NET

OMC (25 – 36)

MOT :

It is based on LCAO theory.

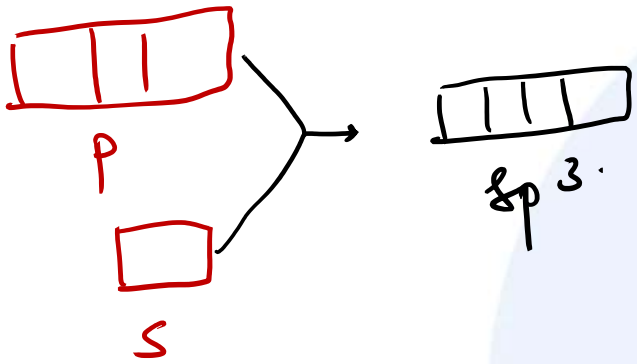
Linear Combination of Atomic Orbital.

When two atomic orbitals undergoes mixing according to LCAO principle, they will form two Molecular Orbitals.

① BMO [Bonding Molecular Orbitals]

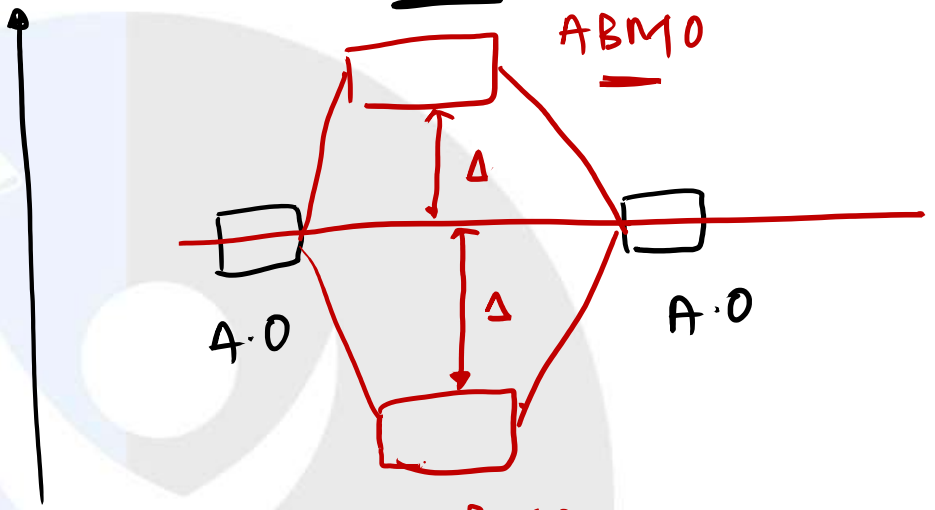
② ABMO (Anti

Hybdn / VBT



Diff energy A.O mix to get the equal. energy hybrid orbital.

MOT



Similar energy A.O mix to give diff. energy M.O.

MOT

① Mixing of Atomic Orbital

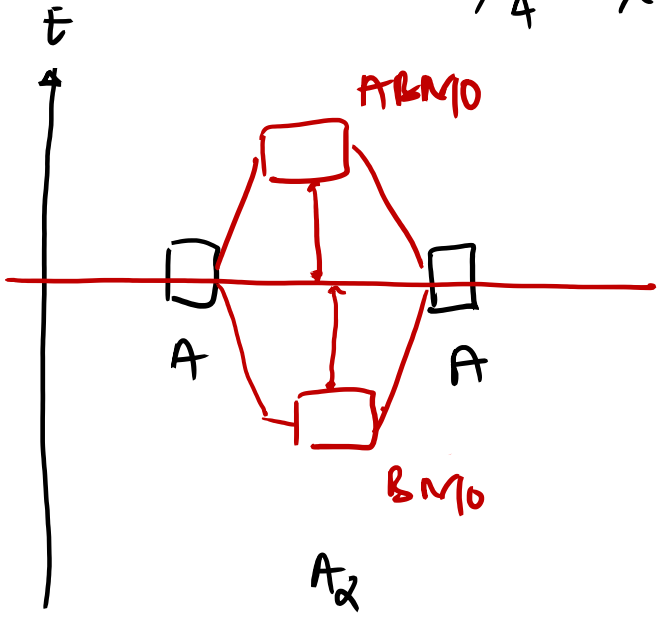
formation of M.O.D

filling of M.O.

