★ Draw the molecular orbital diagram for H_2 molecule.

$H = 1S^1$

$H_2 = \sigma 1S^2$

E (energy)

$\sigma^* 1S$

1S — H-atom

$\sigma 1S$

1S — H-atom
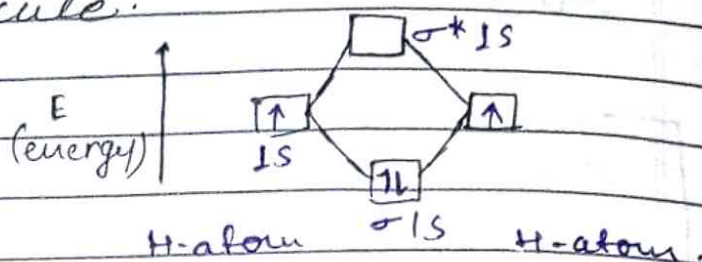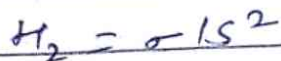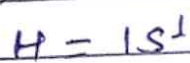
Bond Order :-

$$\frac{\text{No. of } e^- \text{ in bonding molecule} - \text{No. of } e^- \text{ in anti Bonding molecule.}}{2}$$

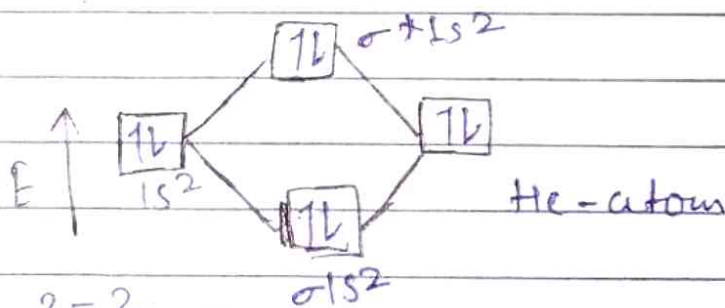Bond order :- $\frac{2-0}{2} = 1$ (for above diagram)

Bond length :-

α Bond order

α Bond strength
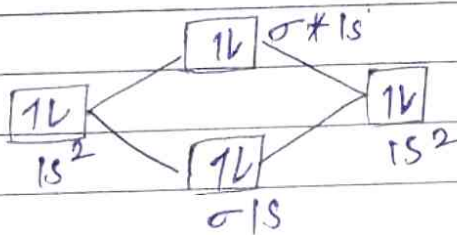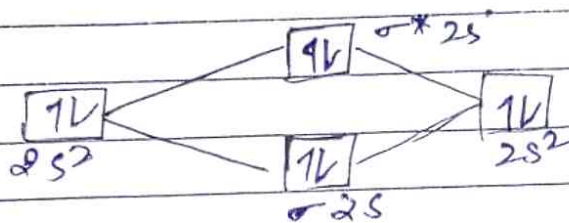
for He_2 molecule

or prove that He_2 does not exist

$He = 1S^2$

$He_2 = \sigma 1S^2 \sigma^* 1S^2$

$\sigma^* 1S^2$

$1S^2$ — He-atom

$\sigma 1S^2$

E
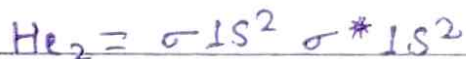
Bond order $= \frac{2-2}{2} = 0$

Draw the molecular Diagram of B_2 molecule —

$5^{B} = 1s^2\ 2s^2\ 2p^1$

$10\ B_2 = \sigma1s^2\ \sigma^*1s^2\ \sigma2s^2\ \sigma^*2s^2\ \pi2px^1 = \pi2p^1$

σ^*2pz

$\pi^*2px = \pi^*2py$

$\pi2px = \pi2py$

σ^*2s

$2s^2$ $2s^2$

$\sigma2s$

σ^*1s

$1s^2$ $1s^2$

$\sigma1s$

B-atom   po† B-atom.

Bond order $= \dfrac{6-4}{2} = 1$

* $\sigma1s < \sigma^*1s < \sigma2s < \sigma^*2s < \pi2px = \pi2py < \sigma2pz <$
$< \pi^*2px = \pi^*2py < \sigma^*2pz$
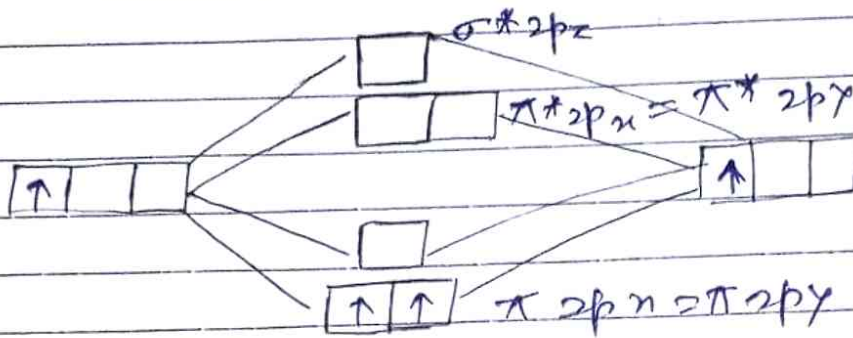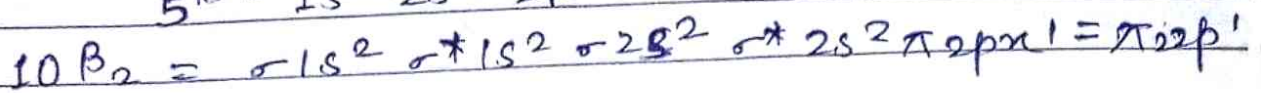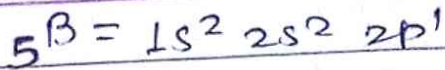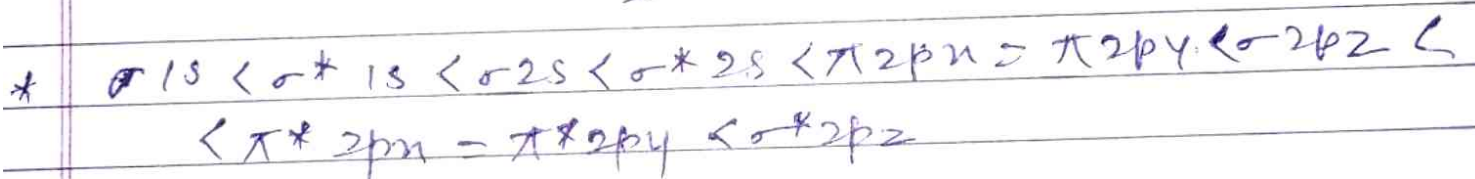
Draw a molecular orbital diagram for Li_2

