- $C_2\psi = +\psi$; $\sigma_v\psi = -\psi$; $\sigma_v'\psi = -\psi$; A_2-type
- $C_2\psi = -\psi$; $\sigma_v\psi = +\psi$; $\sigma_v'\psi = -\psi$; B_1-type
- $C_2\psi = -\psi$; $\sigma_v\psi = -\psi$; $\sigma_v'\psi = +\psi$; B_2-type

Impossible combination

$C_2\psi = -\psi$; $\sigma_v\psi = -\psi$; $\sigma_v'\psi = -\psi$

$C_2\psi = +\psi$; $\sigma_v\psi = +\psi$; $\sigma_v'\psi = -\psi$

$C_2\psi = +\psi$; $\sigma_v\psi = -\psi$; $\sigma_v'\psi = +\psi$

It is not possible to have these three combinations because the above 4 combinations are the only permissible functions that can be deduced from the C_2 multiplication table for water.

Let's Prove that these are the only 4 permissible combination. Is it possible to have a combination that's anti-symmetric w.r.t all the operations of C_{2v}

If for some fxn ψ:

$C_2\psi = -\psi$ & $\sigma_v\psi = -\psi$

$C_2\sigma_v\psi = C_2(-\psi) = \psi$

$C_2\sigma_v = \sigma_v'$ — B_2 type

$\sigma_v' = +\psi$

Consider a situation where

$C_2\psi = +\psi$ & $\sigma_v'\psi = +\psi$

$C_2\sigma_v\psi = C_2(+\psi) = +\psi$

$C_2\sigma_v = \sigma_v'$ → A_1 type

$\sigma_v'\psi = +\psi$

For some fxn, Let's define

$C_2\psi = -\psi$ $\sigma_v\psi = +\psi$ —— B_1 type

$C_2\sigma_v\psi = C_2(+\psi) = -\psi$

$C_2\sigma_v\psi = \sigma_v'$

∴ $\sigma_v' = -f$

$C_2 f = +f$, $\sigma_v f = -f$

$C_2 \sigma_v f = C_2(-f) = -f$

$C_2 \sigma_v = \sigma_v'$ — A_2 type

∴ $\sigma_v' = -f$

By these procedures, one can show that the eqn of symmetry given in eq ① are the only one permitted in C_{2v}. If we include the identity operation E, for which all functions equals to +ve, then symmetries can be written as a 4-dimensional vectors.

$A_1 = (1, 1, 1, 1)$

$A_2 = (1, 1, -1, -1)$

$B_1 = (1, -1, 1, -1)$

$B_2 = (1, -1, -1, 1)$

The 4-D vectors are known as irreducible representation

* Reducible & irreducible representation

Character table for C_{2v} molecule

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	functions
$A(a_1)$	1	1	1	1	z, x^2, y^2, z^2
$A_2(a_2)$	1	1	-1	-1	xy
$B_1(b_1)$	1	-1	1	-1	x, xz
$B_2(b_2)$	1	-1	-1	1	y, yz

IR active

x, y, z (linear) — translational (vibrational motion)

x^2, y^2, z^2 (quadratic) — Raman spectroscopy (vibrational)
(xy, yz, xz)

IR active modes of trans-1,2-dichloroethene

Due to centre of inversion present in the molecule, it'll be A_g, B_g, A_u & B_u - type.

Character table

C_{2h}	E	C_2	$\hat{e}$	$\hat{i}$	σ_h	functions
A_g	1	1		1	1	R_z
B_g	1	-1		1	-1	R_x, R_y
A_u	1	1		-1	-1	z
B_u	1	-1		-1	1	x, y
No of unshifted atom	6	0		0	6	
Contribution/atom	3	-1		-3	1	
Γ reducible representation	18	0		0	6	

R_x, R_z, R_y — Radial form (rotational)

E	C_n	i	σ	S_n
3	$2\cos\theta+1$	-3	1	$2\cos\theta-1$

$$N_{sym} = \frac{1}{h}\left[\Sigma f_i C_i \chi_i\right]$$ — standard reduction formula

where $h \rightarrow$ order of the group (total no of symmetry element)

f_i – reducible representation

C_i – coefficient of the symmetry element

χ_i – character corresponding to the symmetry element in the table.

$$N_{A_g} = \frac{1}{4}\left[(18\times1\times1)+(0\times1\times1)+(0\times1\times1)+(6\times1\times1)\right] = \frac{24}{4} = 6A_g$$

$$= 6A_g$$

$$N_{B_g} = \frac{1}{4}\left[(18\times1\times1)+(0\times1\times-1)+(0\times1\times1)+(6\times1\times-1)\right] = \frac{12}{4}$$

$$= 3B_g$$

$$N_{A_u} = \frac{1}{4}\left[(18\times1\times1)+(0\times1\times1)+(0\times1\times-1)+(6\times1\times-1)\right] = \frac{12}{4}$$

$$= 3A_u$$

$$N_{B_u} = \frac{1}{4}\left[(18\times1\times1)+(0\times1\times-1)+(0\times1\times-1)+(6\times1\times1)\right] = \frac{24}{4}$$

$$= 6B_u$$

Remove the rotational & translational mode from the overall wavefxn.

2n-6
12-6

$\Gamma_M = 6A_g + 3B_g + 3A_u + 6B_u$

$\Gamma_{rot} = A_g + 2B_g$

$\Gamma_{trans} = A_u + 2B_u$

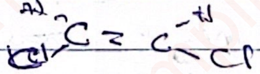
$\Gamma_x = \Gamma_M - (\Gamma_{rot} + \Gamma_{trans})$

$= 5A_g + B_g + \underbrace{2A_u + 4B_u}$

IR active mode = 2 + 4 = 6

<u>Ass</u>

Det. the IR active mode using the character table below.



	E	C_2	σ_v	σ_v'	fxns
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

Pattern of electron cloud det. of shape of molecule
not all molecules can form crystal - X-ray crystallography 3-
- NMR

Laser (categorized based on pulsewidth)
also send light

31/05/2025

What makes a molecule Raman active?

