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1897 : J J Thomson → Electrons have -ve charge

1899 : RA millikan → $e^- = 1.6 \times 10^{-19} C$
$m_{e^-} = 9.1 \times 10^{-31} Kg$

1911 : Rutherford → Established the simplest nuclear model of atom.

1913 : Bohr → Bohr Theorem (N. Prize)

1913 : Moseley → Atomic No.

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Saathi

Defects of Rutherford model

(i) By gradual Emission of 'e' moves towards the nucleus and finally combines with it. So, all the atoms will be unstable.

(2) For continuous radiation of 'e' by the rotating 'e', continuous spectrum is expected discontinuous.

Bohr's Theory

concept → K, L, M, N orbits

Postulates

(i) $mvr = \frac{nh}{2\pi}$

↳ angular momentum

(2) Stationary orbit concept. (No radiation)

Page No.

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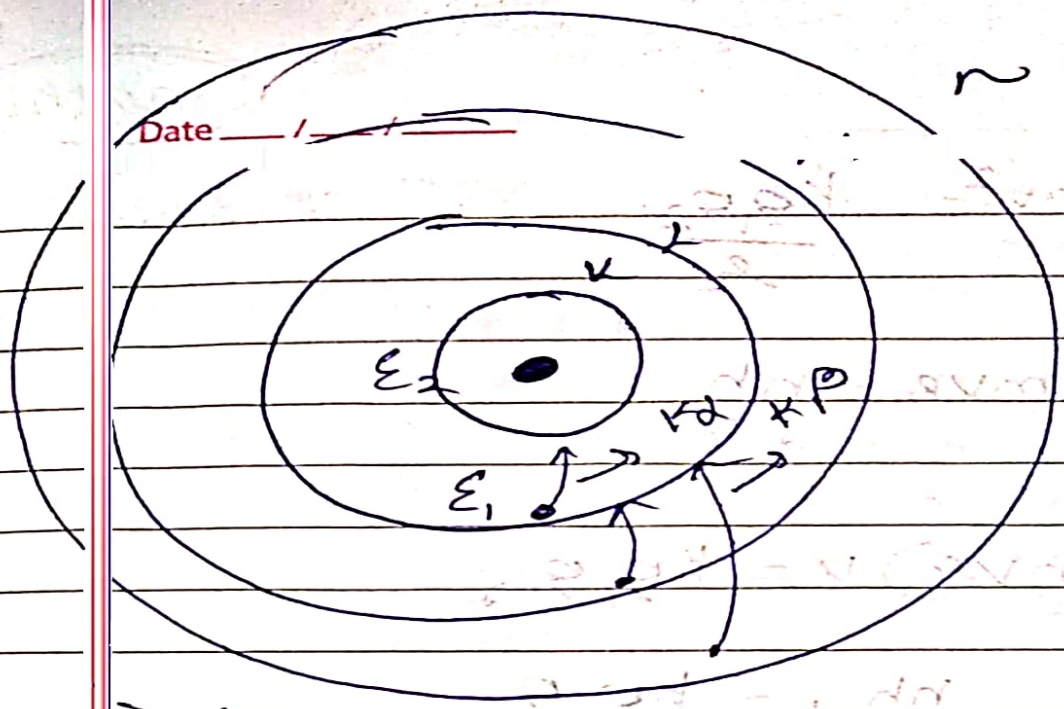
$|E = h\nu|$

Planck's Quantum Theory

Date ___/___/___

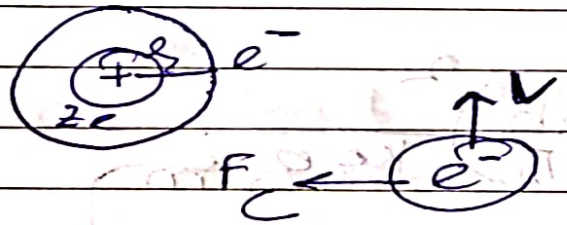


$\lambda = 0.1 A^{\circ} - 10$

'E' is emitted when 'e' moves from one stationary orbit of higher energy to one stationary orbit of lower energy

$E_1 - E_2 \propto \nu$ → frequency

$= h\nu$



$$F_c = \frac{mv^2}{r} = ma$$

$$\frac{mv^2}{r} = \frac{kq_1q_2}{r^2}$$

$$mv^2 = \frac{kq_1q_2}{r}$$

$$mvr = \frac{nh}{2\pi}$$

Page No.

Date ___/___/___

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$$mv^2 = \frac{kq_1q_2}{r}$$

$$mvr = \frac{nh}{2\pi}$$

$$(mvr)v = kq_1q_2$$

$$\frac{nh}{2\pi}v = kq_1q_2$$

$$\boxed{v = \left(\frac{2\pi}{nh}\right)kq_1q_2}$$

$$kq_1q_2\, m\left(\frac{2\pi}{nh}\right)r = \frac{nh}{2\pi}$$

$$r = \left(\frac{nh}{2\pi}\right)^2 \frac{1}{kq_1q_2m}$$

$$\boxed{r = \frac{(h)^2}{(2\pi)^2 kq_1q_2m}\, n^2}$$

$$q_1 = Ze$$

$$q_2 = e$$

Page No. ___

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$$\cancel{E = \left[\frac{-13.6 Z}{n^2}\right]}$$

Date ___/___/___

$$E = U + KE$$

$$KE = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\frac{2\pi}{nh}\right)^2 k^2 Z^2 e^4$$

$$U = -\frac{k q_1 q_2}{r} = -\frac{k Z e^2}{r} = \left(\frac{k Z e^2}{nh}\right) 2\pi m v$$

$$= \left(\frac{k Z e^2}{nh}\right) 2\pi m \left(\frac{2\pi}{nh}\right) k q_1 q_2$$

$$= U = \frac{-k^2 Z^2 e^4 (2\pi)^2 m}{n^2 h^2}$$

$$= -\frac{1}{2} KE$$

Work done in bringing the e^- from infinite to its position of nth Bohr orbit.

$$E = U + KE = -\frac{1}{2} KE$$

$$= \left(-\frac{m Z^2 e^4}{8 \varepsilon_0^2 n^2 h^2}\right) \text{(S.I.)}$$

→ Ionisation potential.

Date ___ / ___ / ___

Saatfull

Explanation of H spectrum Bohr

If an e^- jumps ~~for~~ from one orbit to another orbit
(n_i) (n_f)

$$\Delta E = \frac{m z^2 e^4}{8 \varepsilon_0^2 h^2} \left[-\frac{1}{n_f^2} + \frac{1}{n_i^2} \right]$$

$$E = h\nu = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \bar{\nu} = \frac{m e^4}{8 \varepsilon_0^2 c h^3} z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\boxed{\nu = \frac{c}{\lambda}} = c\bar{\nu}$$

→ R (Rydberg Const.)

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$n_f = 1$ $n_i = 2, 3, 4 \rightarrow$ Lyman series (UV)

$n_f = 2$ $n_i = 3, 4, 5 \rightarrow$ Balmer series (visible)

$n_f = 3$ $n_i = 4, 5, 6 \rightarrow$ Paschen

$n_f = 4$ $n_i = 5, 6, 7 \rightarrow$ Brackett

$n_f = 5$ $n_i = 6, 7, 8 \rightarrow$ Pfund

$n_f = 6$ $n_i = 7, 8, 9 \rightarrow$ Humphrey

$\rightarrow$ GP

discontinuous spectra

It cannot explain Stark & zeeman effect

Page No.

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Date ___/___/___

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Bohr's theory → Nucleus Remains stationary except for rotating its own axis.

True if ⇒

$\boxed{\text{Mass of the nucleus is infinite.}}$

Nucleus is always vibrating about the centre of gravity.

So, the mass of the 'e' will be reduced.

Reduced mass $(\mu) = \boxed{\frac{Mm}{M+m}}$

M = Mass of nucleus

m = " " electron

$$\boxed{R = \frac{e^4}{8\varepsilon_0^2 ch^3}\left(\frac{Mm}{M+m}\right)}$$

$$\frac{Mm}{M+m} = \frac{1}{\frac{1}{M}+\frac{1}{m}} = \frac{M+m}{2}$$

$$\frac{2e+1}{(2+1)^4 e}$$

Page No.

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Date ___/___/___

$$\frac{M+m}{2} \leq \frac{2Mm}{M+m}$$

$$\frac{1}{M} + \frac{1}{m}$$

$$\cancel{\frac{Mm}{M+m} < (Mm)^{1/2}}$$

$$\sqrt{ze} < 1$$

$$\frac{zm_p * m_e}{m_e + zm_p}$$

$$\cancel{(m_p z m_e)} \quad m_p + m_e < 1$$

$$\frac{m_p + m_e}{2} \geq (m_p m_e)^{1/2}$$

$$\cancel{m_p +} \quad (m_p m_e)^{1/2} < m_p m_e$$

$$\therefore m_p + m_e > 2 m_p m_e$$

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right) < \frac{R_1 R_2}{}$$

$$\frac{R_1 R_2}{R_1 + R_2} < R_1 R_2$$

$$\frac{z m_p m_e}{z m_p + m_e} < z m_p, m_e$$

Page No. ____

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Date ___/___/___

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$$E = 13.6\, Z^2/n^2 \text{ eV}$$
$$E = 2.18 \times 10^{-18}\, Z^2/n^2 \text{ J}$$

Quantum Numbers

The minimum characteristics by which an electron can be completely identified in an atom are called quantum no(s).

(1) Principle quantum number (n)
(2) Azimuthal quantum number (l)
or
subsidiary quantum number
(3) magnetic quantum number (m)
(4) spin quantum number (s)

n → Energy & size of electron orbit.

In Bohr's orbit

K	L	M	N	...
n = 1	2	3	4	...

→ he says orbits are circular.

Page No.

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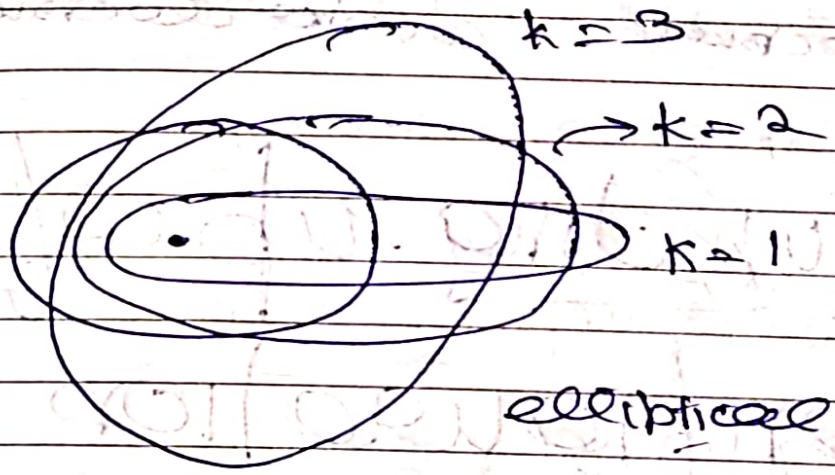
Date ___/___/___

2) $l \rightarrow$ shape of the 'l' orbit.