① Mixing Conditions

(i) A_2 A — A

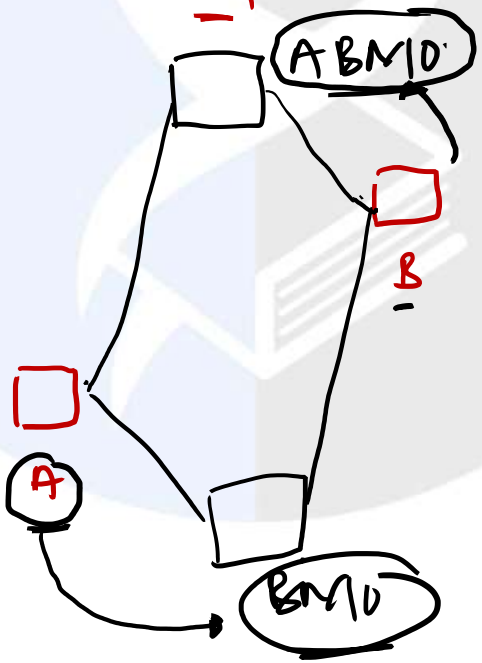
$X_A = X_A \rightarrow \{\Delta E = 0\}$



② AB

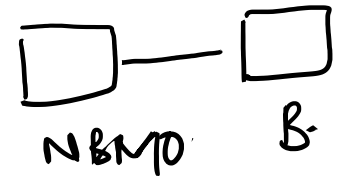
$\Delta E \neq 0$

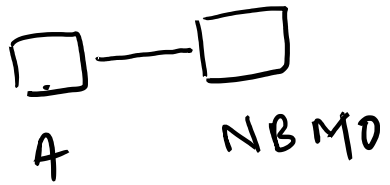
$X_A > X_B$



③ AB

$X_A >>> X_B$





Better Mixing $\propto \frac{1}{\text{Energy gap.}}$

② Formation of MOs. / Pictorial Representation of M.O.

A.O + A.O ⟶ M.O

LCAO

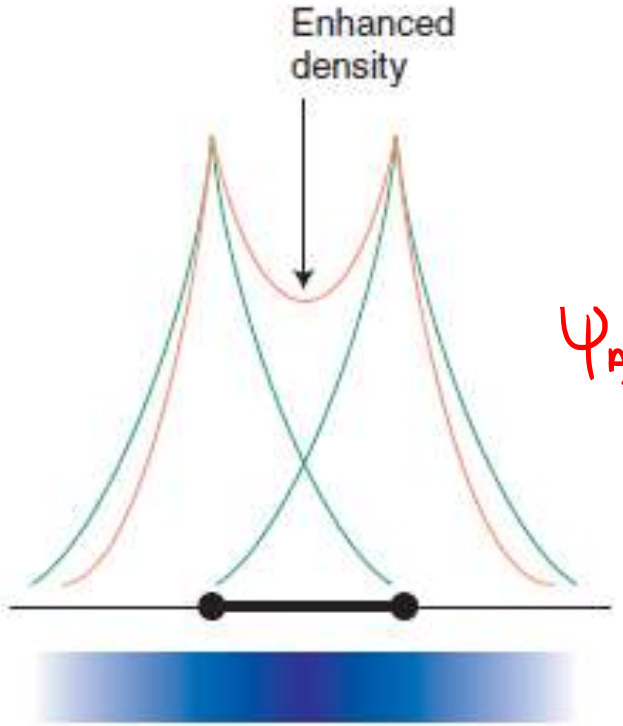
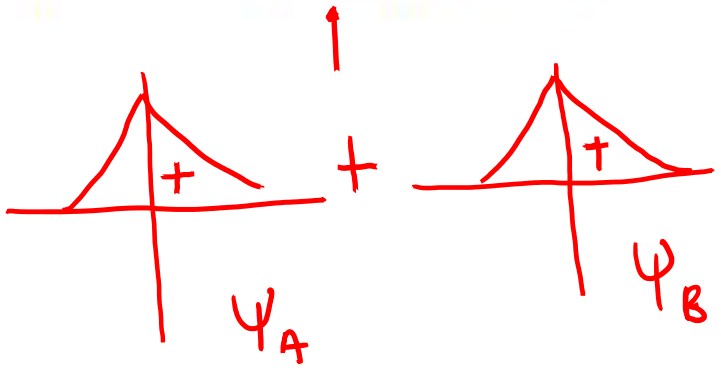


Figure 2.8 The enhancement of electron density in the internuclear region arising from the constructive interference between the atomic orbitals on neighbouring atoms.