A vibrational mode is Raman active if it has the same symmetry component of the molecular polarizability.

Polarizability is the measure of ~~[illegible]~~ ease with which the electron cloud may be distorted. A very dense electron cloud is harder to polarize than a more diffused electron cloud.

Exclusion Rule

If a molecule has an inversion centre, none of its mode can both be Raman and IR active. But a mode may be inactive in both.

This rule applies to only molecules with inversion centre.

Mulliken Symbols

They are short-hand notation system that describe the symmetry of irreducible representation (in a character table).

Γ_{irr}

They're part of the language of symmetry

A - Symmetric with respect to the principal rotation axis. It will have a ~~+~~ 1 in the identity column.

B — antisymmetric w.r.t the principal rotation axis. It will also have a 1 in the identity column.

E - doubly degenerate. It will have a 2 in the identity column.

T — triply degenerate. It'll have a 3 in the identity column.

Subscript

Subscript 1 — symmetric to C_2 rotation ⊥ to the principal axis.

Subscript 2 — antisymmetric to C_2 rotation.

But if there are no ⊥ C_2, 1 designate a representation that is symmetric to a vertical plane and 2 means antisymmetric to a vertical plane

G — Symmetric ~~wrt~~ inversion. (Gerade)

U — antisymmetric to inversion (ungerade)

Superscript (A' A'')

single prime (A') — symmetric w.r.t horizontal mirror plane.

Double prime (A'') — antisymmetric w.r.t horizontal mirror plane. when such distinction are possible

However, note that there are cases when

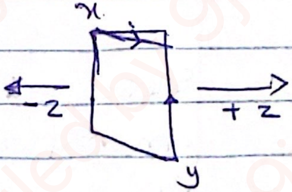
Single, double & triple prime are assigned arbitrar

Matrix Method of solving Symmetry Operation

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \xrightarrow{E} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \xrightarrow{C_2^x} \begin{bmatrix} x \\ -y \\ -z \end{bmatrix}$$

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \xrightarrow{\sigma_{xy}} \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$



$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \xrightarrow{i} \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

Find the product of $C_2^x \sigma_{xy}$

✓ σ_{xz} , σ_{yz} , C_2^y , C_2^z (show for all)

$$C_2^x \sigma_{xy} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \longrightarrow C_2^x \begin{bmatrix} x \\ y \\ -z \end{bmatrix} \rightarrow \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

σ_{xz} – reflection in xz plane :

$$\begin{aligned} \sigma_{xy} \cdot S_4^z &= \sigma_{xy} \cdot C_4^z \, \sigma_{xy} \\ &= \sigma_{xy}^2 \cdot C_4^z \\ &= E \cdot C_4^z = C_4^z \end{aligned}$$

x, y　　x
y　　$-y$
-z　　z

Matrix Representation of Symmetry Operation

A matrix is an array of number:

Row (n-row)

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \cdots & a_{3n} \\ \vdots & \vdots & \vdots & & \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{bmatrix}$$

Column
(m-column)　　　　$n \times m$ matrix

If the no of element in a row is equal to the no of element in a column, such a matrix is called a square matrix.

- Diagonal matrix:- When only the diagonals are non-zero numbers.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = M$$

- Unit Matrix:-

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = M$$

Cn 8h

CHM 310

Prof. Owoyomi’s Part

06/03/2025

Covalent Bond

formed as a result of 2 participating atom coming together to share electron so as to -

tendency to attain a stable octet configuration is the driving force for bond.

The molecule formed is more stable than the individual atom, so how do we account for such stability ?

Valence Bond Theory
Molecular Orbital Theory

Molecular Orbital theory

Born-Oppenheimer Approximation

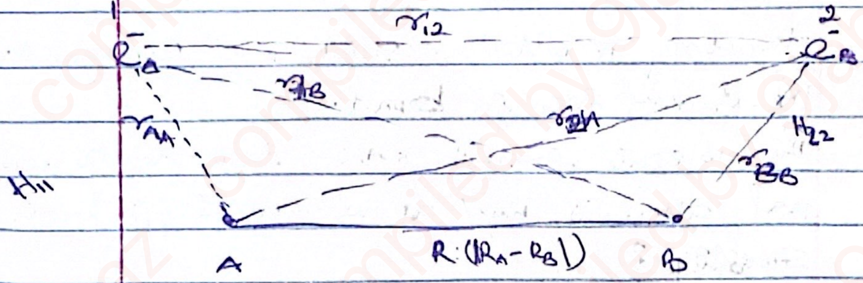
1 amu = 1.6605×10^{-27} kg

mass of electron = 9.109×10^{-31} kg

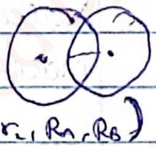
For any electronic motion, the nuclei is stable

* total hamiltonian is taken as a composite form of both electronic motion & nuclear motion.

The simplest neutral molecule is the hydrogen molecule.



The molecular Schrödinger eqn for this system is:



$$\hat{H}\psi(r_1, r_2, R_A, R_B) = E_T\,\psi(r_1, r_2, R_A, R_B)$$

Where the hamiltonian

$$-\frac{\hbar^2}{2M_1}\nabla_1^2 - \frac{\hbar^2}{2M_2}\nabla_2^2 - \frac{\hbar^2}{2m_{e_1}}\nabla_{e_1}^2 - \frac{\hbar^2}{2m_{e_2}}\nabla_{e_2}^2 + \frac{e^2}{R} - \frac{e^2}{r_{AA}} - \frac{e^2}{r_{BB}}$$
$$- \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} + \frac{e^2}{r_{12}}$$

Proton - proton repulsion

electrostatic attraction

electron - electron repulsion.