This was proposed by Sommerfield. Some of the orbits are elliptical.

The shape of the ellipse $= \frac{\text{L. of M.A.}}{\text{L. of Minor axis}} = \frac{n}{k}$



elliptical orbits

$\frac{4}{1}, \frac{4}{2}, \frac{4}{3}$

Orbits → orbitals

$n=1$, $l=0$ (s)

$n=2$, $l=0$ (s), 1 (p)

n, $l = 0, 1, 2, \ldots n-1$

3) $m \rightarrow$ orientation of l orbital in the n orbit w.r.t. external magnetic field given by (inde)

Value of $m \Rightarrow -l$ to $+l$ includes 0 (zero)

$m \rightarrow (2l+1)$

Page No.

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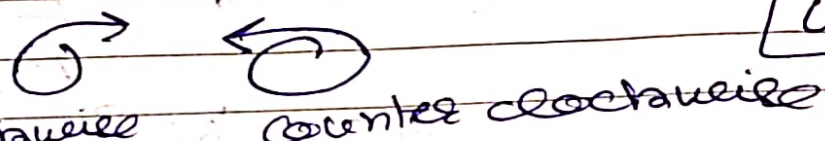
Date ___/___/___

$l = 3$, $m = 0, \pm 1, \pm 2, \pm 3$

4) s → Spin of the e^- in an orbital

Same cloud sm



Building up of Electron Configuration of an atom

With increase in atomic number, electronic configuration of an atom develop based on 3 principles

(1) Aufbau Principle
(2) Pauli's Exclusion principle
(3) Hund's rule.

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not a scientist

Date / /

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Aufbau Principle

→ german (building up/construction)

The orbital are filled up with the 'E' in order of increasing E. that means orbitals of lowest E will be filled up first.

$\boxed{n+l \text{ rule}}$

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f 5g
6s 6p 6d 6f 6g
7s

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s

Lower (n+l) value will have lower E.

if (n+l) value is same then lower n value will have lower energy.

Page No.

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1 + 3 + 5 + 7

Date ___/___/___

Pauli Exclusion Princ

No two e^-(s) in an atom can have all the 4 QN same.

Hund's Rule of max. multiplic

'e' enter into the degenerate atomic orbitals in such a way as to contain max no. of unpaired 'e' with their spins parallel.

p_x	p_y	p_z
↑	↑	↑

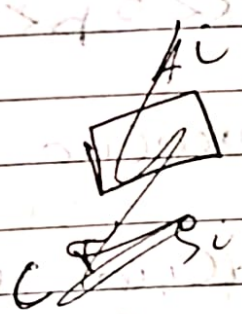
✓

p_x	p_y	p_z
↑	↑	↓

✗

p_x	p_y	p_z
↑↓	↑	

✗



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Chemical Bonding

Combination of atoms.

Covalent bonding / co-ordinate covalent bonding (coordination compound)

Ionic bond (NaCl)

A covalent bond is the bond established b/w two atoms by overlap of their atomic orbitals. Each containing one unpaired e^- of opp. spin.

Covalent bonds are directional in nature.

$O \rightarrow 2s^2\ 2p^4$ $\quad$ $2s^2$ [↑↓] $\quad$ $2p^4$ [↑↓] [↑] [↑]

$H \rightarrow 1s^1$ $\quad$ [↑] $\quad$ s $\quad$ px py pz

↓ s

1 unpaired e^- $\quad$ 2 unpaired e^-(s)

So, 2p orbitals of O atom overlap with two 1s orbitals of H atom and forms two O-H bonds.

Page No.

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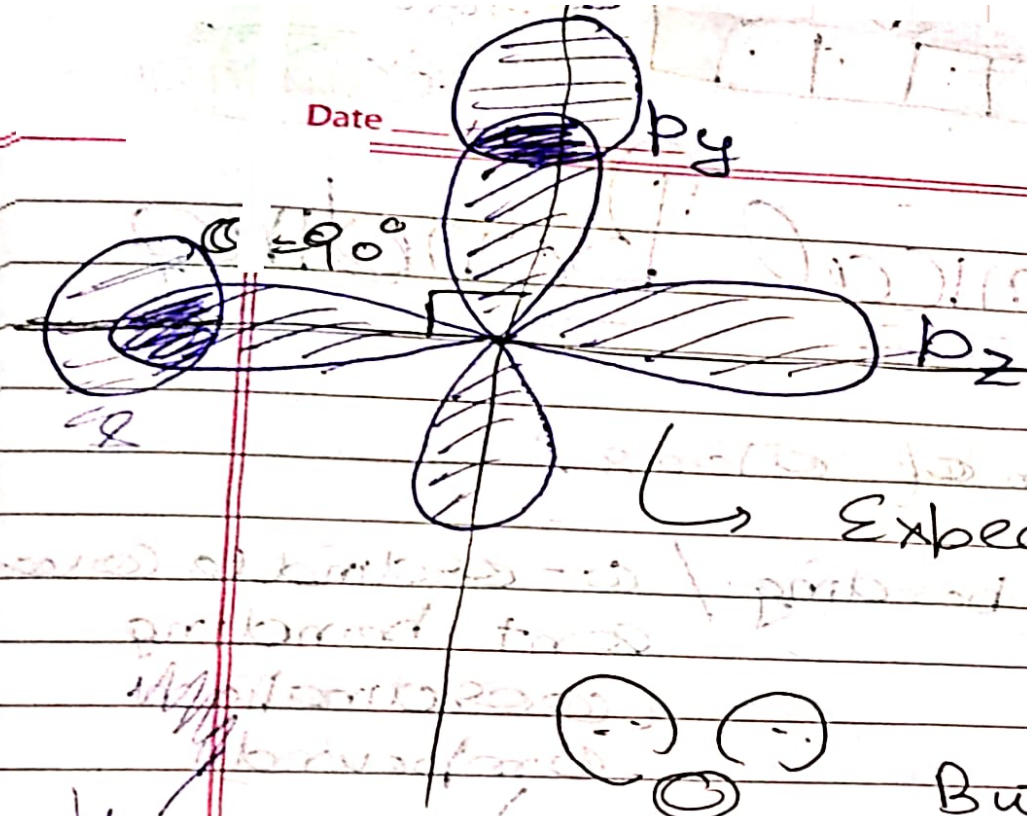
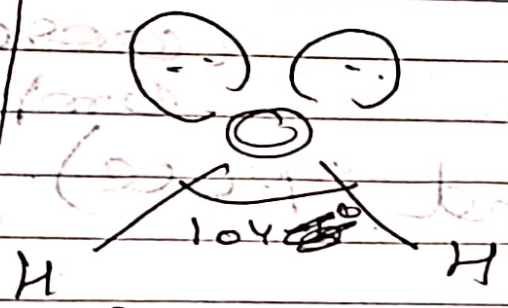


Expected θ = 90°



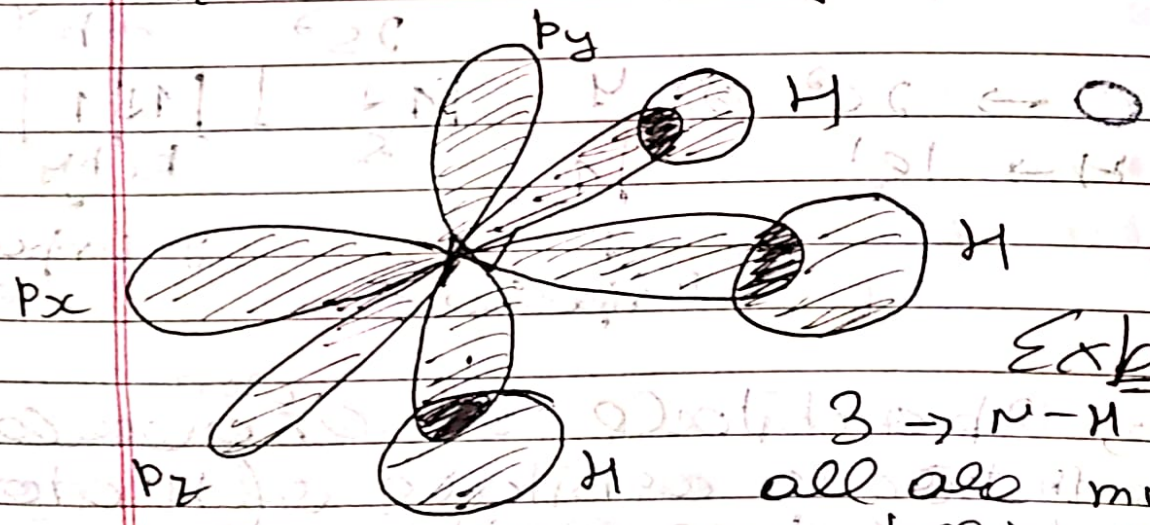
But measured θ = 104.5°

Bent or V shape

NH_3 $2s^2$ $2p^3$

N → [↑↓] [↑ | ↑ | ↑]

H → $1s^1$ [↑]



Expected

3 → N–H bonds all are mutually perp.

Page No.

Date ___/___/___

measured

$\theta = 107.3^\circ$

So, final geometry is determined by other factors.

1. Hybridization

2. Mutual repulsion of bonding e^- cloud.

3. Influence of lone pair or unshared e^-(s) on bonding e^-(s)

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Unpairing & Promotion of e^- Prior to bond formation (V.B.T.)

Ground state

Be

[↑↓]	[↑↓]	[ ] [ ] [ ]
$1s^2$	$2s^2$	$2p$

↓

Valence shell

Excited state

[↑↓]	[↑]	[↑] [ ] [ ]
$1s^2$	$2s^1$	$2p^1$

↓

valence shell

Ground state

B $1s^2$ $2s^2$ $2p^1$

G.S. [↑↓] [↑↓] [↑] [ ] [ ]

Page No. ____

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F

Date ___/___/___

$1s^2$	$2s^2$			
↑↓	↑	↑	↑	

E.S.