$Li = 1s^2\ 2s^1$

$Li_2 = \sigma1s^2 \cdot \sigma^*1s^2\ \sigma2s^2$

$\boxed{7L}\ \sigma^* 2s$

$\boxed{1}$ $\boxed{1}$

$\boxed{7L}\ \sigma\ 2s$

$\boxed{7L}\ \sigma^* 1s$

$\boxed{7L}$ $\boxed{1L}$

$\boxed{7L}$ $\sigma\ 1s$

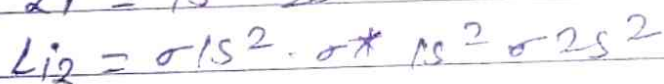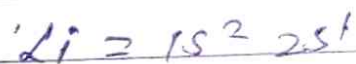di atom   Li-atom.
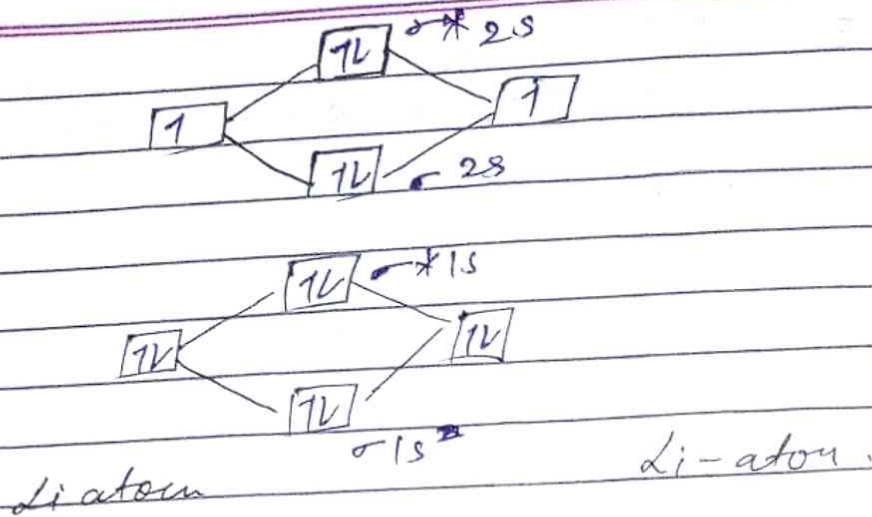
$$\text{Bond order} = \frac{4-2}{2} = 1$$

$*$ Draw the molecular diagram for N_2 molecule -

$$N = 1s^2\ 2s^2\ 2p^3$$
$$N_2 = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p^2 u$$
$$\sigma 2p^2 z$$

$\boxed{\ }\ \sigma^* 2pz$

$\boxed{\quad}$

$\boxed{1|1|1}$ $\sigma^* 2p x\ \sigma^* 2p y$ $\boxed{1|1|1}$
$2p^3$ $\boxed{7L}$ $2p^3$

$\boxed{7L|7L}\ \pi 2p^2 u = \pi 2p^2 y$

$\boxed{7L}\ \sigma^* 2s^2$

$\boxed{1L}$ $\boxed{7L}$

$\boxed{7L}\ \sigma 2s^2$

$\boxed{7L}\ \sigma^* 1s^2$

$\boxed{7L}$ $\boxed{7L}$ $\qquad$ Bond order $= \dfrac{10-4}{2} = 3$

$\boxed{7L}\ \sigma 1s^2$
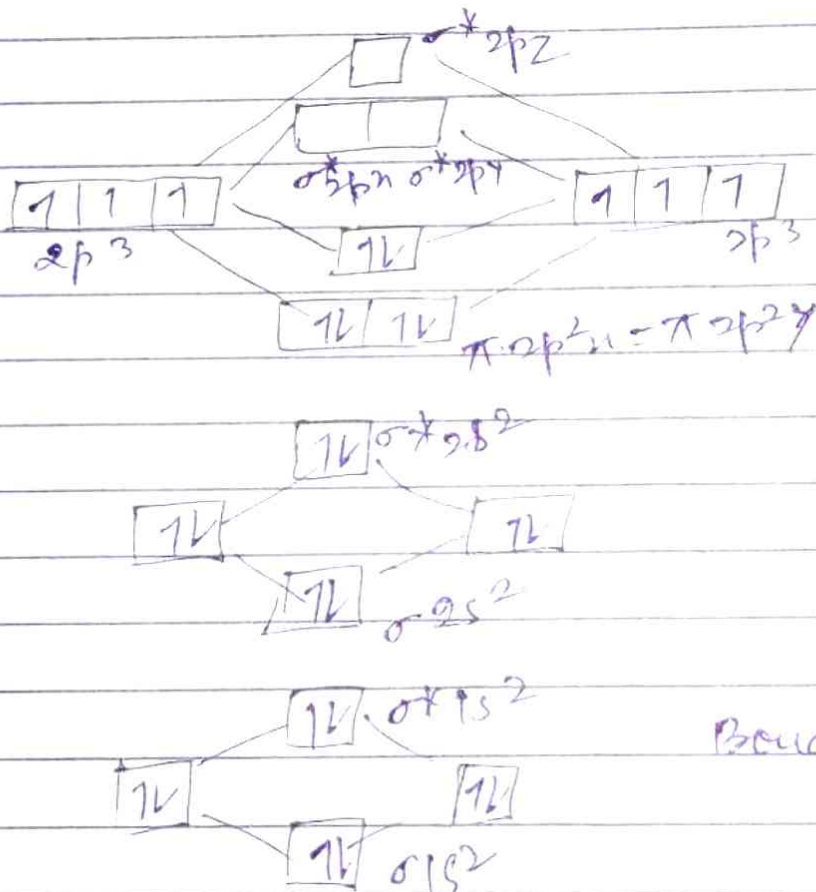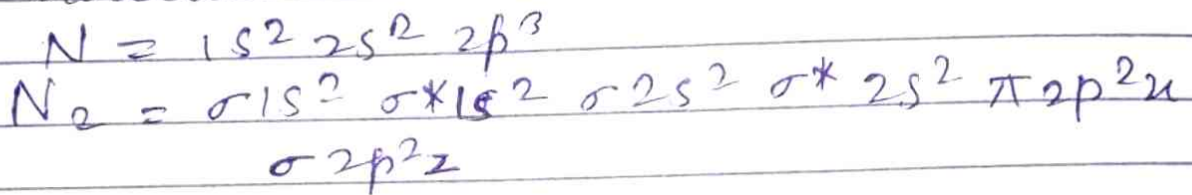
Shortcut for Bond order :-