08/05/2025

MO - nuclear

Linear Combination of Atomic Orbital - I
[LCAO] - MO Method

This method is based on the idea that a wave function for a molecule can be written as a linear combination of atomic wavefns, i.e.,

$$\psi = \sum a_i \phi_i$$

where ψ = molecular wavefxn

ϕ_i = atomic wavefns for the various atom that make up a molecule.

a_i = a measure of the contribution of the ith atom to the molecule.

For a diatomic molecule, e.g. H_2,

$$\psi_+ = a_1\phi_1 + a_2\phi_2$$

It can also be shown that this is also a possibility

$$\psi_- = a_1\phi_1 - a_2\phi_2$$

a_1 & a_2 ≡ weighting factor.

(How do we det- the value of the coeff.?

This can be done by employing the Variation method.

$$\langle E \rangle = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

where $d\tau$ = volume element.

$$= \frac{\int (a_1\phi_1 + a_2\phi_2)^{*} \hat{H} (a_1\phi_1 + a_2\phi_2)\, d\tau}{\int (a_1\phi_1 + a_2\phi_2)^{*} (a_1\phi_1 + a_2\phi_2)\, d\tau}$$

$$= \frac{\int (a_1\phi_1 + a_2\phi_2) \hat{H} (a_1\phi_1 + a_2\phi_2)\, d\tau}{\int \left[a_1^2\phi_1^2 + a_1 a_2 \phi_1 \phi_2 + a_2 a_1 \phi_2 \phi_1 + a_2^2 \phi_2^2\right] d\tau}$$

$$= \frac{\int (a_1\phi_1 + a_2\phi_2)^{*} \hat{H} (a_1\phi_1 + a_2\phi_2)\, d\tau}{\int \left(a_1^2 \phi_1^{*}\phi_1 + \cancel{2} a_1 a_2 \phi_1^{*}\phi_2 + a_2 a_1 \phi_2 \phi_1 + a_2^2 \phi_2^{*}\phi\right) d\tau}$$

$$= \frac{\int (a_1\phi_1 + a_2\phi_2)^{*} (a_1 \hat{H}\phi_1 + a_2 \hat{H}\phi_2)\, d\tau}{\int (a_1^2\phi_1^2 + a_2^2\phi_2^2) + (a_1 a_2 \phi_1 \phi_2 + a_2 a_1 \phi_2 \phi_1)\, d\tau}$$

$$= \int (a_1$$

$f_1 = f_2$ $\overset{=0}{=1}$

$f_1 \neq$

$$= \frac{\int (a_1\phi_1^* + a_2\phi_2^*)(a_1\hat{H}\phi_1 + a_2\hat{H}\phi_2)\, d\tau}{}$$

$$= \frac{\int a_1^2 \phi_1^* \hat{H} \phi_1 + a_1 a_2 \phi_1^* \hat{H} \phi_2 + a_2 a_1 \phi_2^* \hat{H} \phi_1 + a_2^2 \phi_2^* \hat{H} \phi_2}{\int a_1^2 \phi_1^* \phi_1 + 2 a_1 a_2 \phi_1^* \phi_2 + a_2 a_1 \phi_2^* \phi_1 + a_2^2 \phi_2^* \phi_2 \, d\tau}$$

$$= \frac{a_1^2 \int \phi_1^* \hat{H} \phi_1 + 2 a_1 a_2 \int \phi_1^* \hat{H} \phi_2 + a_2^2 \int \phi_2^* \hat{H} \phi_2 \, d\tau}{a_1^2 \int \phi_1^* \phi_1 + 2 a_1 a_2 \int \phi_1^* \phi_2 \, d\tau + a_2^2 \int \phi_2^* \phi_1 \, d\tau}$$

$$\int \phi_1^* \hat{H} \phi_2 \, d\tau = \int \phi_2^* \hat{H} \phi_1 \, d\tau$$

$$\int \phi^* \phi \, d\tau = \int \phi \phi \, d\tau$$

Let $\int \phi_1^* \hat{H} \phi_1 \, d\tau = H_{11}$ $\quad \int \phi_2^* \hat{H} \phi_2 \, d\tau = H_{22}$

$\int \phi_1^* \hat{H} \phi_2 = H_{12}$ $\quad \int \phi_2^* \phi_2 \, d\tau = S_{22}$

$\int \phi_1^* \phi_1 = S_{11}$ $\quad \int \phi_2^* \phi_1 \, d\tau = S_{21}$

$\int \phi_1^* \phi_2 = S_{12}$

The integral H_{11} & H_{22} rep. the energies with which an electron is held in atoms 1 & 2 respectively.

H_{11} & H_{22} = Coloumbic integrals

The integral H_{12} & H_{21} are known as exchange integral indicative of the attraction that nucleus 1 has for electron 2 & vice versa.

S_{21}, S_{12}, S_{11} & S_{22} are known as Overlap integral.

Therefore, the expectation value of energy of MO formed from linear combination of atom 1 & atom 2 can be written in a more compact form as.

$$\langle E \rangle = \frac{a_1^2 H_{11} + 2a_1a_2H_{12} + a_2^2 H_{22}}{a_1^2 S_{11} + 2a_1a_2S_{12} + a_2^2 S_{22}}$$

where $S_{11} = S_{22} = 1$ provided ϕ_1 & ϕ_2 are normalised atomic wave fxn.