$\psi_{AB} = \psi_A + \psi_B$

Constructive interference



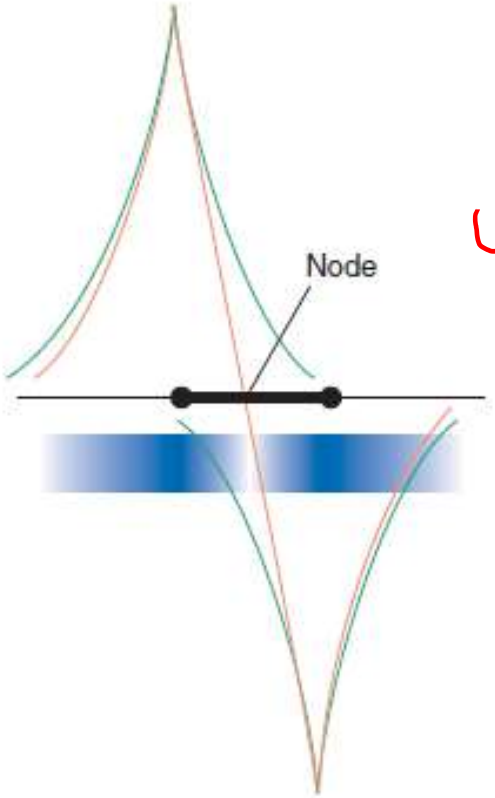
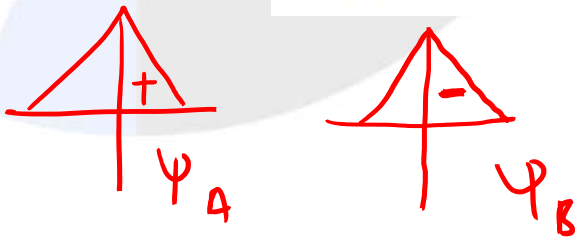


Figure 2.9 The destructive interference that arises if the overlapping orbitals have opposite signs. This interference leads to a nodal surface in an antibonding molecular orbital.

$\psi_{AB} = \psi_A - \psi_B$

Destructive Interference



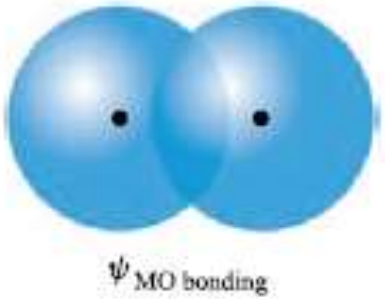
IfAS

Overlapping

① Head to head overlapping → ABMO

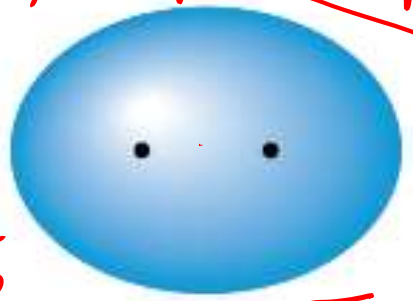
↳ σ_{1s}, σ^*_{1s}, σ_{2pz} / σ^*_{2pz} → BMO

1s 1s



is equivalent to

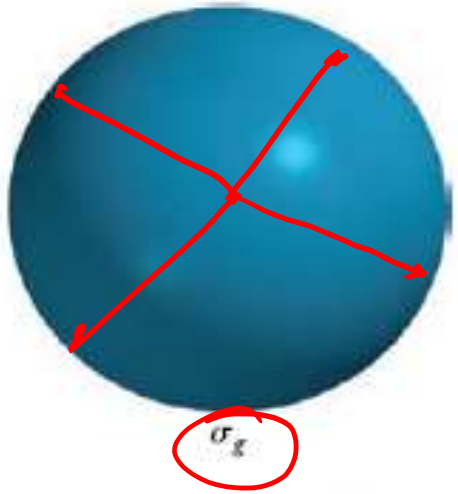
Constructive interference



σ_{1s} BMO

(a)