(N₂, CO)	NO	O₂	O₂⁻	
14	15	16	17	18
3	2.5	2	1.5	1

Bond order

* when head to head or end to end overlapping then sigma bond formed

* when side to side overlapping then Pi (π) bond formed.

HOMO = Higher occupied molecular orbital
LUMO = Lower unoccupied molecular orbital.

For d-orbital :-

d_{xy} d_{yz} d_{zx}		$d_{x^2-y^2}$ d_{z^2}
⇓		⇓
Non-axial		axial
π-bond formed		δ (delta). σ bond formed.

for 14e⁻ and less than 14e⁻ :-
$\sigma^* 2p_z > \pi^* 2p_x = \pi^* 2p_y > \sigma 2p_z > \pi 2p_x = \pi 2p_y$

for greater than 14e⁻ :-
$\sigma^* 2p_z > \pi^* 2p_x = \pi^* 2p_y > \pi 2p_x = \pi 2p_y > \sigma 2p_z$

Shortcut for bond order

e^-	8	9	10	11	12	13	14
B.O	0.0	0.5	1.0	1.5	2	2.5	3

e^-	15	16	17	18	19	20
BO	2.5	2.0	1.5	1	0.5	0

Delocalisation → (movement in any area)
Localisation → (Particular area movement

Aromiticity :- An organic molecule containing a cyclic with delocalised $P\pi$ (e⁻) which confers out exceptional stability

Aromatic :- Burn with sooty flame. (Black flame)

(i) Compound should be cyclic

(ii) Compound should be planar (when sp^2 hybridise angle → 120°)

(iii) Compound should be conjugated (double or π bond at alternate position)

(iv) Compound must follow Huckel's Rule.
   $(4n+2)\pi e^-$ n {0,1,2,3}
                    ↳ non conjugated   negative nitrogen
   or

conditions for Aromaticity — If (-ve) charge participated in delocalisation so (-ve) charge considered with π·bond planar. structure.
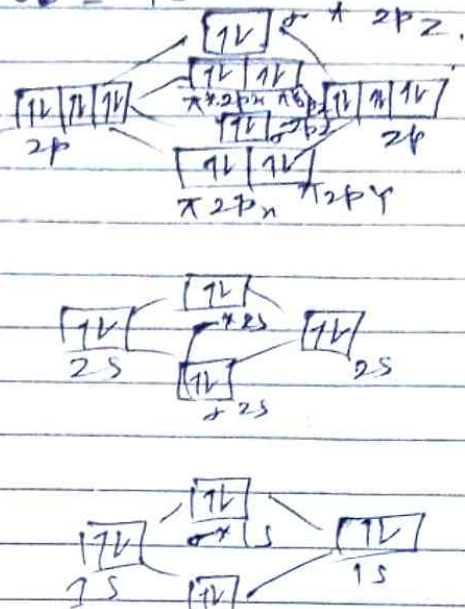
Mot diagram for homol

① $N_2^\oplus$:-
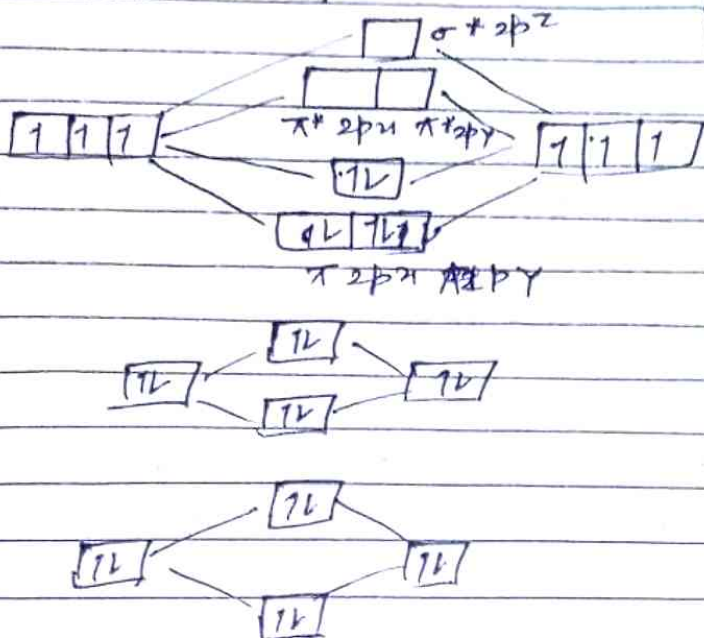
$N = 1S^2 \, 2S^2 \, 2p^3$

Bond order $= \dfrac{10-4}{2} = 3$

O^{2-}

$O_2^{2-} = 1S^2 \, 2S^2 \, 2p^6$

Bond order $= \dfrac{N_b - n_a}{2} : \dfrac{10-10}{2} = 0$

Postulates of molecular orbital theory

MOT was purposed by Hund and Mulliken in 1932 and it explains the formation of covalent bond in a better way.