No. of bonds formed by an atom = no. of unpaired e⁻'s

Be → 2 unpaired e → 2 bond
B → 3 " " → 3 "
C → 4 " " → 4 "

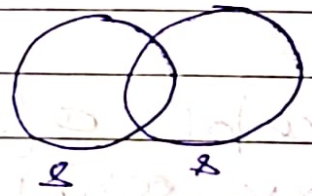
Why hybridization is necessary?

	2s	2p		
C (G.S.)	↑↓	↑	↑	
C (E.S.)	↑	↑	↑	↑

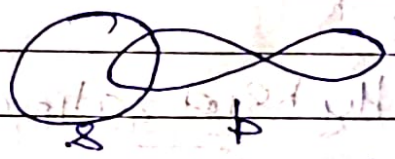
2s, 1s → 1 C–H bond

2p 1s → 3 C–H bond

Overlap & bond strength

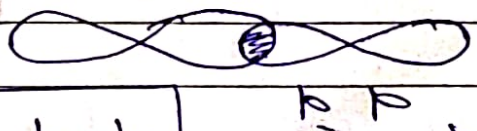


Non-directional



partial directional

Bonding strength



s–s < s–p < p–p

Directional

Page No.

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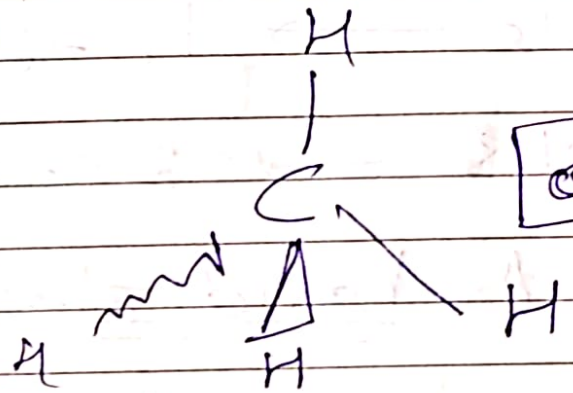
Date ___ / ___ / Stability

H_2O		HF	
H_2S		H–Cl	
H_2Se		H–Br	
H_2Te	↓ decreases	H–I	↓ obv

Down the table valence shell orbital become larger in size so, the overlap becomes poorer so stability decreases.

It is found that all C–H bonds have same bond lengths.



$\boxed{\theta = 109.28^\circ}$

Hybridization → Concept of mix of atomic orbitals (s of C with 3p of before overlap)

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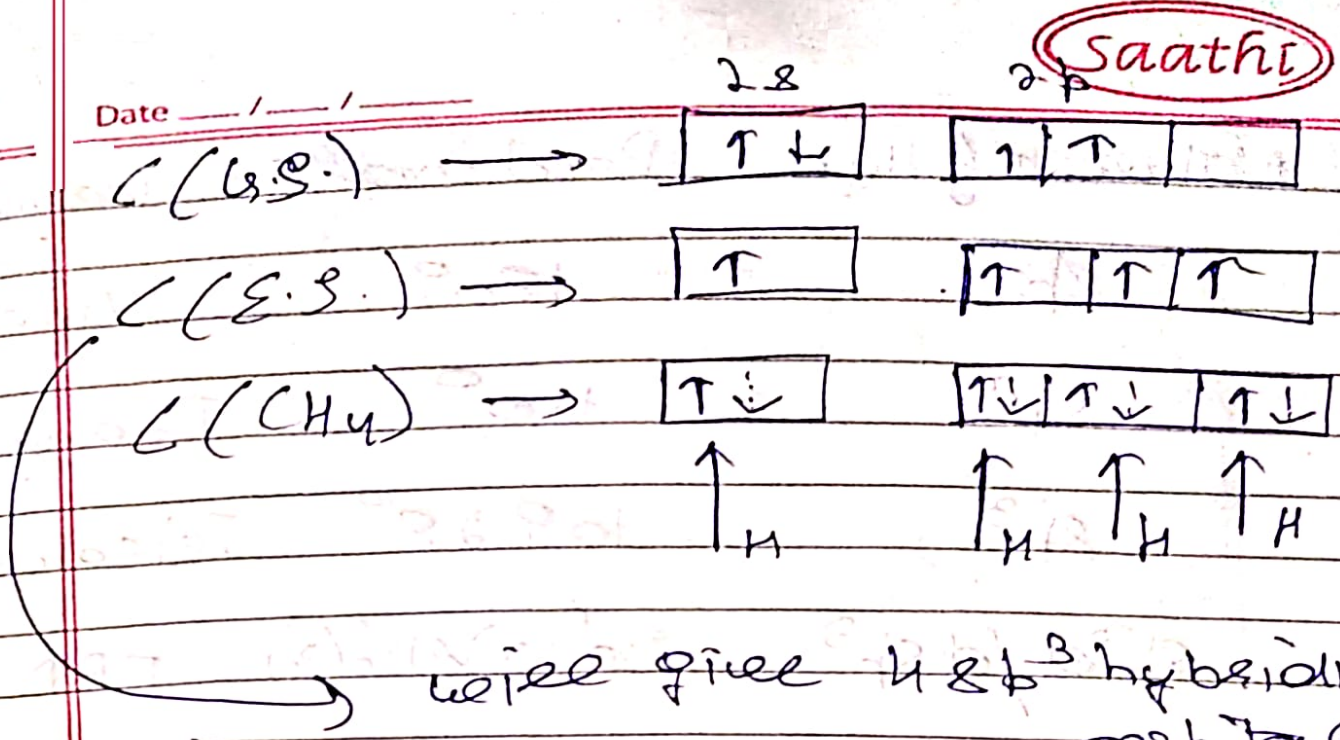

will give 4 sp^3 hybridised orbitals.

Hybridization :-

The concept of mixing of definite no. of atomic orbitals of comparable shapes & E in the valence shell of an atom just before ~~containing~~ ~~with~~ combining with other atoms to produce the same no. of atomic orbitals having definite orientation in space surrounding the central atom is called hybridization.

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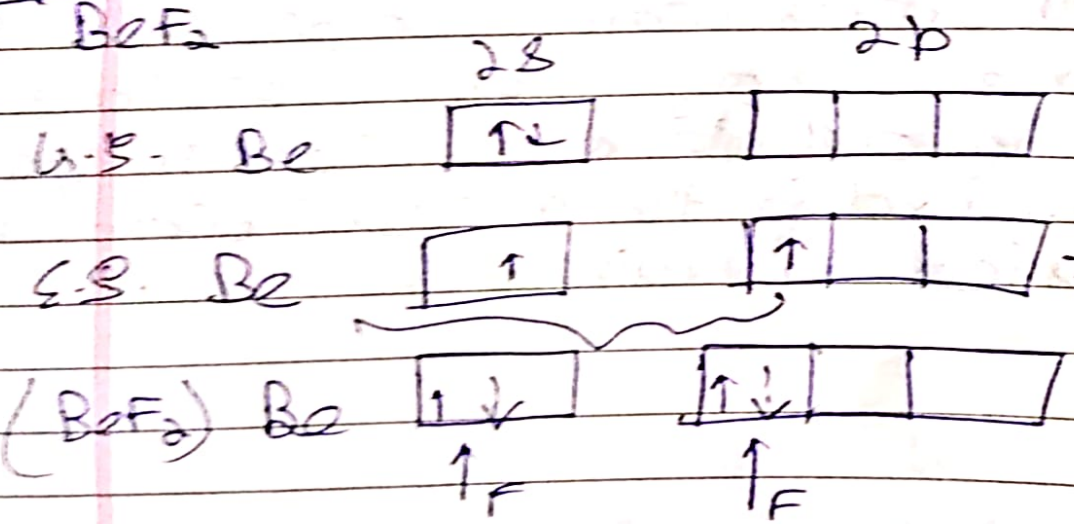
Nature of Hyb.	Bond angle	Geometry
sp	180°	Linear
sp^2	120°	Triangular
sp^3	109.28°	Tetrahedral
sp^3d / dsp^3	$90^\circ(2), 120^\circ(3)$	TBP
sp^2d / dsp^2	90°	Sq. pla
sp^3d^2 / d^2sp^3	90°	Octahed

Eg. 15)