13/05/2025 Therefore

$$E = \frac{a_1^2 H_{11} + 2a_1a_2H_{12} + a_2^2 H_{22}}{a_1^2 + 2a_1a_2S_{12} + a_2^2}$$

$$\left(\frac{\partial E}{\partial a_1}\right)_{a_2} = 0 \quad \& \quad \left(\frac{\partial E}{\partial a_2}\right)_{a_1} = 0$$

$$a_1(H_{11}-E) + a_2(H_{12}-S_{12}E) = 0$$
$$a_1(H_{21}-S_{21}E) + a_2(H_{22}-E) = 0$$
} secular eqn

For non-trivial solution

The solution gives (non-trivial) a secular determinant

$$\begin{vmatrix} H_{11}-E & H_{12}-S_{12}E \\ H_{21}-S_{21}E & H_{22}-E \end{vmatrix} = 0$$

$$(H_{11}-E)^2 - (H_{12}-S_{12}E)^2 = 0$$

OR

$$(H_{11}-E)^2 = (H_{12}-SE)^2$$

$$H_{11}-E = \pm(H_{12}-SE)$$

$$E_b = \frac{H_{11}+H_{12}}{1+S}$$ — bonding energy

$$E_a = \frac{H_{11}-H_{12}}{1-S}$$ ← anti-bonding energy

For these two energy states, E_b is referred to as symmetric or bonding state & E_a is referred to as the anti-symmetric or anti-bonding state.

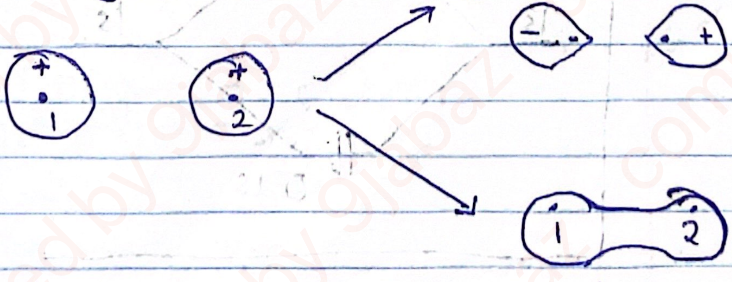


fig. : Electron density diagram of M.O from 2. Atomic Orbital.

from the secular eqn

$a_1 = a_2$ Symmetric state

$a_1 = -a_2$ anti-symmetric state

The wavefxn corresponding to the binding engy

$$\psi_2 = a_1\phi_1 + a_2\phi_2 = \frac{1}{(2+2S)^{1/2}}(\phi_1 + \phi_2)$$

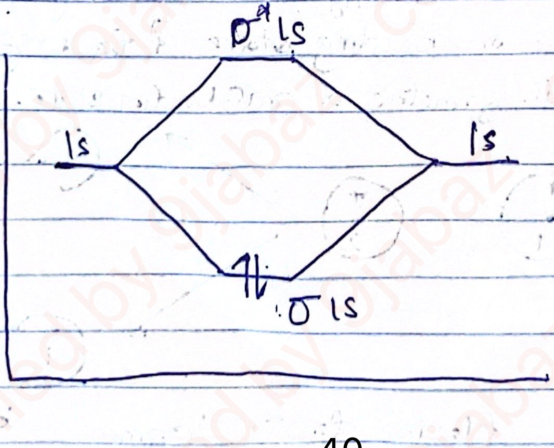
However

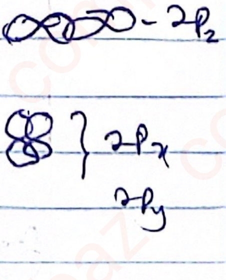
$$a_1 = a_2 = \psi = a_1(\phi_1 + \phi_2)$$

$$= \frac{1}{\sqrt{2+2S}}$$

$$\int \psi^2 d\tau = 1$$

$$\int a_1^2(\phi_1 + \phi_2)^2 d\tau = 1$$





The filling fro of e^-s into of molecular orbital for diatomic molecular follows the trend below

$$\sigma 1s \quad \sigma^* 1s \quad \sigma 2s \quad \sigma^* 2s \quad \left\{\begin{matrix}\pi 2p_x \\ \pi 2p_y\end{matrix}\right. \quad \sigma 2p_z \quad \left\{\begin{matrix}\pi^* 2p_x \\ \pi^* 2p_y\end{matrix}\right. \quad \sigma^* 2p_z$$

However, the trend above follows from Li_2 to N_2. but from O_2, F_2, Ne, there's a little amendment. They follow the trend below

$$\sigma 1s \quad \sigma^* 1s \quad \sigma 2s \quad \sigma^* 2s \quad \sigma 2p_z \left\{\begin{matrix}\pi 2p_x \\ \pi 2p_y\end{matrix}\right. \left\{\begin{matrix}\pi^* 2p_x \\ \pi^* 2p_y\end{matrix}\right. \quad \sigma^* 2p_z$$

Spectroscopy evidence shows that $\sigma 2p_z$ is of a slightly lower energy.

The Configuration of Li molecule is

$\sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2$

Li — Li [The strength of the bond is measured by the bond order].

Bond order (B.O) = $\frac{N_b - N_a}{2}$

N_b – no of electron in bonding orbital for Li

$B.O = \frac{4-2}{2} = 1$

The fact that it's a non-zero bond order shows that it's possible to 've a Lithium molecule.

4 $Be_2 \rightarrow$ 8 electrons.

$\sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2 \; \sigma^* 2s^2$

$B.O = \frac{4-4}{2} = 0$

therefore, it's impossible for Be_2 (Beryllium molecule) to occur since the bond order which measures of stability & the strength of bond is zero.

Will Be_2^- or Be_2^+ exist ?

5 $B_2 \rightarrow$ 10 electron

$\sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2 \; \sigma^* 2s^2 \begin{cases} \pi 2p_x^1 \\ \pi 2p_y^1 \end{cases}$

$B.O = \frac{6-4}{2} = 1$

$_6C_2$ — 12 electrons

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2 \begin{cases} \pi 2p_x^2 \uparrow\downarrow \\ \pi 2p_y^2 \uparrow\downarrow \end{cases}$

$B.O = \frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$

Since the B.O is 2, the bond is $C=C$.

$_7N_2$ — 14 electrons

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2 \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases} \sigma 2p_z^2$

$B.O = \frac{10-4}{2} = 3$

that is, $N \equiv N$

$_8O_2$ → 16 electrons

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2 \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases} \begin{cases} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{cases}$

$B.O = \frac{10-6}{2} = 2$

$O=O$

This can also be used to det. whether a molecule is diamagnetic

In a system where all e^-s are paired, we're diamagnetic.
While if there's unpaired electron, it is said to be paramagnetic.