② Sidewise overlapping

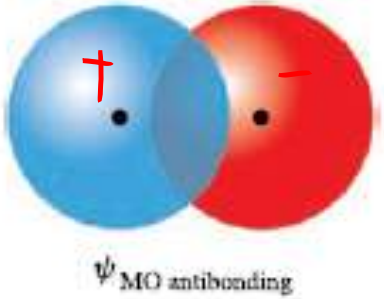


→ cos ✓

→ gerade

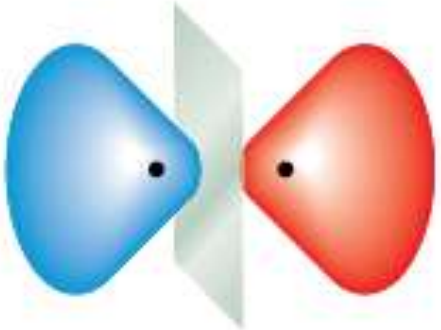
→ $\sigma_{1s} \equiv \sigma_g$

Destructive Interference

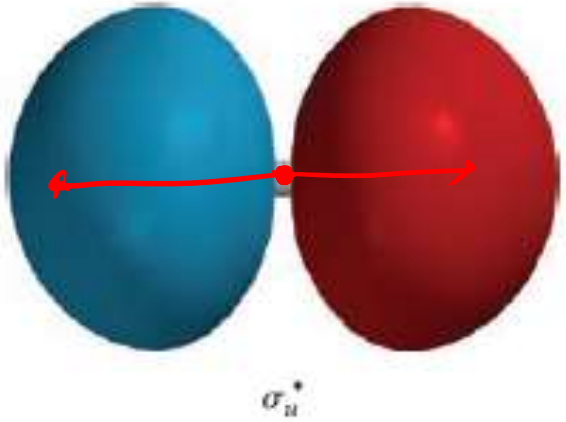


1s 1s

is equivalent to



σ^*_{1s} / ABMO

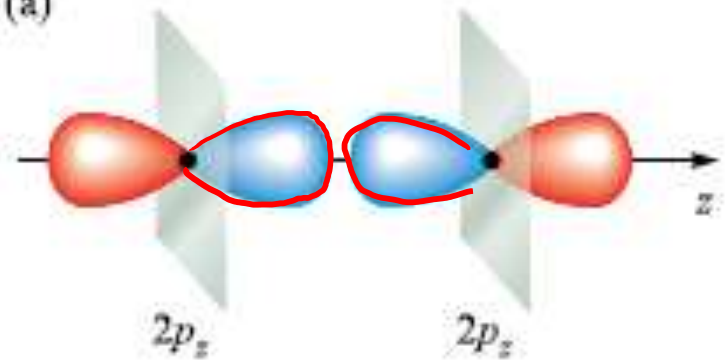


→ cos X

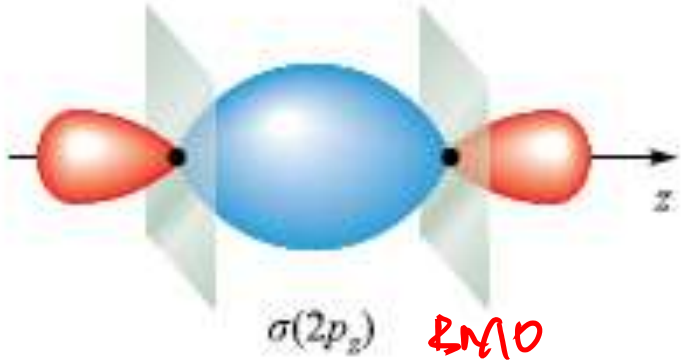
→ Ungerade

→ $\sigma^*_{1s} \equiv \sigma^*_u$

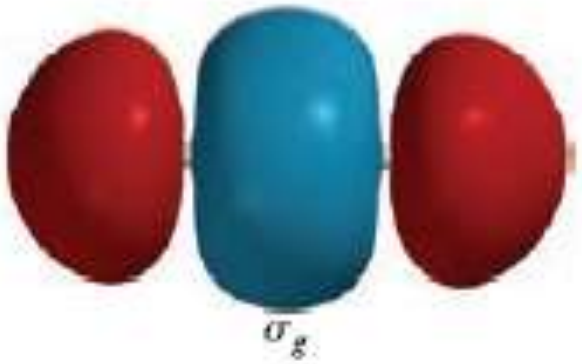
(a)