BeF_2



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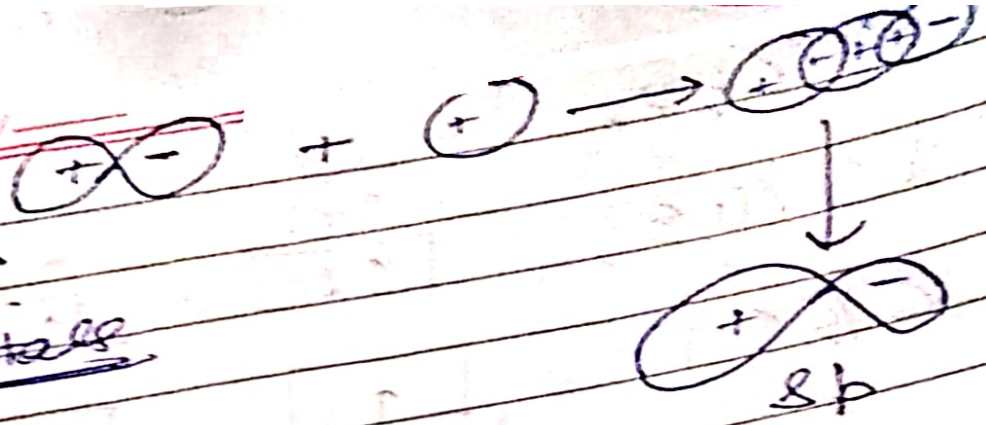
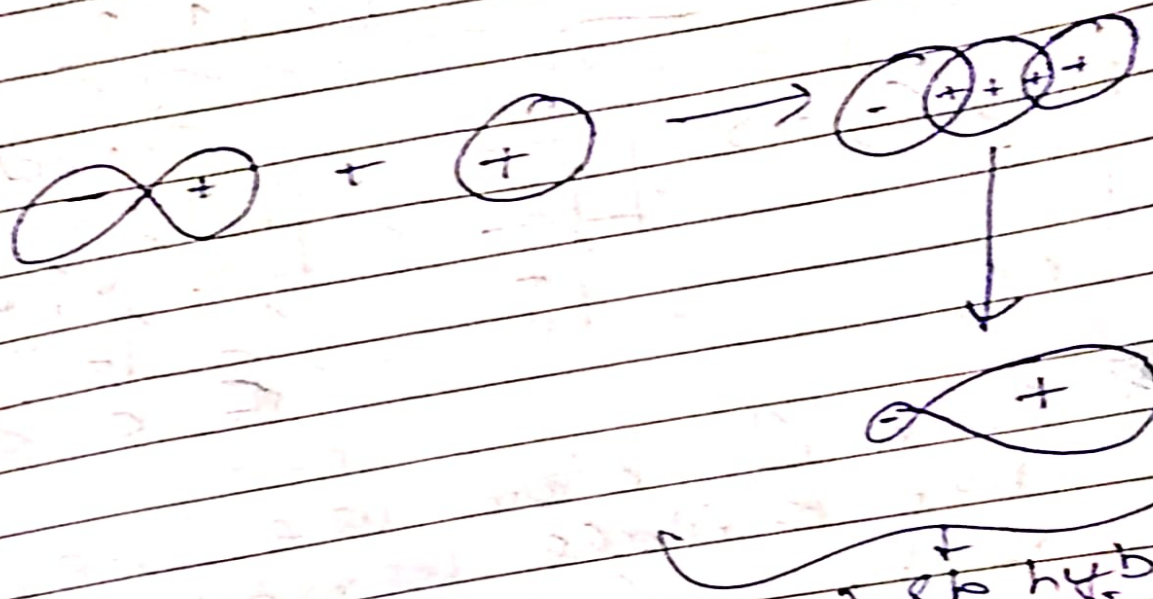
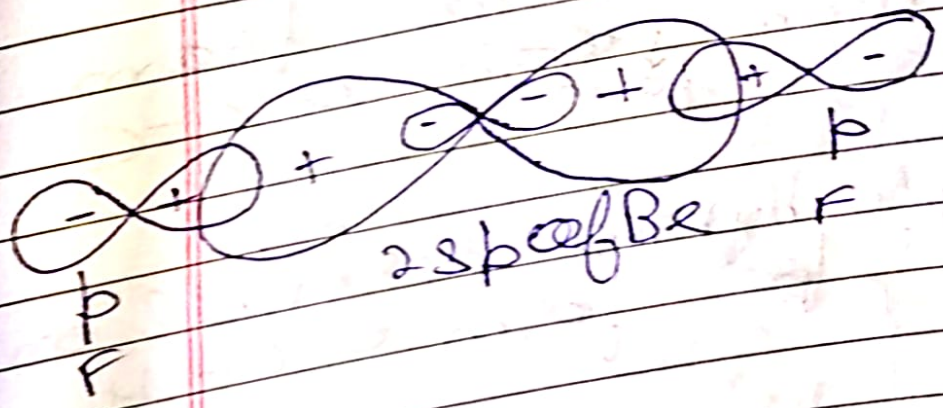
one s
one p → sp hyb. orbitals





2 sp hyb. orbitals



F—Be—F

Page No.

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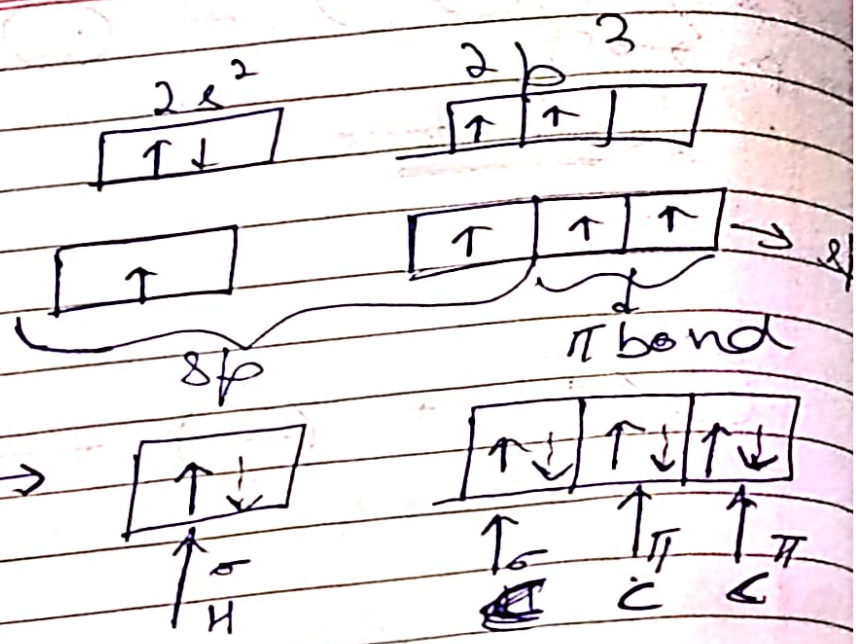
H — C ≡ C

Date ___/___/___

C_2H_2



☆ Each 'C' atom uses 2 sp hyb. orbitals formed by 1 2s 1 2p.

☆ 1 sp hyb. orbital from each 'C' atom form a C–C bond.

☆ Other 'sp' hybrid orbitals of each 'C' form a C–H σ bond.

☆ A linear arrangement is obtained.

Page No.

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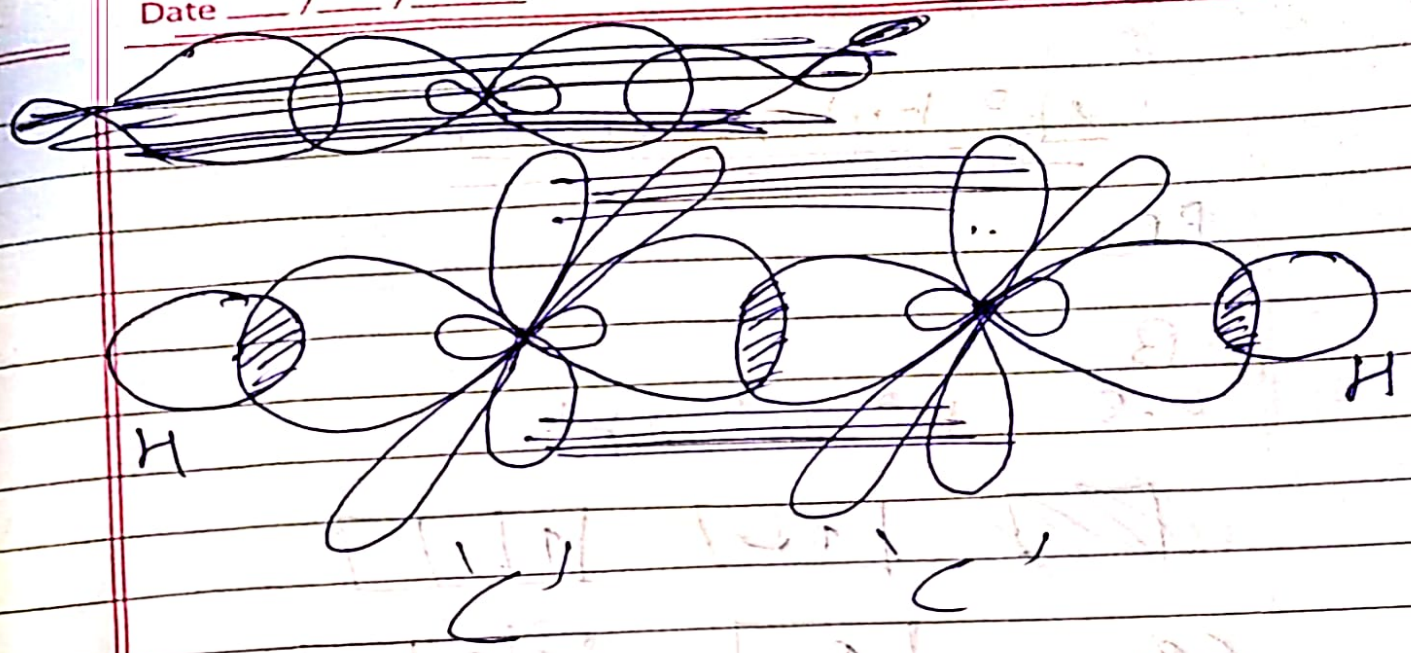

~~2-2p orb~~

☆ 2 2p atomic orbitals remained on each C are excluded from hyb. They go for lateral overlap to form 2 C-C π bond

Page No.

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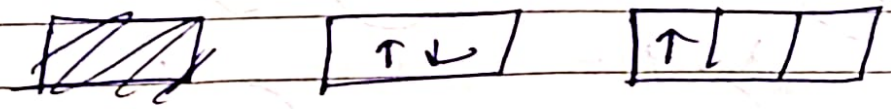
Date 20 / 8 / 19

sp^2 hybridization

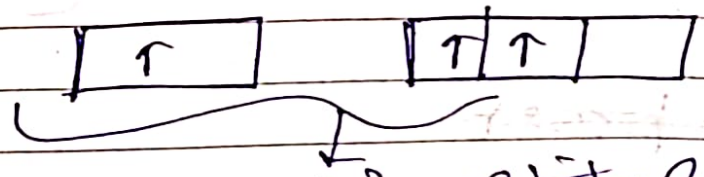
BF_3

B

G.S. $2s^2\ 2p^1$

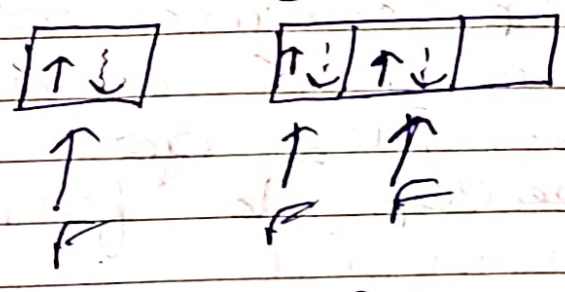


E.S.

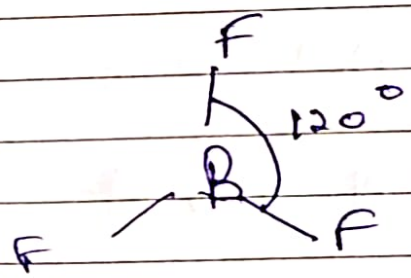


sp^2 orbitals

$BF_3 \longrightarrow$



overlap of 3 sp^2 hyb. orbitals of B with 3 2p orbitals of 3F atoms to form 3σ bonds.