20/05/2025 **Heteronuclear Diatomic Molecule**

$$\overset{\delta^+}{H} \twoheadrightarrow \overset{\delta^-}{X}$$

There are 3 possibilities

$A - B$

$A^+ - B^-$

$A - B^+$

Each of these structure contribute a substantial amount to the overall stability of the molecule.

$$\psi_{molecule} = a_1\psi_{A-B} + a_2\psi_{A^+-B^-} + a_3\psi_{A^--B^+}$$

Where a_1, a_2 & a_3 are the weighing coeff.

These possible structures are called resonance structure.

For an homonuclear diatomic molecule such as H_2, the ionic component contribute equally to the

Overall wavefxn such that

$a_1 >> a_2 \approx a_3$ – homonuclear diatomic molecule, since a_2 & a_3 contribute equally

& contribution of ionic component is very small in an homonuclear system but in an heteronuclear system

H – F

$$\psi_{molecule} = a_1\psi_{H-F} + a_2\psi_{H^+-F^-} + \boxed{a_3\psi_{H^--F^+}}$$ (hypothetically)

Via the presence of F, the last structure is unrealistic.

Therefore, there are only 2 combinations for heteronuclear diatomic molecules. The wavefxn therefore can be written as

$$\psi_{molecule} = \psi_{covalent} + \lambda\psi_{ionic}$$

where λ is a measure of the degree of ionicity of the molecule

How do we measure λ?

λ, lambda, is a measure of the dipole moment which in turn is a measure of the ionic character of the molecule. The percent ionic character of any molecule is expressed as

$$\% \text{ ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100$$

The percentage ionic character can also be related to λ as

$$= \frac{\lambda^2}{(1+\lambda^2)} \times 100$$

Therefore,

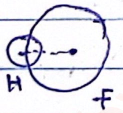
$$\frac{\lambda^2}{1+\lambda^2} = \frac{\mu_{obs}}{\mu_{ionic}}$$

How do we determine μ ?

$\mu = e \cdot r =$ (electronic charge × distance)

where r = intermolecular distance = bond length

ml.



For example, for HF, the observed dipole moment is 1.91D while the theoretical dipole moment is 4.41D.

$$\frac{\lambda^2}{1+\lambda^2} = \frac{\mu_{obs}}{\mu_{ionic}} = \frac{1.91}{4.41} = 0.43$$

$$\lambda^2 = 0.43 + 0.43\lambda^2$$
$$\lambda^2 - 0.43\lambda^2 = 0.43$$
$$0.57\lambda^2 = 0.43$$
$$\lambda^2 = 0.43/0.57 = 0.75$$
$$\lambda = 0.87$$

$$\Psi_{HF} = \Psi_{covalent} + 0.87\Psi_{ionic}$$

That is HF appears to be 43% ionic and 57% covalent, such that the overall molecule is a hybrid of the covalent and ionic structure.

In reality, a pure covalent bond does not exist.

The implication of this statement is that the bond dissociation energy for the pure covalent bonds and the bond dissociation energy for the actual covalent bond are not the same.

Resonance stabilization energy (RSE)

$$= BDE_{actual} - BDE_{covalent}$$

The bond dissociation energy for pure actual covalent bonds minus the bond dissociation energy for the ~~actual~~ pure covalent bond

Resonance Stabilization Energy therefore can be determined as

$$RSE = BDE_{AB} - \left(\frac{BDE_{AA} + BDE_{BB}}{2}\right)$$

$$= \underbrace{BDE_{AB}}_{\text{actual bond}} - \underbrace{\left[\frac{1}{2}\left[BDE_{AA} + BDE_{BB}\right]\right]}_{\text{Pure covalent bond}}$$

The RSE is always a +ve entity, i.e the actual BDE is always greater than the predicted covalent BDE.

Recall that, the ionic structure of any molecule is related to the electronegativities of the combining atoms

Therefore, the resonance stabilization energy can also be determined in terms of electronegativities of the atom, i.e,

$$RSE = 23.06|\chi_A - \chi_B|^2$$

$$= 23.06\,|\Delta_{EN}|^2$$

Possibility only if molecules can be isolated in vacuum.

The HS bond moment/dipole moment is 0.68D and the bond length is 1.37 Å. What's the percent ionic character of the HS bond.

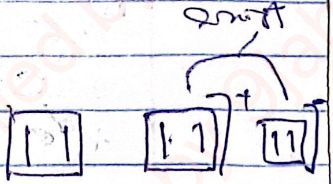
22/05/2025

$F_2 = 142$ pm } Explain of diff in these bond
$F_2^+ = 132$ pm } length

$F_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \begin{cases} \pi 2p_x^2 & \pi^* 2p_x^2 \; \sigma^* 2p_z^2 \\ \pi 2p_y^2 & \pi^* 2p_y^2 \end{cases}$

$B.O = \frac{10-8}{2} = 1$ (F_2)

$B.O(F_2^+) = \frac{10-7}{2} = 1.5$

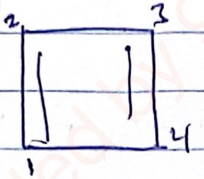


Since the RSE of Cyclobutan-1,2-diene is zero, it's been impossible to synthesize it, i.e. it does not exist.

Hückel - Molecular Orbital Theory

In the Hückel MOT, the basic assumption is that the sigma & pi part of the bonding in molecules can be separated.