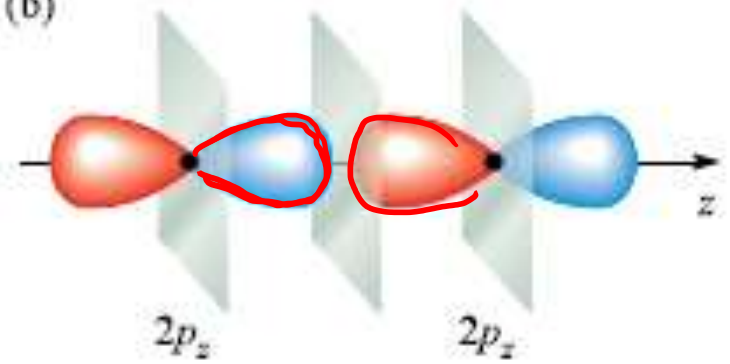
C.I



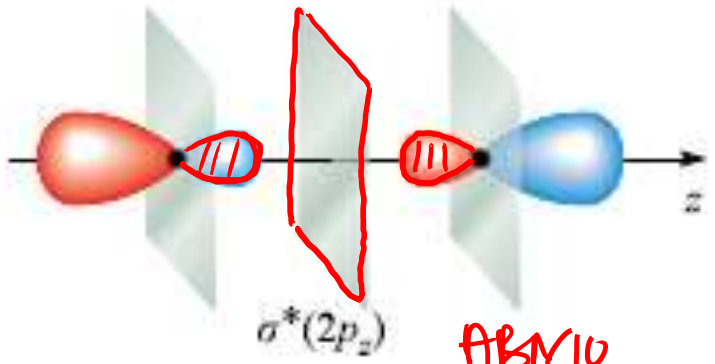
BMO



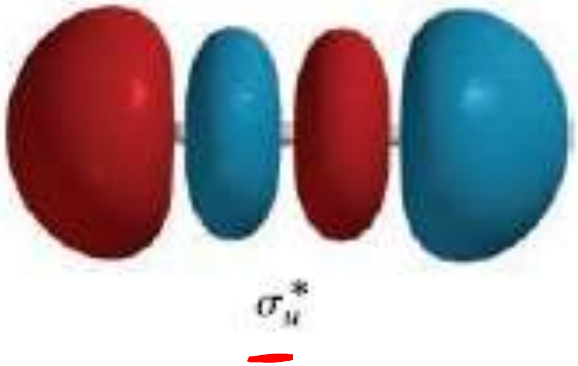
(b)