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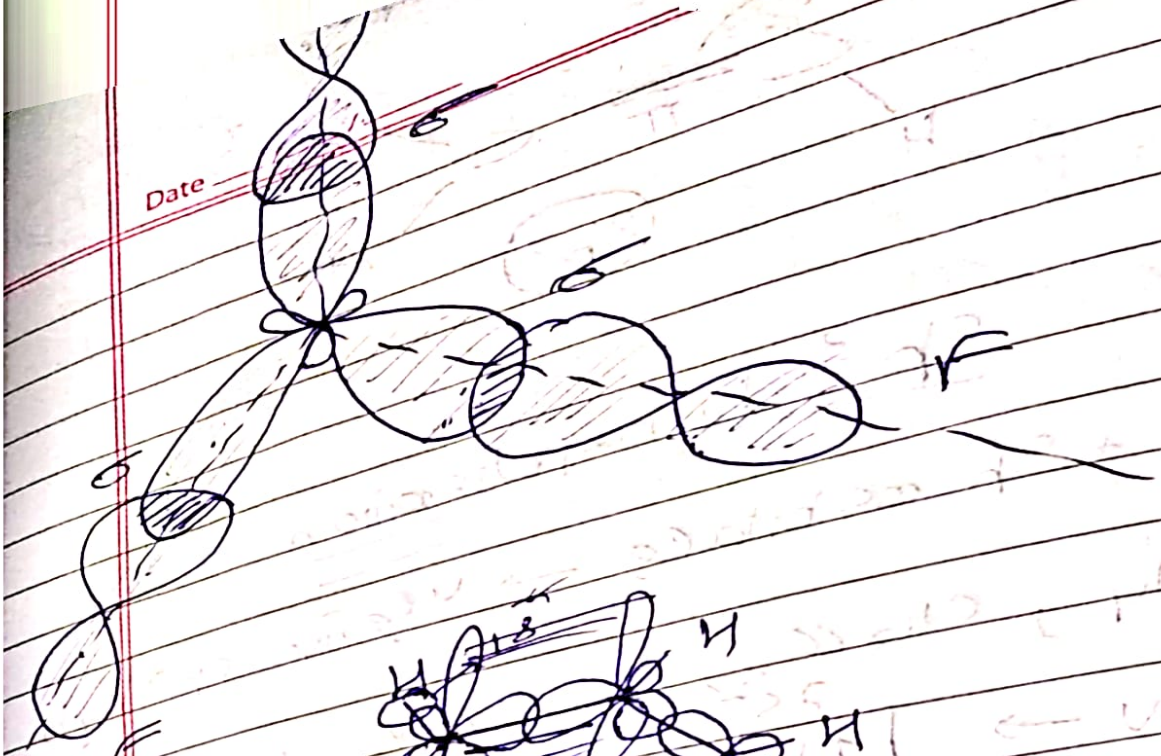

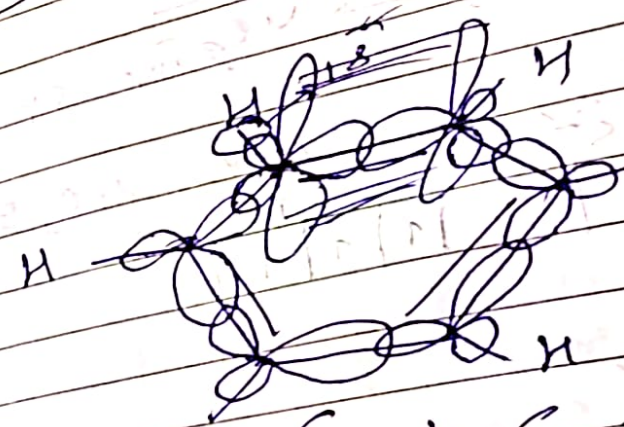

(each C is sp^2 hybridised)

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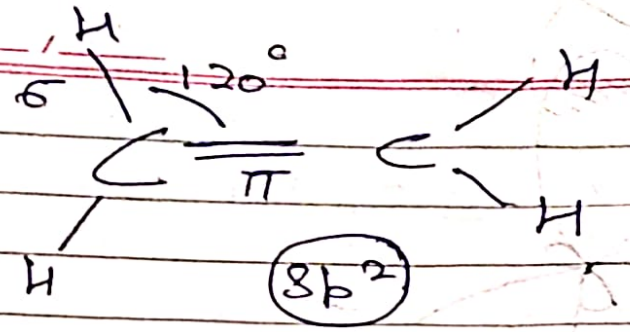
$1s^2\ 2s^2\ 2p^3$

Date ___/___/___

eg.



sp^3 hybridisation

1s + 3p orbitals → 4 equiv. sp^3 hyb.

CH_4, CH_2Cl_2, CF_4, NH_3, H_2O, SO_4^{2-}, ClO_4^-

N → (G.S.)

2s	2p		
↑↓	↑	↑	↑

(E.S.) →

↑↓	↑↓	↑↓	↑↓
lone pair	σ	σ	σ

sp^3

sp^3d hybridisation

P → (G.S.)

3s	3p			3d				
↑↓	↑	↑	↑					

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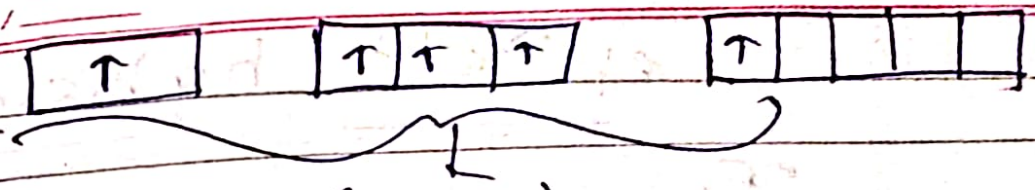
sp^3

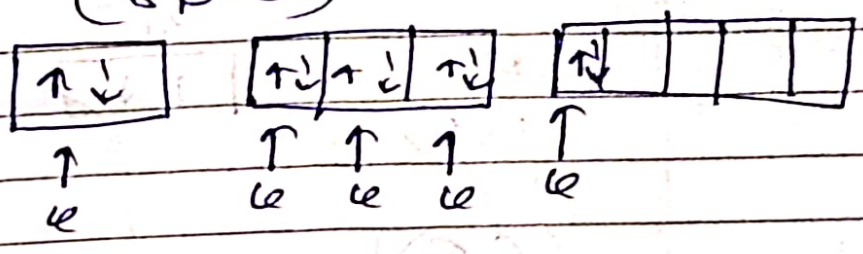
Date ___/___/___

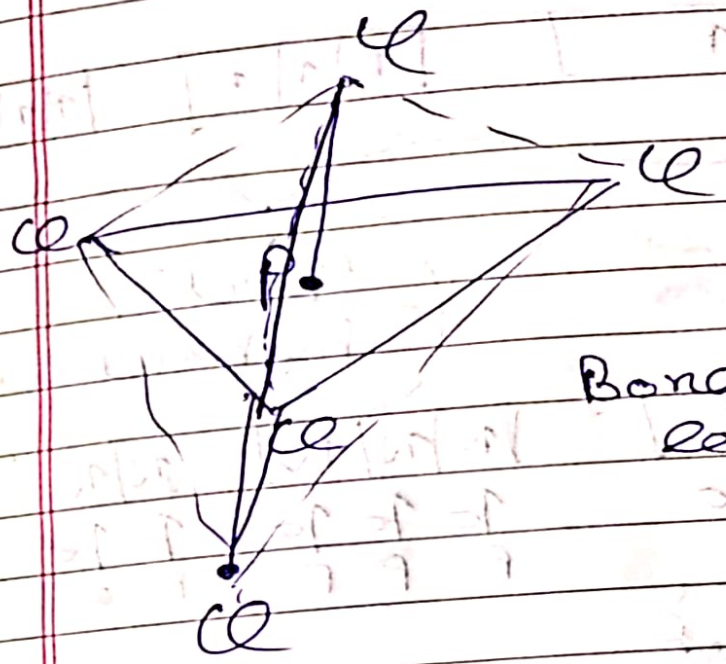
P → (G.S.)



(sp^3d)

P in PCl_5 →





Bond epical (axial) (P–Cl) length

✓

equal axial (P–Cl)

Page No.

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Date ___/___/___

sp^3d^2 hybridisation

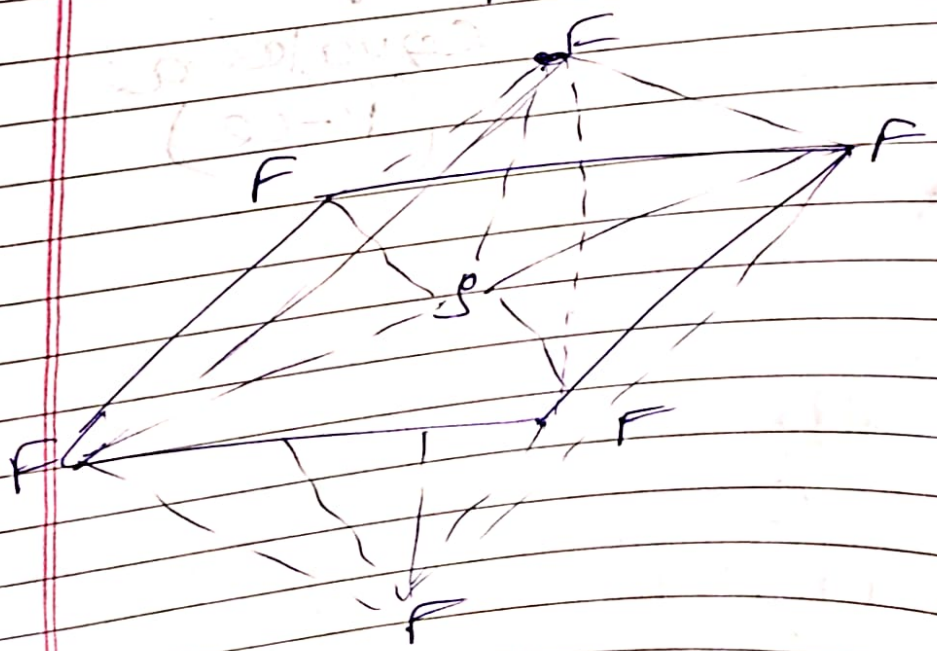
SF_6

	$3s^2$	$3p^4$	$3d$
S (G.S.)	↑↓	↑↓ ↑ ↑	
(E.S.)	↑	↑ ↑ ↑	↑ ↑

(sp^3d^2 hybridisation)

SF_6

	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓
	↑σ	↑σ ↑σ ↑σ	↑σ ↑σ
	F	F F F	F F



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Types of molecules — Types of molecules

Types of Molecules	No. of V.-shell pairs: BP	LP	Total	Hyb.	Shape	Eg.
AX_2	2	0	2	sp	linear	$BeCl_2$
	2	1	3	sp^2	bent (T.planar)	$PbCl_2$
	2	2	4	sp^3	bent (T_d)	H_2O
	2	3	5	sp^3d	Linear (TBP)	XeF_2

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Types of Molecules	No. of val. e⁻ pairs BP	LP	Total	Hyb.	Shape	Ex.
AX_3	3	0	3	sp^2	Trigonal planar	BF_3
	3	1	4	sp^3	Trigonal pyramidal (Tetrahedral)	NH_3
	3	2	5	sp^3d	T shape (Trigonal BP)	ClF_3
AX_4	4	0	4	sp^3	Tetrahedral	CH_4
	4	1	5	sp^3d	See saw (TBP), Tdistorted	$TeCl_4$
	4	2	6	sp^3d^2	Square planar (octahedral)	XeF_4

Page No.