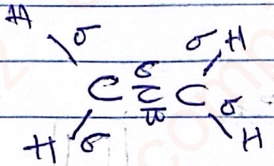
Another important assumption is that the overlap of orbitals on non-adjacent atom is assumed to be zero



$S_{13} = S_{24} = 0$

$S_{12} = S_{23} = S_{34} \neq 0$

In addition to this, the interaction energy between non-adjacent atoms is assumed to be zero i.e H_{13} & $H_{24} = 0$



The wave fxn for the BO can be written as

$$\psi_{CH}(\sigma) = a_1\phi(1s) + a_2\phi(sp^2)$$

$$\psi_{CC}(\sigma) = a_1\phi(sp^2) + a_2\phi(sp^2)$$

$$\psi_{CC}(\pi) = a_1\phi(P_1) + a_2\phi(P_2)$$

The Corresponding secular determinant for this molecule is

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - E \end{vmatrix} = 0$$

since $S_{11} = S_{22} = 1$

$\bar{e}$ & proton interaction

If we assume that the Coulomb integral

$H_{11} = H_{22} = \alpha$ Coulomb integral – bonding energy

$H_{12} = H_{21} = \beta$ Exchange integral

$\Downarrow$

electron in atom 1 & nucleus in atom 2 interaction.

In this, we've assumed that the Overlap integral is zero

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Dividing through by β & assuming $\frac{\alpha - E}{\beta} = x$;

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$x^2 - 1 = 0 \Rightarrow x = \pm 1$$

$\frac{\alpha - E}{\beta} = +1 \quad (x = 1)$

$\Rightarrow \alpha - E = \beta \Rightarrow E_1 = \alpha - \beta$

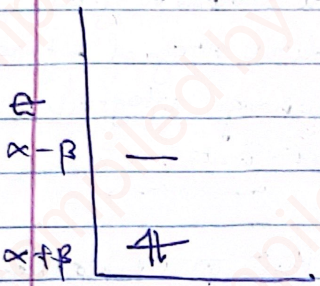
$\frac{\alpha - E}{\beta} = -1 \quad (x = -1)$

$\Rightarrow \alpha - E = -\beta \Rightarrow E_2 = \alpha + \beta$

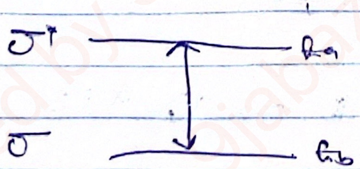
Both α & β are -ve energies

$8.2\times10^{-19}\,J$ $\quad E = \frac{hc}{\lambda}$ $\quad \frac{1}{cm} \times \frac{100cm}{1m}$

$1.6\times10^{-19}\,J = 1\,eV$ $\quad 2eV$



Suppose that a diatomic molecule X2 contains a single sigma bond. The binding energy of an electron in the valence shell of atom X is -10.0eV Spectroscopically, it's observed that promotion of an electron ~~to~~ the antibonding state leads to an absorption band at 16100 cm⁻¹. Using a value of 0.10 for the Overlap integral, det. the value of the exchange integral.



$E_a - E_b = 16100\ cm^{-1}$

$\Delta E = 16100\ cm^{-1}$

$\Delta E = hc\bar{\nu} = 6.626\times10^{-34}\,Js \times 2.99\times10^{10}\,cm\,s^{-1} \times 16100\,cm^{-1}$

$\alpha = -10.0$

$S = 0.10$

$H_{12} = ?$

Columb integral = bonding energy - H_{11}

3.2×10^{-1}

-19

$\Delta E = 3.2\times10^{-19}\,J$

$1.6\times10^{-19}\,J = 1\,eV$

$3.2\times10^{-19}\,J = \frac{3.2\times10^{-19}}{1.6\times10^{-19}}\,eV$

$= 2\,eV$

$E_a - E_b = \left(\frac{H_{11} - H_{12}}{1-S}\right) - \left(\frac{H_{11} + H_{12}}{1+S}\right) = 2\,eV$

$\frac{-10.0\,eV - H_{12}}{1-0.10} - \left(\frac{-10.0\,eV + H_{12}}{1+0.10}\right) = 2\,eV$

$\frac{-10.0\,eV - H_{12}}{0.90} - \left(\frac{-10.0\,eV + H_{12}}{1.10}\right) = 2\,eV$

$\frac{-11 - 1.10H_{12} - (-9.0 + 0.9H_{12})}{0.99} = 2\,eV$

~~$1.98 = -11 - 0.1H_{12}$~~

$1.98 = -11 + 9 - 2.0H_{12}$

$1.98 + 2 = -2.0H_{12}$

$H_{12} = -1.99\,eV$

OR

$\frac{(1+S)(H_{11} - H_{12}) - (1-S)(H_{11} + H_{12})}{1-S^2} = \Delta E$

$(\cancel{H_{11}} - H_{12} + H_{11}S - \cancel{H_{12}S}) - (\cancel{H_{11}} + H_{12} - H_{11}S - \cancel{H_{12}S})$

$= \Delta E(1-S^2)$

$2H_{11}S - 2H_{12} = \Delta E(1-S^2)$

$$2H_{11}S - \Delta E(1-S^2) = 2H_{12}$$

$$H_{12} = H_{11}S - \frac{\Delta E}{2}(1-S^2)$$

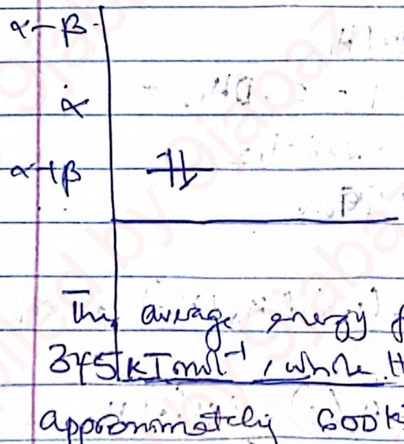
$$(-10\cdot0)(0\cdot1) - \frac{2}{2}(1-0\cdot01)$$

$$= -1 - 0\cdot99$$

$$= -1\cdot99\,eV$$

Parallel overlapping of 2p-orbitals gives [illegible]

The resonance stabilization energy, RSE, will then therefore be equal to:



$$RSE = 2(\alpha+\beta) - 2\alpha$$

$$= 2\beta$$

The energy, 2β, is called delocalisation energy or RSE.