(i) The atomic orbital overlapping to form new orbital called molecular orbital as a result atomic orbital use their individual identity.

(ii) Only those atomic orbital can combine to form molecular orbital which has compairable energy and proper orientation.

(iii) The no. of molecular orbital is equal to the no. of combining atomic orbital
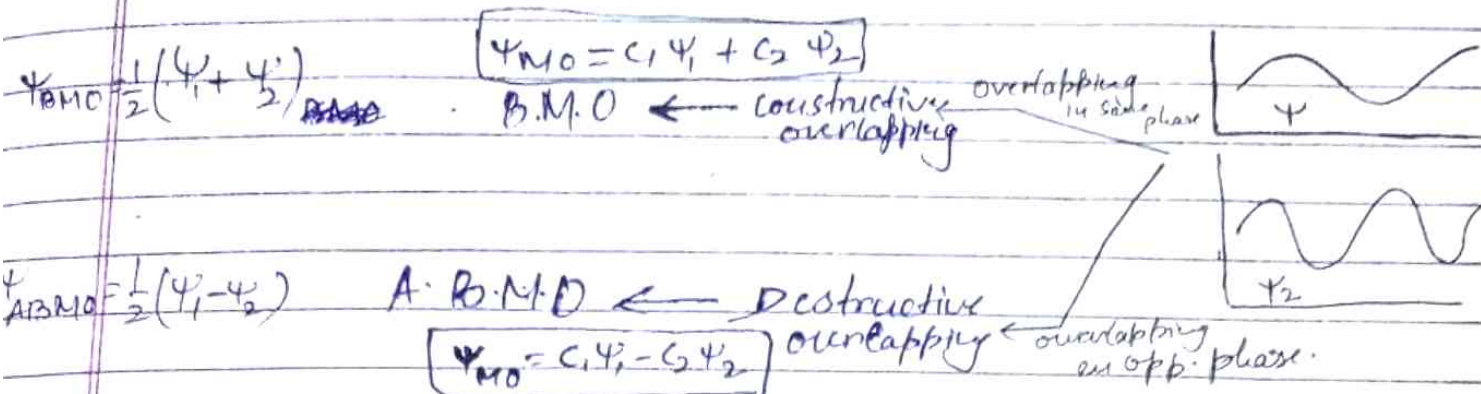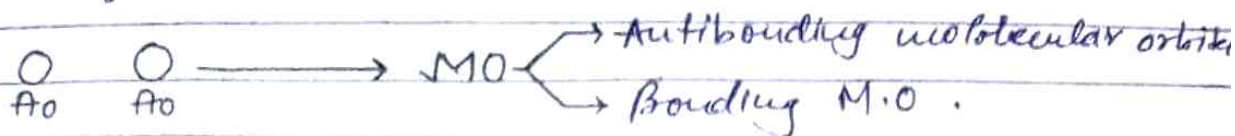
(iv) There are two types of molecular orbital are formed which are called as bonding molecular orbital and antibonding orbital.

(V) The bonding molecular orbital has Lower energy and greater stability.

(IV) Antibonding molecular orbital has higher energy and Lower stability

(VII) The filling of molecular orbital takes

place according to the same rule as goes for the ~~molecular~~ atomic orbital.

O   O ⟶ MO ⟨ → Antibonding molecular orbital
AO   AO   → Bonding M.O.

$\Psi_{BMO} = \frac{1}{2}(\Psi_1 + \Psi_2')$ ~~BMO~~ $\boxed{\Psi_{MO} = C_1\Psi_1 + C_2\Psi_2}$ B.M.O ⟵ constructive overlapping ⟵ overlapping in same phase

$\Psi_{ABMO} = \frac{1}{2}(\Psi_1 - \Psi_2)$ A.B.M.O ⟵ Destructive $\boxed{\Psi_{MO} = C_1\Psi_1 - C_2\Psi_2}$ overlapping ⟵ overlapping en opp. phase.

⭐ Schroudinger wave equation.

Schroudinger presented the wave properties of e^- in the form of an eqn called ~~schroudinga~~ wave equation.

Its soln basically gives information about the probability of e^- at different places around the nucleus in the atom.
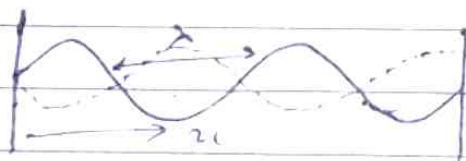
consider the motion of e^- as stationary wave

$$\Psi = A\sin\left(\frac{2\pi u}{\lambda}\right) - (I)$$

Now differenciate eqn (I) with respect to u

$$\frac{\delta\Psi}{\delta u} = A\,2\pi\cos\left(\frac{2\pi u}{\lambda}\right) - (II)$$

Further of diff eqn ② with respect to x

$$\frac{\delta^2 \psi}{\delta x^2} = A\left(\frac{2\pi}{\lambda}\right)^2 \cdot \sin\left(\frac{2\pi x}{\lambda}\right) \quad \text{—(iii)}$$

$$\frac{\delta^2 \psi}{dx^2} = \frac{-4\pi^2 \psi}{\lambda^2} \quad \text{—(iv)}$$

$$\frac{\delta^2 \psi}{\delta x^2} - \frac{4\pi^2 \psi}{\lambda} = 0 \quad \text{—} *$$

* Total energy

$$E = KE + PE$$
$$= \frac{1}{2} m^2 v$$
$$E - v = KE$$

$$\therefore \quad \lambda = \frac{h}{mv}$$

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

putting value of λ in eq $*$

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0$$

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{8\pi^2 m (mv^2)}{2h^2} \psi = 0$$