Date / /

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AX_5	5	0	5	sp^3d	Trigonal bipyramidal	PCl_5
	5	1	6	sp^3d^2	sq. pyramidal (octahedral)	BrF_5
	~~5~~	~~1~~				
AX_6	6	0	6	sp^3d^2	octahedral	SF_6

$\boxed{sp^3d^3 \rightarrow IF_7}$ → distorted octahedral

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Saathi

Valence shell Elec. Pair Repulsion Theory (VSEPR theory)

Gillespie & Nyholm 1957

Mutual interaction among the 'e's orients the orbitals in space to an equilibrium position where repulsion becomes minimum. The stereochemistry of the central atom in a molecule is then determined by the repulsive interaction of the electron pairs of valence shell (those were will bond pairs and one pairs).

Postulates

* LP e⁻(s) repel each other more strongly than BP 'e's.

LP-LP > LP-BP > BP-BP

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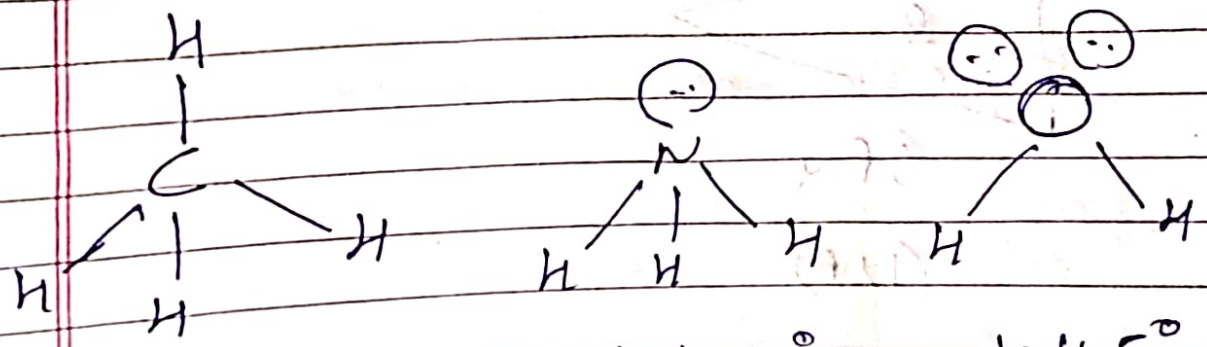
4. Lone pair is conc. (relatively closer) around the central atom while a BP is pulled out between two bonded atoms. As such the repulsion becomes greater when a LP is involved.



109.28 107.3° 104.5°

bp-bp interactions tend to 'open' the bond angles and are weaker and hence ultimate angles are smaller.

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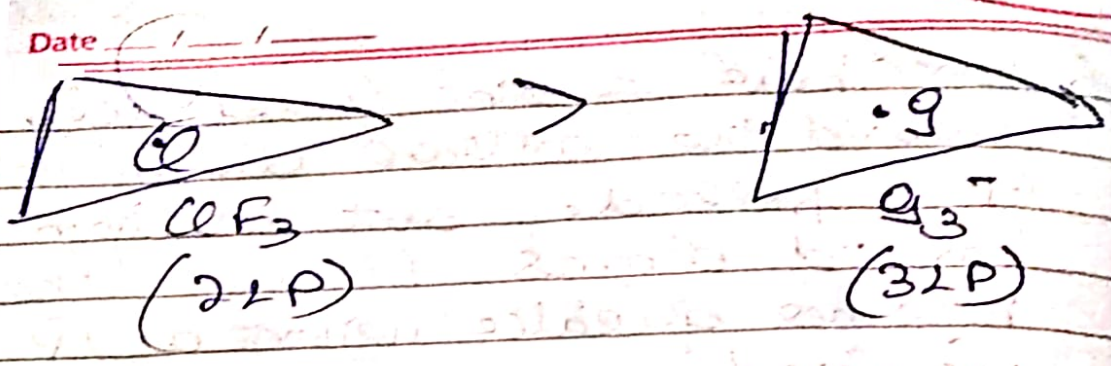
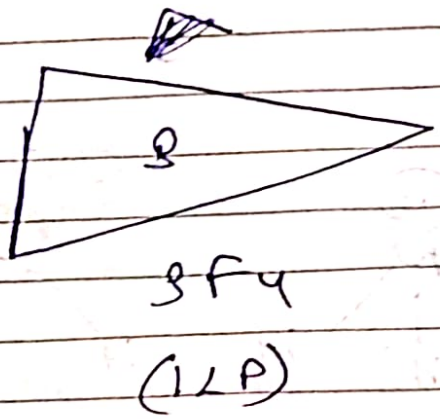
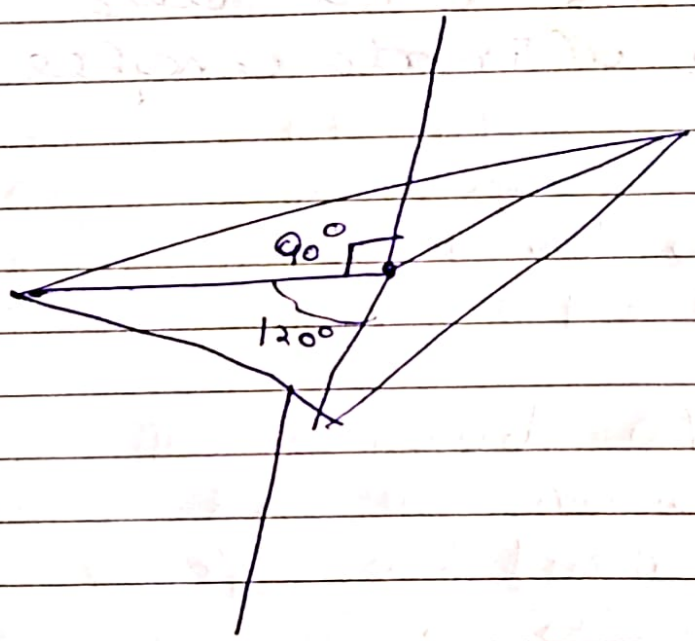




Consider a lpv (ligand) in the equitorial position



2 equitorial neighbours are at 90°
2 axial " " are at 180°

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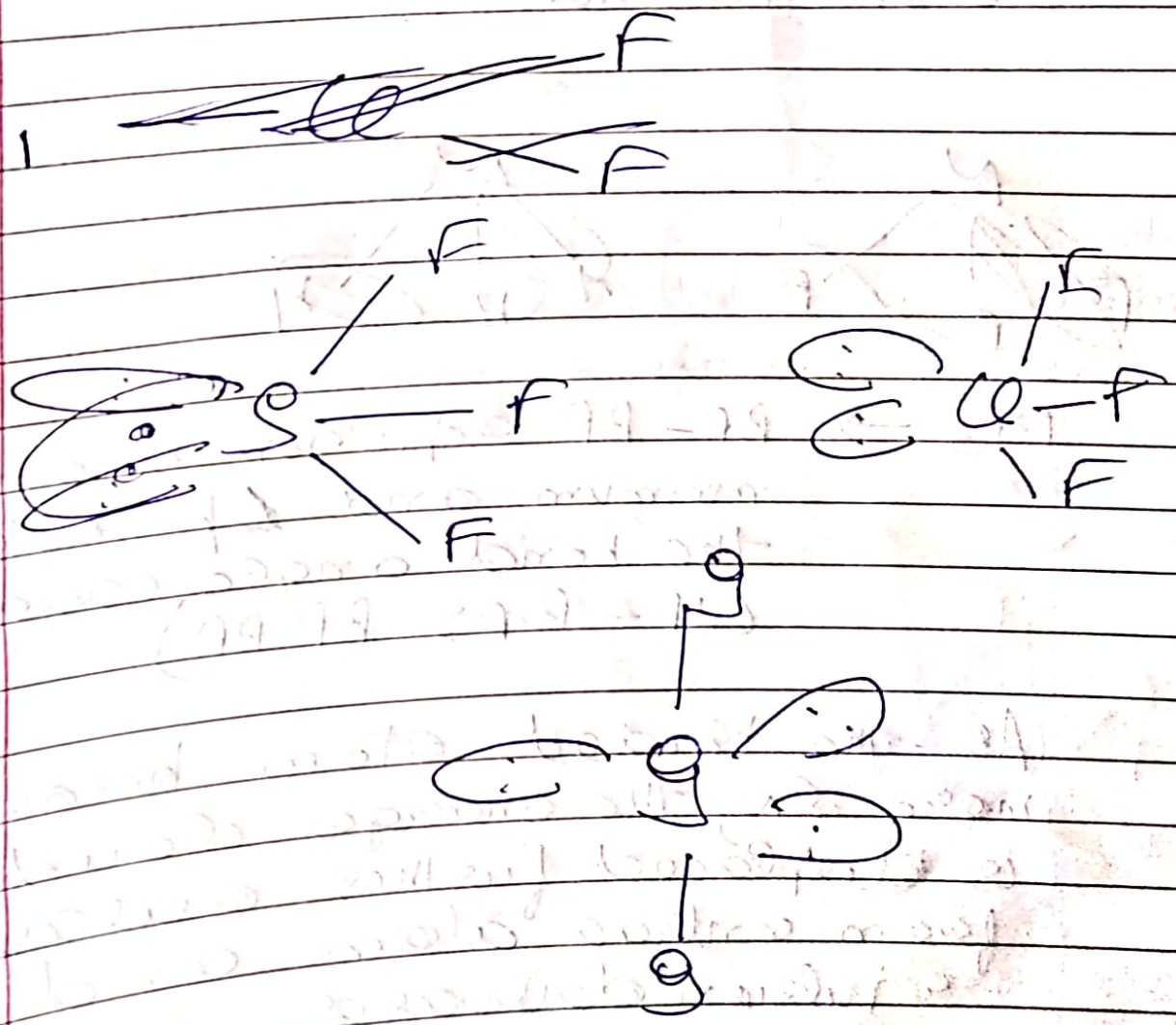
Repulsion b/w the bond and/or LP of e^-(s) decreases greatly as their angular seperation increases.