The average energy for a C−C is approximately 345KJmol⁻¹, while that of a typical C=C is approximately 600KJmol⁻¹

Contributes

Therefore, the ~~bond~~ pi-bond energy is about 255KJmol⁻¹

$$\frac{\alpha - E}{\beta} = x$$

$2\beta = 255$ kJmol^{-1}

$\beta = 1{\cdot}25$ kJ mol^{-1}

$\psi_b = a_1\phi_1 + a_2\phi_2$; $\int \psi^2 d\tau = 1$

$\Rightarrow \int a_1^2\phi_1^2 + \int 2a_1^* a_2 \phi_1 \phi_2 \, d\tau + \int a_2^2 \phi_2 \, d\tau = 1$

For normalised atomic wavefxn:

$\Rightarrow a_1^2 + a_2^2 = 1$

Since $a_1(\alpha - E) + a_2\beta = 0$

$a_1\beta + a_2(\alpha - E) = 0$

$a_1 x + a_2 = 0$

$a_1 + a_2 x = 0$

Given that $x = -1$ for the bonding state

$\Rightarrow a_1 = a_2$

$a_1^2 + a_2^2 = 1 \Rightarrow 2a_1^2 = 1 \Rightarrow a_1 = 1/\sqrt{2}$

$\Rightarrow \psi_b = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$

$2a_1^2 = 1 \Rightarrow a_1^2 = 1/2 = a_2^2$ or

This means that ½ of the bonding electron will be on C_1 & ~~of~~ on localised on C_1 & the remaining goes to localised on C_2.

The electron density therefore will be equal to

$2(1/2) = 1$

Another important property for describing bonding in a molecule is the bond order which gives the e's population in terms of the no of pi bonds btw 2 bonding atoms.

a_1 & a_2

The product of the $\overset{\uparrow}{\text{Coeff.}}$ of the atomic wavefxn gives the density of the bond btw them. The bond order between atom x & y written as B_{xy} is given as :-

$$B_{xy} = \sum_{i=1}^{n} a_x a_y P_i$$; where a_x & a_y are the Coeff. on the atomic wavefxns.

n → no of populated orbitals & P_i → population, i.e. no of e's in that orbital

The bond order of C=C in ethylene

$$B_{CC} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right)\cdot 2 = 1$$, i.e there's only one pi-bond in ethylene.

~~The~~ Allyl System

$$\left.C=C-C \longleftrightarrow C-C=C\right\} \Rightarrow C \overset{\cdots}{=} C \overset{\cdots}{=} C$$

$$\left[C \overset{\cdots}{=} C \overset{\cdots}{=} C\right]^+$$

$$\left[C \overset{\cdots}{=} C \overset{\cdots}{=} C\right]^-$$

$H_{11} = H_{22} = H_{33} = \alpha$

$H_{12} = H_{21} = H_{32} = H_{23} = \beta$

$H_{13} = H_{31} = 0$

$$\begin{vmatrix} H_{11}-E & H_{12} & 0 \\ H_{21} & H_{22}-E & H_{23} \\ 0 & H_{32} & H_{33}-E \end{vmatrix} = \begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix} = \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$x \quad 1 \quad 0$

$1 \quad x \quad 1$

$x(x^2 - \overset{x}{1}) - x = 0$

$x^3 - 2x = 0$

$x(x^2 - 2) = 0$

$x = 0$.

$x^2 - 2 = 0 \Rightarrow x^2 = 2 \Rightarrow x = \pm\sqrt{2}$

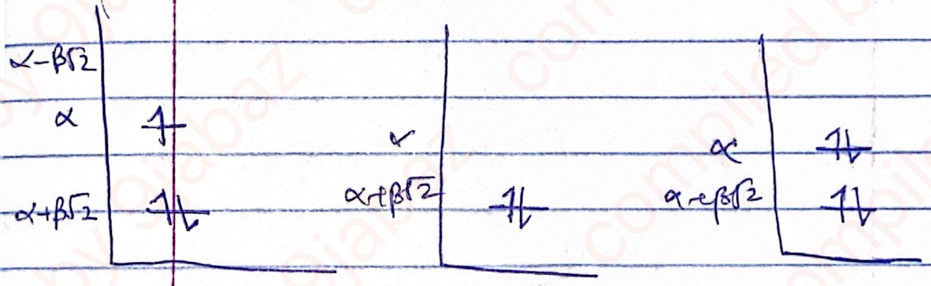
$\therefore x = 0, \sqrt{2}$ & $-\sqrt{2}$

$\frac{\alpha - E}{\beta} = x$ when $x = 0$; $E = \alpha$

$x = +\sqrt{2}$; $E = \alpha - \beta\sqrt{2}$

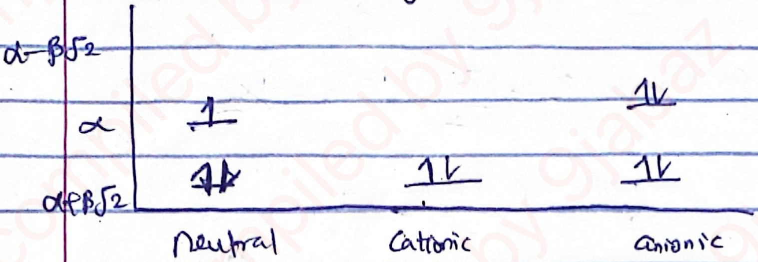
$x = -\sqrt{2}$; $E = \alpha + \beta\sqrt{2}$

~~A~~ Neutral allylic has 3 pi-e's



Neutral radical　　cation　　anion

For the neutral allylic orbital, there are three pi electrons, how are they distributed?