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{8\pi m}{h^2} (KE) \psi = 0$$

$$\boxed{\frac{\delta^2 \psi}{\delta x^2} + \frac{8\pi m}{h^2} (E-v) \psi = 0} \Rightarrow \text{Schroudinger wave eq.}$$

It is along the x-axis.

$$\boxed{\frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + \frac{\delta^2 \psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(E-v)\psi = 0}$$

∇ laplacian operator

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E-v)\psi = 0$$

$$\left\{ \nabla^2 + \frac{8\pi^2 m}{h^2}(E-v) \right\} \psi = 0$$

schrondinger wave equation.
in term of laplacian operator

$$\frac{8\pi^2 m}{h^2}(E-v)\psi = -\nabla^2 \psi$$

$$(E-v)\psi = \frac{-\nabla^2 h^2}{8\pi^2 m}\psi$$

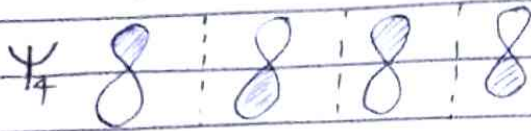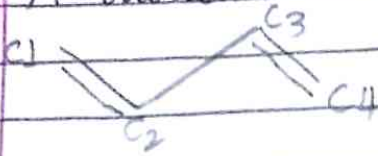$$E\psi = v\psi - \frac{\nabla^2 h^2}{8\pi^2 m}\psi$$

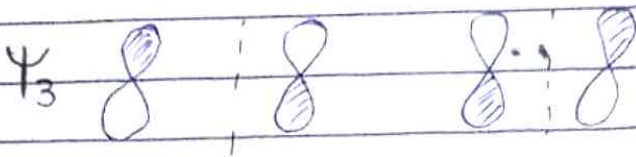$$E\psi = \underbrace{\left(v - \frac{\nabla^2 h^2}{8\pi^2 m} \right)}_{\hat{H}}\psi$$

$\Rightarrow$ $E\psi = \hat{H}\psi$ where $\hat{H}$ = Hamiltonian operator.

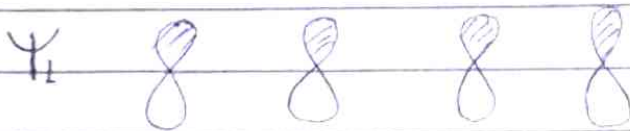# π molecular orbitals of 1,3 Butadiene :-

Ψ_4

Bonding = 0
Antibonding = 3
Nodes = 3

Ψ_3

Bonding = 1
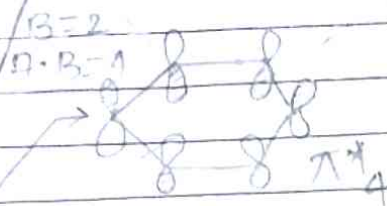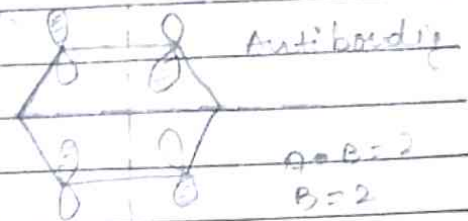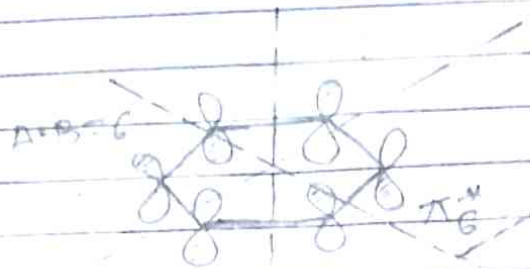Antibonding = 2
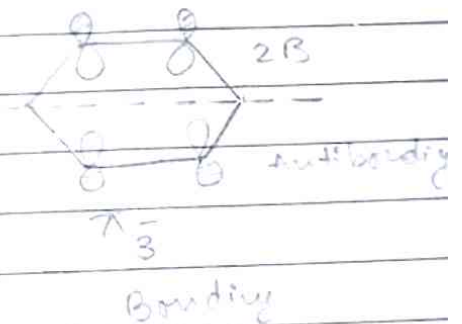Nodes = 2

Ψ_2
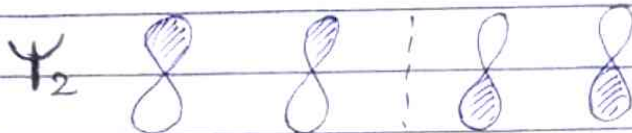
Bonding = 2
Antibonding = 1
Nodes = 1
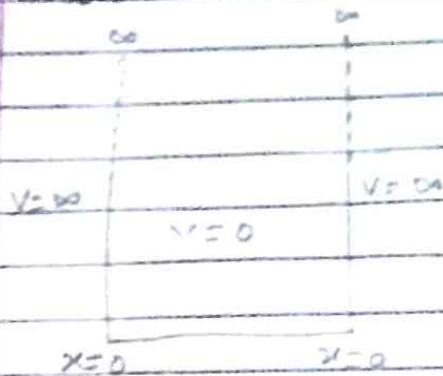
Ψ_1

Bonding = 3
Antibond = 0
Nodes = 0

π M.O of Benzene

A+B=6

π_6^*

Antibonding

A+B=3
B=2

B=2
A-B=1

π_4^*

Non-Bonding

B=4
A-B=2

2B

Antibonding

π_2

π_3^-

Bonding

Particle in 1-D box :—

$$V = \infty \qquad \qquad V = \infty$$
$$V = 0$$
$$x = 0 \qquad \qquad x = a$$

The height of the walls are taken as ∞ because we consider the particle lies within the walls.

We consider only one particle inside the box. So, there is no force. thus potential inside the box is zero.