As such the equitorial group will experience 2 strong repulsions from axial neighbours (90°) and two weak repulsion from the two equitorial neighbours (at 120°).



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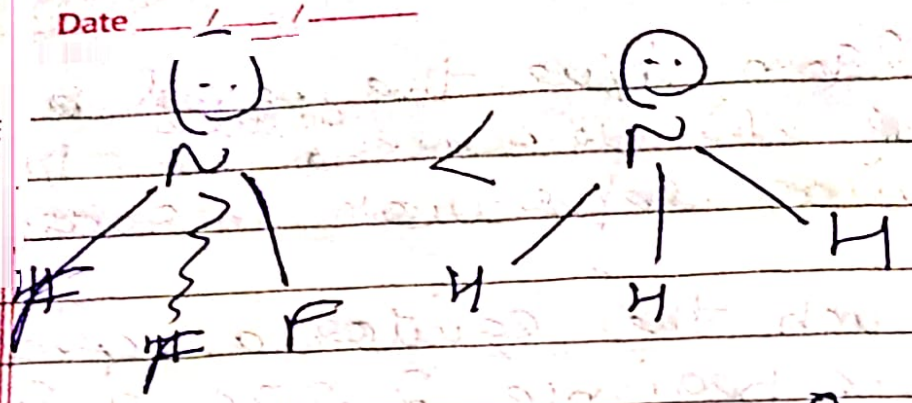
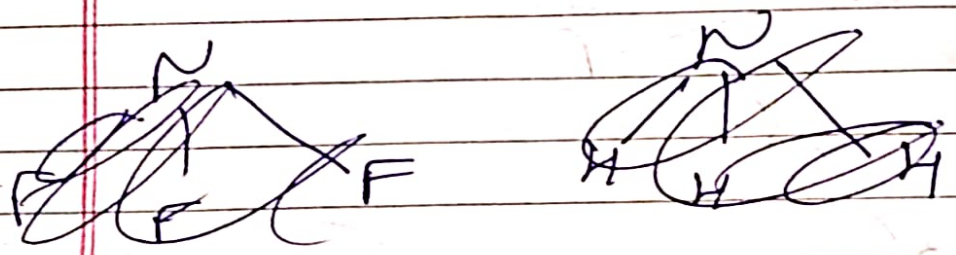
Q



102° 107.3°

Repulsion by a BP decreases as the electronegativity of the atom bonded to the central atom increases.



NF_3 → BP–BP repulsion become minimum and LP makes the bond angle least. (LP–BP > BP–BP)

As the bonded atom becomes more EN, the charge cloud is displaced further away from central atom and repulsion decreases.

Page No.

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Date ___/___/___

* Multiple bond orbitals repeal orbitals more strongly than single bond orbital.

O = PF_3 102.5°

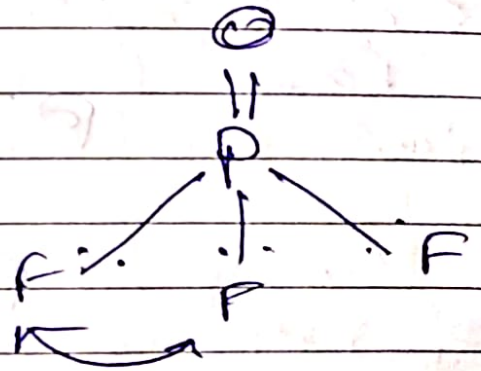
O = PCl_3 103.5°

O = PBr_3 108.5°

Multiple bonds Orbitals

Multiple bond orbitals repel other orbitals more strongly than single bond orbitals.

O = PF_3 102.5°
O = PCl_3 103.5°
O = PBr_3 108.5°



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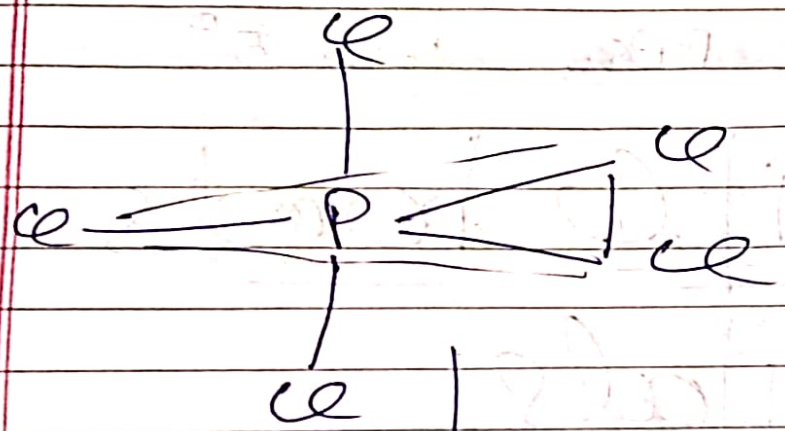
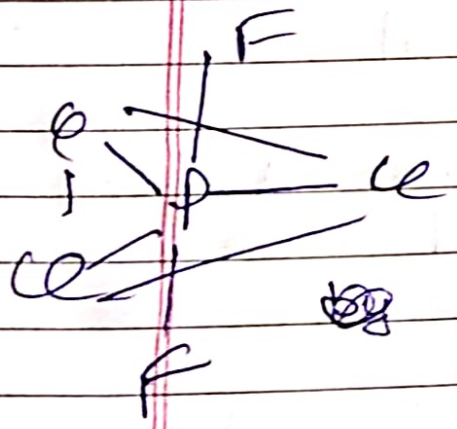
The bond pairs are removed from the phosphorous (P) atom (moving from Br → F). bp-bp repulsions becomes min. & the repulsion from multiple double bond makes the bond angle least.

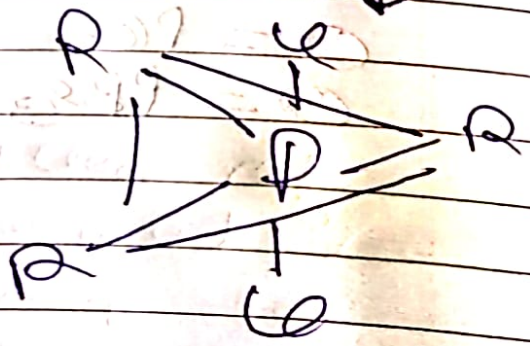


sp^3d

2F



3R



R ≥ Alkyl grp.

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By taking advantage of VSEPR theory Bent's rule appears electro-negative atom pulls the shared e^- pairs towards it A electropositive atom repels the e^- pair away from it.

Bent's Rule

A more EN atom or substituent prefer to combine with those hyb. orbitals which has less s character and vice versa.

sp^3d

$\Downarrow$

$(sp^2) + (p_z - d_{z^2})$

$\downarrow$ 33% s character

$\downarrow$ 0% s character.

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Octet / Electronic Theory Valency

Every element has a tendency to occupy the inert electronic configuration of the nearest inert gas given by Kossel & Lewis (1916)

drawbacks

→ directional nature of covalent bond.

→ bond angles

→ geometry of central molecule

VBT

Pauling & Slater

① A covalent bond are of 2 type (σ, π) both being formed by orbital overlap.

② Distortion due to LP (VSEPR)

③ Concept of hyb.

④ Resonance.

Page No.