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$$\begin{vmatrix} a_1x & a_2 & 0 \\ a_1 & a_2x & a_3 \\ 0 & a_2 & a_3x \end{vmatrix} = 0$$

$a_1x + a_2 = 0$ — ①

$a_1 + a_2x + a_3 = 0$ — ⓘⓘ

$a_2 + a_3x = 0$ — ⓘⓘⓘ

$\boxed{\text{when } x = -\sqrt{2}}$

$-a_1\sqrt{2} + a_2 = 0$

$a_1 - a_2\sqrt{2} + a_3 = 0$

$a_2 - a_3\sqrt{2} = 0$.

$a_2 = a_1\sqrt{2}$

$a_2 = a_3\sqrt{2} \Rightarrow a_1\cancel{\sqrt{2}} = a_3\cancel{\sqrt{2}} \Rightarrow a_1 = a_3$

$a_1^2 + a_2^2 + a_3^2 = 1$

$a_1^2 + (a_1\sqrt{2})^2 + a_1^2 = 1$

$a_1^2 + 2a_1^2 + a_1^2 = 1$

$4a_1^2 = 1$

$a_1 = \frac{1}{2} = a_3$

$a_2 = \frac{1}{2} \times \sqrt{2} \Rightarrow a_2 = \frac{\sqrt{2}}{2}$

$a_1 = \frac{1}{2}, \quad a_2 = \frac{\sqrt{2}}{2}, \quad a_3 = 1/2$

$\psi = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$

$\boxed{\text{When } x = 0}$

$a_1 \times 0 + a_2 = 0$

$\Rightarrow a_2 = 0$

$a_1 = a_3$

$a_1^2 + a_2^2 + a_3^2 = 0$

$a_1^2 + a_3^2 = \phi$

$a_1^2 + a_1^2 = \phi$

$2a_1^2 = 1 \Rightarrow a_1 = \frac{1}{\sqrt{2}} = a_3$

$a_1 = \frac{1}{\sqrt{2}}, \quad a_2 = 0, \quad a_3 = \frac{1}{\sqrt{2}}$

Since $a_2 = 0$

$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$

$= \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$

when $x = +\sqrt{2}$

$a_1\sqrt{2} + a_2 = 0$ $\quad , a_2 = -a_1\sqrt{2}$

$a_1 + a_2\sqrt{2} + a_3 = 0$

$a_2 + a_3\sqrt{2} = 0 \qquad a_2 = -a_3\sqrt{2}$

$-a_1\sqrt{2} = -a_3\sqrt{2}$

$a_1 = a_3$

$a_1^2 + a_2^2 + a_3^2 = 1$

$a_1^2 + (-a_1\sqrt{2})^2 + a_3^2 = 1$

$a_1 + 2a_1^2 + a_1^2 = 1$

$4a_1^2 = 1$

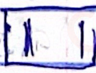
$a_1 = \frac{1}{2} = a_3$

$a_2 = a_1\sqrt{2}, \quad a_2 = -\frac{1}{2} \times \sqrt{2} \Rightarrow a_2 = -\frac{\sqrt{2}}{2}$

$a_1 = \frac{1}{2}, \quad a_2 = -\frac{\sqrt{2}}{2}, \quad a_3 = 1/2$

$\varphi = \frac{1}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$

Assignment

$H_2C=CH-CH=CH_2$,  , 

a cyclobutadien

1. Obtain the HMO for these molecules, its cation and its anion

2- For each of the HMO's in no. 1, calculate the corresponding electron density @ each C atom and also, the bond order in each system.

3. Determine the RSE, and always each of the species in the order of relative stability.

5-06-2025

electron density is the square of the coefficient of the atomic wave function multiplied by the occupancy.

$$\psi_1 = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$

$$\psi_2 = \frac{\sqrt{2}}{2}\phi_1 + 0\phi_2 - \frac{\sqrt{2}}{2}\phi_3$$

$$\psi_3 = \frac{1}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$

neutral

$ED(C_1) = 2(0.5)^2 + 1\left(\frac{\sqrt{2}}{2}\right)^2 = 1$

$ED(C_2) = 2\left(\frac{\sqrt{2}}{2}\right)^2 + 1(0)^2 = 1$

$ED(C_3) = 2\left(\frac{1}{2}\right)^2 + 1\left(-\frac{\sqrt{2}}{2}\right)^2 = 1$

$$\psi_1 = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$

Anion

$ED(C_1) = 2\left(\frac{1}{2}\right)^2 + 2\left(\frac{\sqrt{2}}{2}\right)^2 = 1.5$

$ED(C_2) = 2\left(\frac{\sqrt{2}}{2}\right)^2 + 2(0)^2 = 1.0$

$ED(C_3) = 2\left(\frac{1}{2}\right)^2 + 2\left(-\frac{\sqrt{2}}{2}\right)^2 = 1.5$

Question

(i) Calculate the ED for the cation

(ii)

(iii) For a molecule X, where the molecular wave function is given as; $\psi_{molecule} = \psi_{covalent} + 0.15\psi_{ionic}$
Calculate the % ionic character of the X–Y bond.
If the bond length is 1.50 Å, what is μ (dipole moment)?

(iv) For the molecule ICl; $\psi_{ICl} = \psi_{covalent} + 0.53\psi_{ionic}$
If the μ (dipole moment) for ICl is 0.65 D, what is the internuclear distance?

ABE = IN

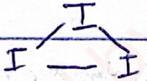
(v) The covalent radii of F and Cl atoms are 0.72 and 0.99 Å respectively, what will be the expected bond distance for ClF molecule?

(vi) The bond energy in C_2^- is 2.2 eV > C_2

$$\left.\begin{array}{l}\Delta BE \equiv BE\,C_2^- - B.E\,C_2 = 2.2\,eV \\ \text{and } \Delta BE \equiv BE(O_2) - B.E\,(O_2^-) = 1.1\,eV\end{array}\right\}\text{Explain ???}$$

(Vii) Two possible structures of I_3^+ are;

I–I–I and



Use the Huckel Molecule orbital calculation to determine which structure is more likely.

(Viii) Perform Huckel Molecular Orbital Calculation for bicyclobutadiene.