ψ is a wave function which gives every information about the particle. so we have Schrodinger wave equation.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad \text{—①}$$

If we consider $V = \infty$

So, above eqn becomes:—

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - \infty)\psi = 0$$

On neglecting E in comparison to ∞

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(-\infty)\psi = c$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}\infty\psi = c$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{8\pi^2 m \psi}{h^2}$$

$$0 = \frac{8\pi^2 m}{h^2}\psi \qquad \boxed{\psi = 0}$$

13

This proves that the particle cannot go outside the box.

Now, for the particle within the box.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

If consider V=0

$$\frac{\partial^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-0)\psi = 0$$

$$\frac{\partial^2 \psi}{dx^2} + \left(\frac{8\pi^2 m E}{h^2}\right)\psi = 0$$

let $\frac{8\pi m E}{h^2} = k^2$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$$

$\psi = A\sin kx + B\cos kx$ (A & B are constant)

In the above eqⁿ is 2nd order diff. eqⁿ so, the general solution for the eqⁿ will be eq (11)

when $x=0$, $\psi = 0$

Putting the value of $x=0$ and $\psi = 0$ ~~in eq~~ ②

$\psi = 0$ in eqⁿ ⑪

$0 = A\sin k(0) + B\cos k(0)$

$0 = 0 + B$

$\boxed{B = 0}$

Now at $x = 0$, $\psi = 0$:-

Putting the value of $x = a$ and $\Psi = 0$ in eqn (ii)

$$0 = A \sin k(a) + B \cos k(a)$$
$$0 = A \sin ka + 0$$
$$\boxed{0 = A \sin ka}$$

$\rightarrow$ $\sin n\pi = \sin ka$

on compairing :-

$$n\pi = ka$$
$$\boxed{k = \frac{n\pi}{a}}$$

$$k^2 = \frac{8\pi m E}{h^2}$$

$$\frac{n^2 \pi}{a^2} = \frac{8\pi^2 m E}{h^2}$$

$$\boxed{E = \frac{n^2 h^2}{8ma^2}} \longleftarrow \text{(iv)}$$

$$\Psi = A \sin kx - \underset{\underset{0}{\downarrow}}{I B \cos kx}$$

$$\Psi = A \sin kx \quad \longrightarrow \text{(v)}$$

Putting value of k in eqn (v)

$$\boxed{\Psi = A \sin \left(\frac{n\pi x}{a} \right)} \longrightarrow \text{(vi)}$$

The value of constant a can be determined by using the normalisation condⁿ.

$\Rightarrow$ $$\boxed{\int \Psi \Psi' dx = 1}$$

$$\int A \sin \left(\frac{n\pi x}{a} \right) A \sin \left(\frac{n\pi x}{a} \right) dx.$$

$$\int_{0}^{a} A \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$\underbrace{A^2 \int_{0}^{a} \sin^2\left(\frac{n\pi x}{a}\right) dx}_{\frac{a}{2}} = 1$$
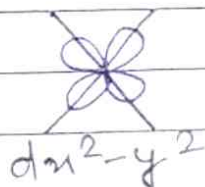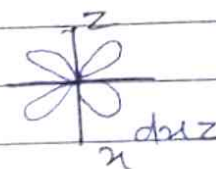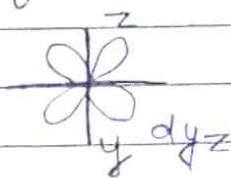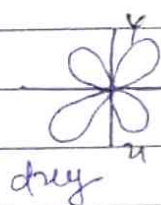
$$A^2 \frac{a}{2} = 1$$

$$\Rightarrow \boxed{A = \sqrt{\frac{2}{a}}}$$

$$\longrightarrow \Psi = A \sin kx$$

$$\Rightarrow \boxed{\Psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)}$$

CFT (Crystal Field Theory) :-

* Orientation of d- orbitals

d_{xy}

d_{yz}

d_{xz}

$d_{x^2-y^2}$

d_{z^2}
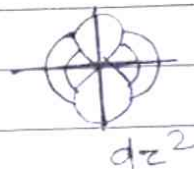
CFS for coordination number $\gg$ 6

CFS For square planar

$d_{x^2-y^2}$

$\Delta_{sq.}$

$d_{x^2y^2}$

$d_{x^2y^2}$ d_{z^2}

d_{z^2}

d_{xy}

exited d-level

d_{x^2}

d_{z^2}

Free metal
d-orbitals.