D.I

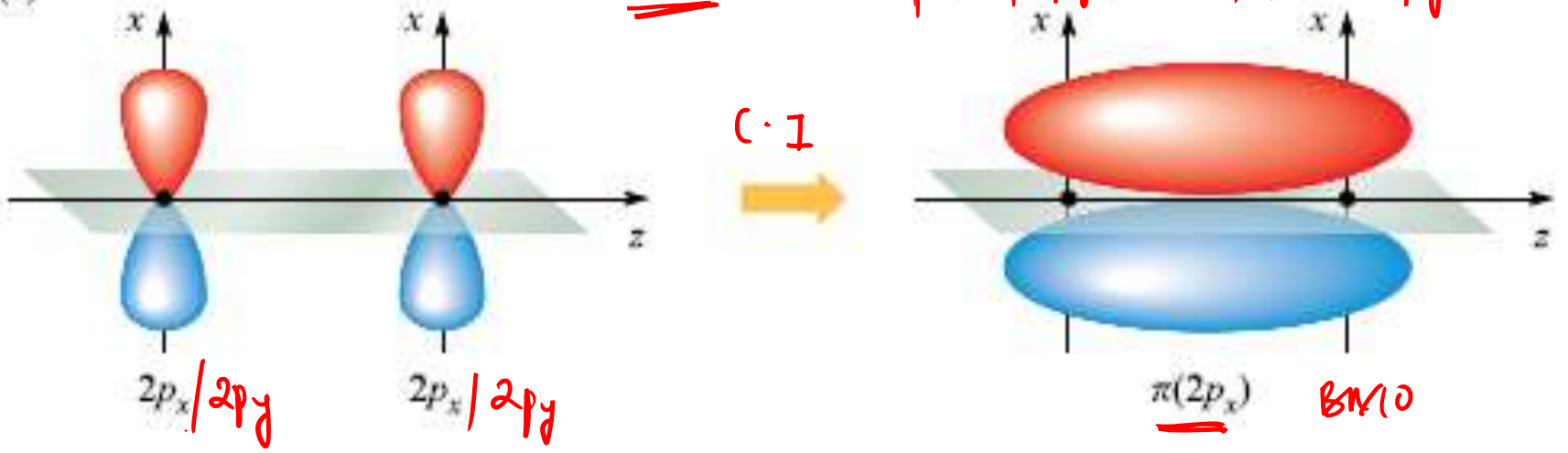


ABMO

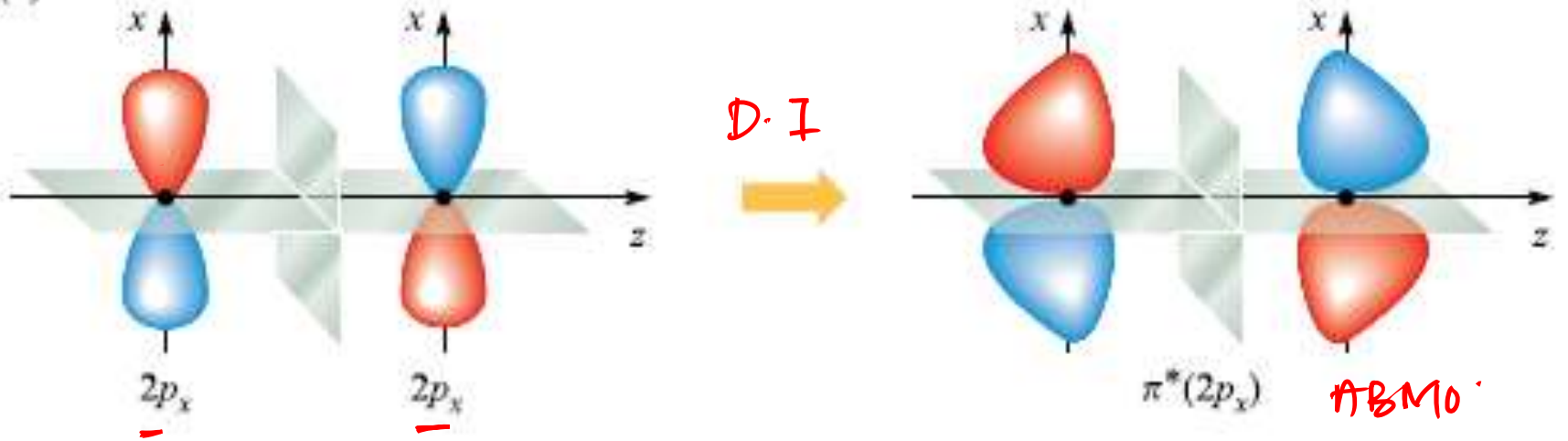


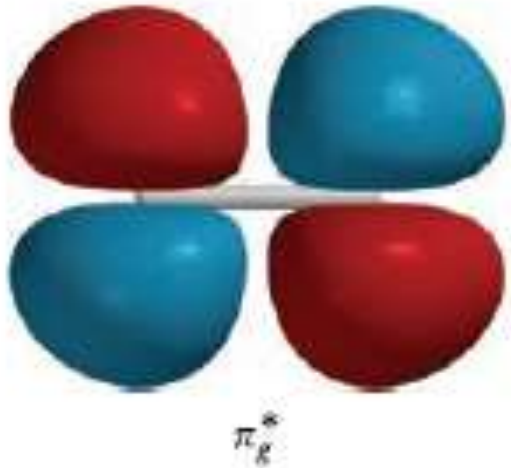
π M.O → π2px, π2py, π*2px, π*2py

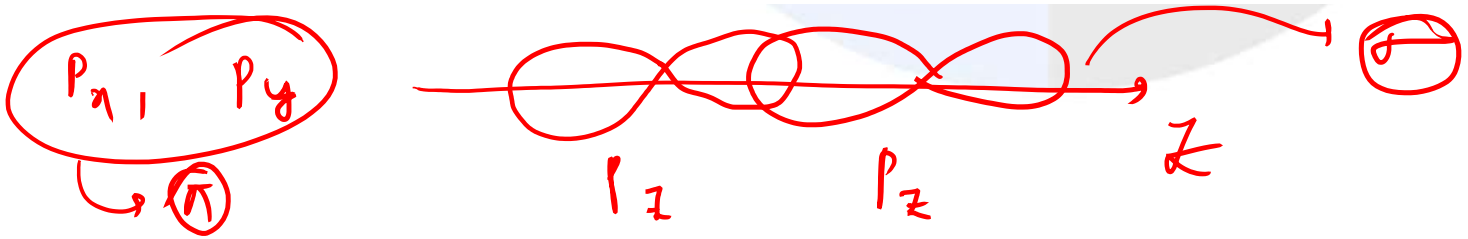
(c)



(d)







MOD

(Break 5 min)

① Homonuclear Diatomic MOD

→ A_2 Eg H_2, Li_2, B_2, O_2 F_2 etc.