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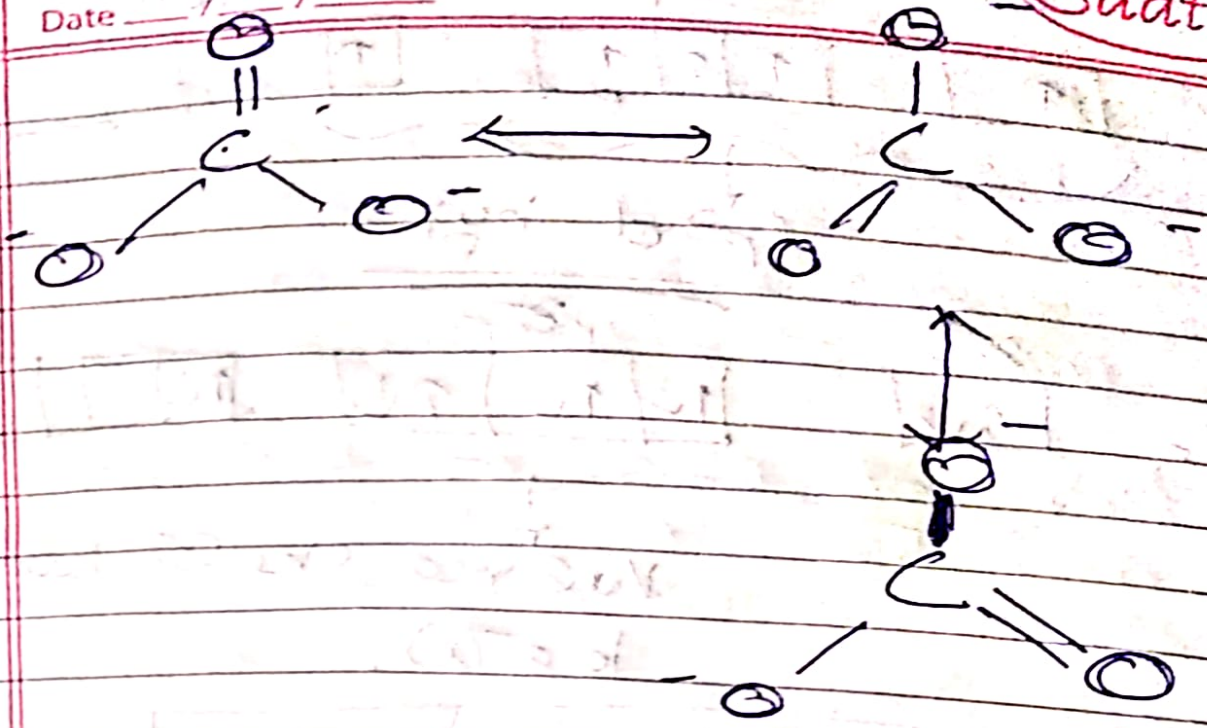
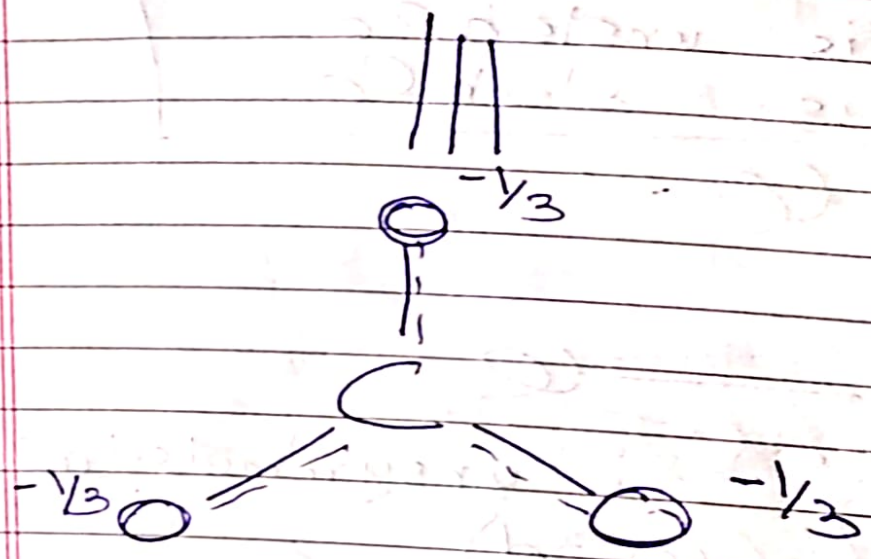
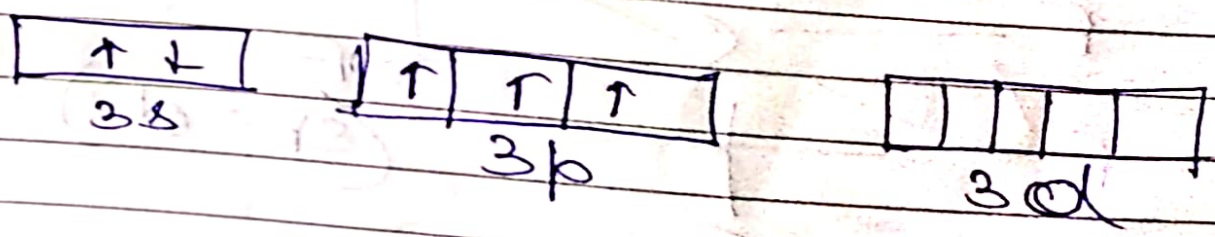




PCl_5 is not formed according to electronic theory of valency

. Valence shell e^-

U.S.



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Saathi

Es

3s	3p			3d				
↑	↑	↑	↑	↑				

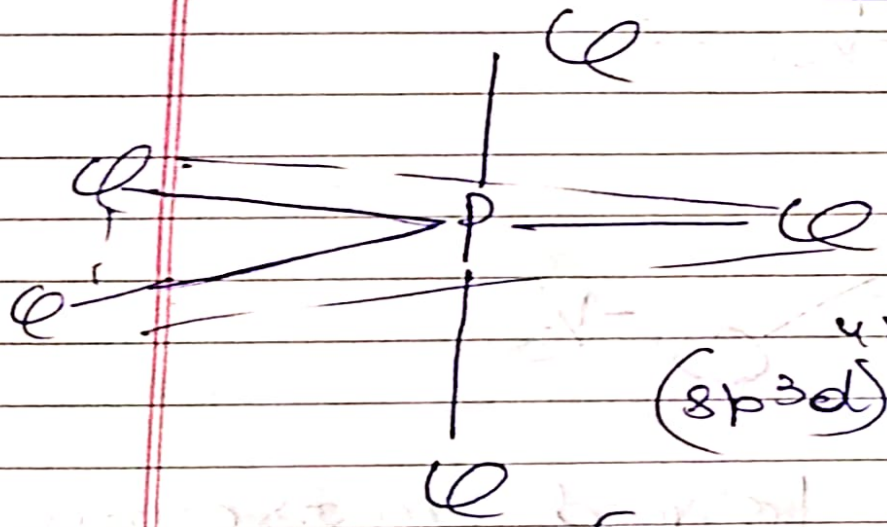
sp^3d hyb.

PCl_5

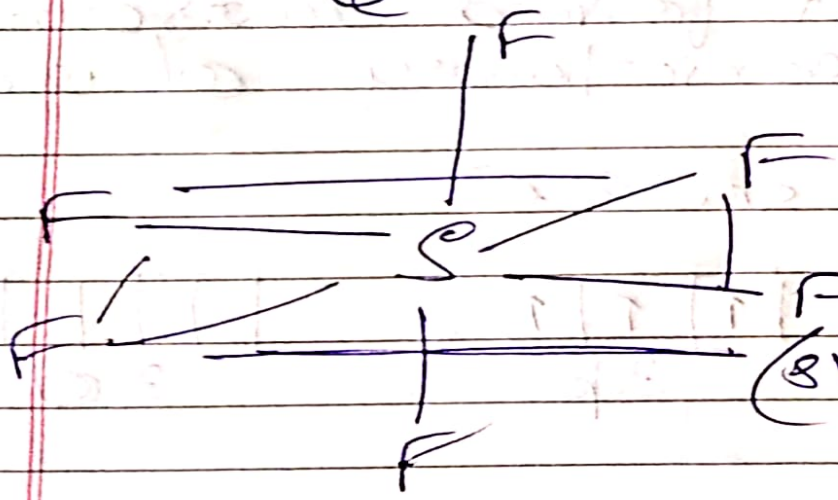
3s	3p			3d				
↑↓	↑↓	↑↓	↑↓	↑↓				

Valence shell has 10 e^-(s).

1. PCl_5 is unstable
   SF_6 is stable



unsymmetrical
(sp^3d)



symmetrical
(sp^3d^2)

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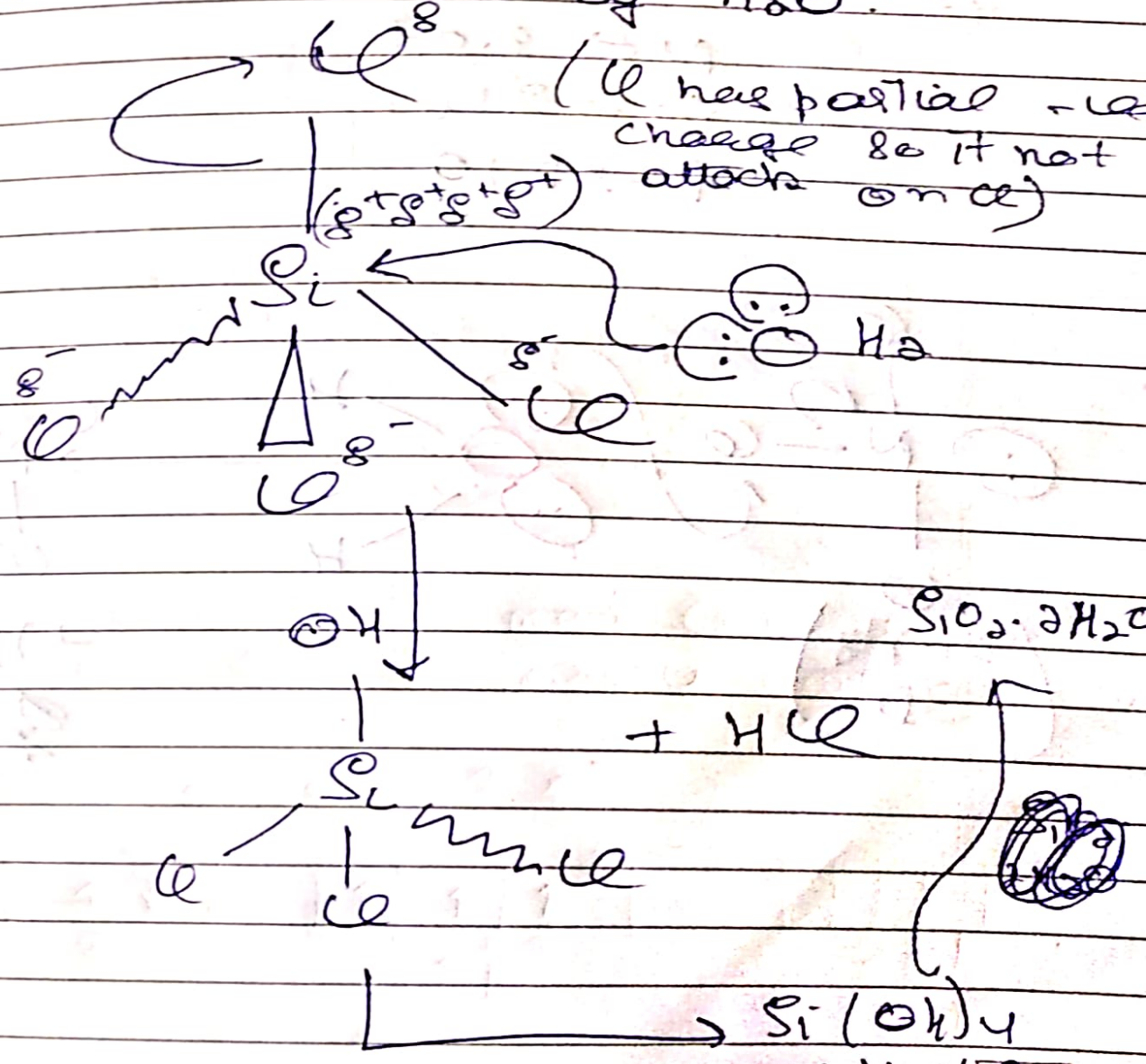
2. disproportion

$$2H_2O_2 \xrightarrow[\text{Light}]{} 2H_2O + O_2$$

3. CCl_4 does not hydrolyse
$SiCl_4$ does hydrolyse

because $CCl_4 \rightarrow$ No empty d/
$Si \rightarrow$ empty 3d orbital

Hydrolysis $\rightarrow$ Nucleophillic attack by H_2O.



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