d_{yz} d_{zx}

d_{y_z} d_{zx}
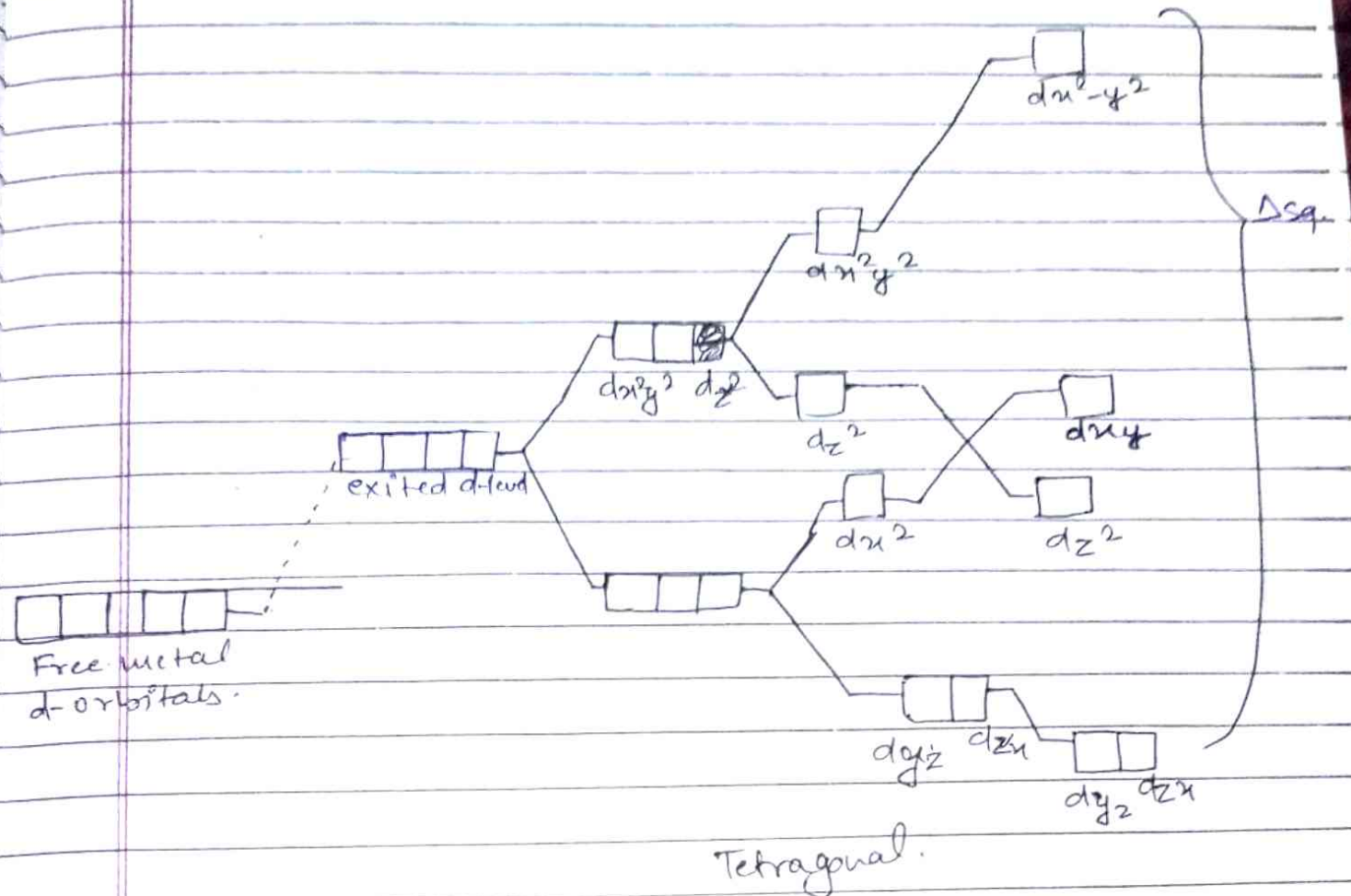
Tetragonal.

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* Main Points of CFT (crystal field theory):-
① CFT Considered the transition metal ion and
the ligands as point charges and the bonding
b/w them is purely ionic (electrostatics).

② If the ligands with the metal ions then the
intraction of ligands with the metal ion will
be similar to the intraction b/w two opposite
point charges.

In a free metal atom or ion all the five d-orbitals are degenerate in nature i.e they have same energy when the metal ion is surrounded by the ligands for the complex formation even due to electrostatic repulsion exerted by the ligands, the degeneracy of the d-orbitals is lost and it splits into two groups of different energy. They type of splitting of d-orbitals into two groups of diff. energy is k/a Crystal field splitting.

Crystal field splitting in Octahedral complexes.

In octahedral geometry all the six ligands are present at the axis. When the metal ion is surrounded by the ligands Octahedrally than the orbitals having orientation along the axis expriences greater repultion form the ligand while the d-orbitals having orientation in b/w the axis expriences less repultion from the ligands.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which lies directly in the path of ligand exprience greater repultion so that their energy increases whereas the orbitals d_{xy}, d_{yz} and d_{xz} do not lie directly in the path of ligand exprience less

repulsion due to which their energy is lower. Hence, the d-orbitals splits into 2 group of different energy which is termed as the t_{2g} & e_g level is termed as crystal field statoth stabilization energy which is indicate by Δ_0 and the magnitude of Δ_0 depends upon the nature of ligands. The CFSE is also measured in terms of Dq.
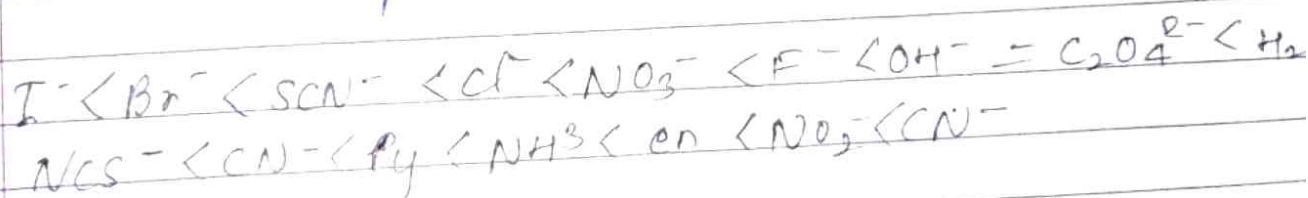
* **Strong field & weak field ligands:-**
The ligands which cause greater CF spliting of d-orde orbitals give rise to larger value of Δ_0 are k/a strong field ligands.
The ligands which cause smaller CF spliting of d-orbitals give rise to lower value of Δ_0 are k/a weak field ligands.

Spectrochemical series :-
The spliting power of diff. ligands is experimentally determined and the ligands are arranged in increasing order of increasing power so that a series is obtained which is k/a spectrochemical series.

$$I^- < Br^- < SCN^- < Cl^- < NO_3^- < F^- < OH^- = C_2O_4^{2-} < H_2$$
$$NCS^- < CN^- < Py < NH^3 < en < NO_2^- < CN^-$$

Distribution of e^- in t_{2g} and e_g lev
① If the ligands are weakfield ligands then the value of Δ_0 will be smal so the filling of e^- occurs in

a way that all the t_{2g} & e_g orbitals are 1st signally field and then often pairing start.

② In such cases the metal ion consists greater no. of unpaired e^-. so that it has larger value of spin quantum no. and so such complexes are 3did to be **high spin complexes.**

③ If the ligands are strong field ligands than the value of Δ_0 will be larger and so the filling of e^- occurs in such a way e^- are first paired in t_{2g} orbital & that then e_g orbitals are filled thus, such complexes have min. no. of unpaired e^- and so they have less value of spin quantum no. and such complexes are said to be **Low spin complexes.**

* CF splitting in tetrahedral complexes :-
The tetrahedral geometry can be explained by considering a tetrahedron placed inside a cube such that different axis pass through the face of the cube. In such case the atom is present at the centre of the cube by the four ligands occupy the alternate corner of the cube.

The orbitals d_{xy}, d_{yz} and d_{zx} lies directly in the path of the ligands so that these orbitals experiences greater repulsion from the ligands and so the energy of these orbital increased increases as compared to excited d-level. The orbitals $d_{x^2-y^2}$ and d_{z^2} do not lie directly in the path of ligand and so they experiences less repulsion from the ligand and hence the energy of these orbital is lowered has compared to excited d-level. Hence, under the influence of tetrahydral excited d-level splits into two groups.

where the groups consists of d_{xy}, d_{yz} and d_x is said to be t_2 level while the other group consist of $d_{x^2-y^2}$ and d_{z^2} is said to be e-level. and the energy diff. b/w these two levels is said to be tetrahedral spliting energy

Formula for calculating CFSE

In O_h complexes:-

$$\Delta_0 = (-4p + 6q)Dq$$

or

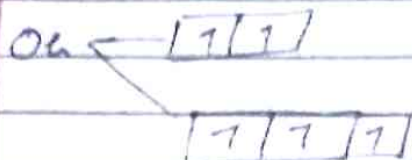$$\Delta_0 = (-0.4p + 0.6q)\Delta_0$$

In T_d complexes

$$\Delta_{Td} = (-6p + 4q)Dq$$

or

$$\Delta_{Td} = (-0.6p + 0.4q)\Delta_{Td}$$

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Calculate CFSE for d^5 configuration in Octahedral complexes of weak field as well as strong field ligands.
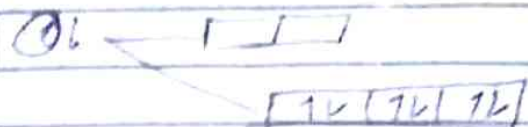
weak field	strong field
O_h ⟨ [↑][↑] [↑][↑][↑]	O_h ⟨ [ ][ ][ ] [↑↓][↑↓][↑↓]
$\Rightarrow -0.4 \times 3 + 0.6 \times 2$ $= -1.2 + 1.2$ $\boxed{\Delta_0 = 0}$	$\Rightarrow -0.4 \times 5 + 0.6 \times 0$ $\Rightarrow -2.0 + 0$ $\Rightarrow \boxed{\Delta_0 = -2.0}$

Calculate CFSE for d^3 configuration in octahedral complexes of weak field as well as strong field ligand.
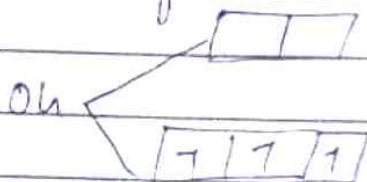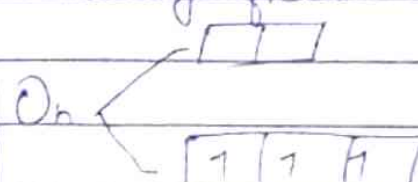
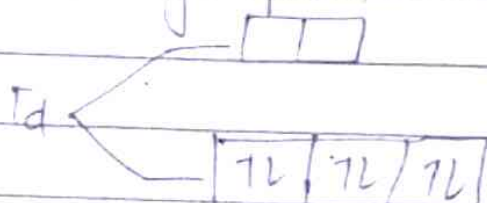| weak field	strong field
O_h ⟨ [ ][ ] [↑][↑][↑]	O_h ⟨ [ ][ ] [↑][↑][↑]
$\Delta_0 = -0.4 \times 3 + 0.6 \times 0$ $= -1.2 + 0$ $= -1.2$	$\Delta_0 = -0.4 \times 3 + 0.6 \times 0$ $= -1.2 + 0$ $\underline{\Delta_0 = -1.2}$

Calculate CFSE for d^6 in Td complex:-

weak field :-	Strong field
Td ⟨ [↑][↑] [↑↓][↑][↑]	Td ⟨ [ ][ ] [↑↓][↑↓][↑↓]
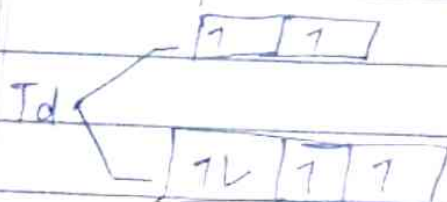
$$\Delta_{Td} = -0.6 \times 4 + 0.4 \times 2$$
$$= -2.4 + 0.8$$
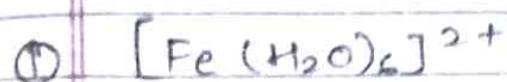$$\boxed{\Delta_{Td} = -1.6}$$

$$\Delta_{Td} = -0.6 \times 6 + 0.4 \times 0$$
$$= -3.6 + 0$$
$$\boxed{\Delta_{Td} = -3.6}$$

Ex:- ① $[Fe(H_2O)_6]^{2+}$ ∘   ② $[Co(CN)_6]^{3-}$

① $[Fe(H_2O)_6]^{2+}$

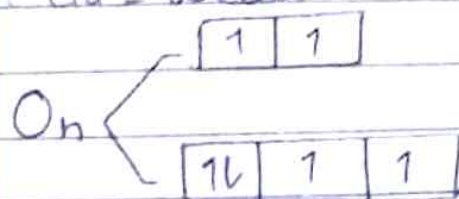→ $x + 2 = 0$

$x = +2$

$Fe^{2+} = 3d^6$

Field = weak

$$O_h \begin{cases} \boxed{1 \quad 1} \\ \\ \boxed{1\downarrow \quad 1 \quad 1} \end{cases}$$

$\Delta_0 = 0.4 \times 4 - 0.6 \times 2$

$[Co(CN)_6]^{-3}$

$x - 3 = 0$

$x = 3$