② Heteronuclear diatomic MOD

→ AB Eg: $CN^{\ominus}$, $OH^{\ominus}$, HF, CO, NO.

① Homonuclear Diatomic MOD

→ H_2, He_2, Li_2, B_2, C_2, N_2, O_2, F_2

O_2, F_2 → 8+8 = (16)

$\leq 14\ e^{\ominus}$

Unsymm MOT

s-p mixing

2121 MOT

$> 14\ e^{\ominus}$

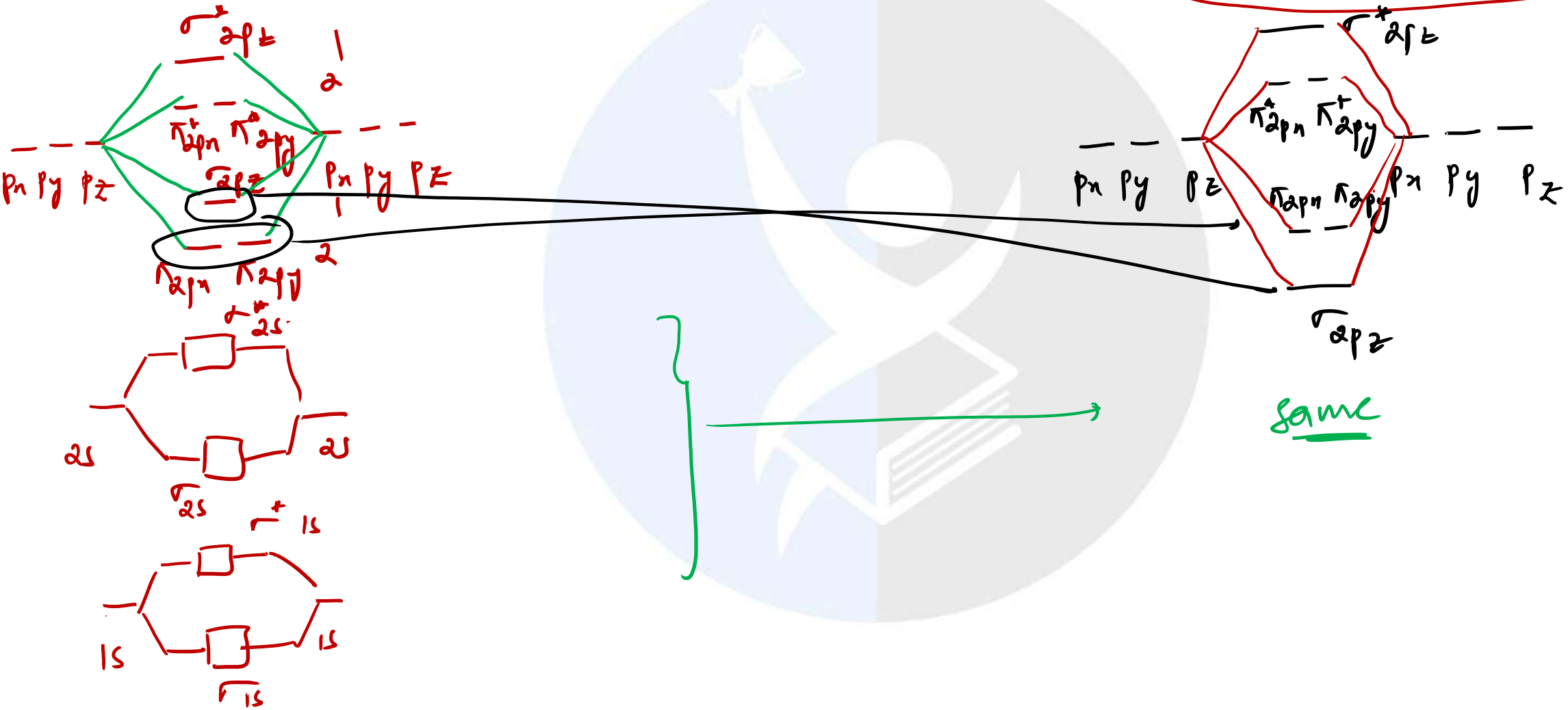
Symm MOT

No sp mixing

1221 MOT

Unsymm MOT / sp mixing / ≤ 14 e⊖ / 2121 MOT

Symm MOT / no sp mixing / > 14 e⊖ / 1221 MOT



same

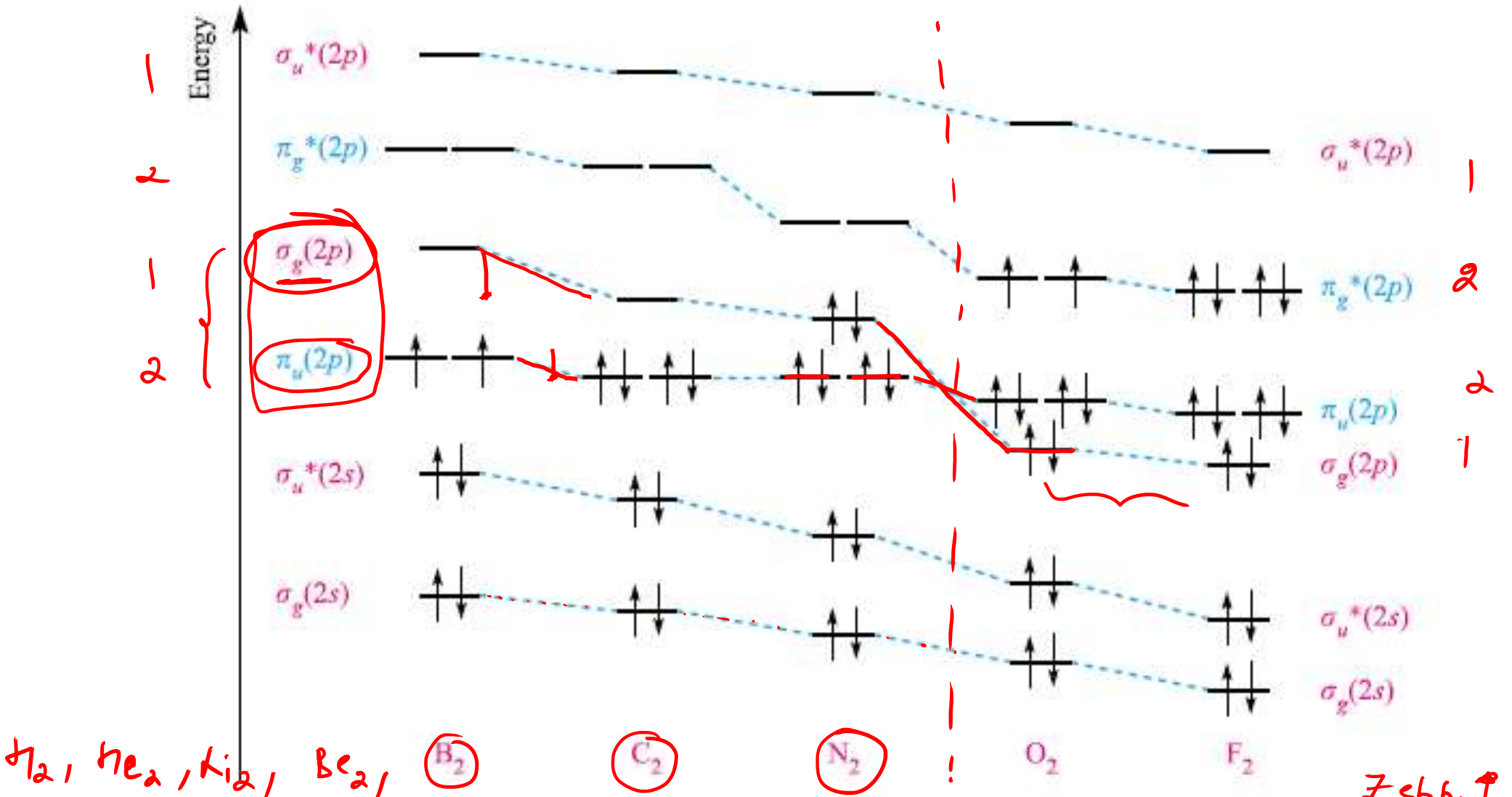
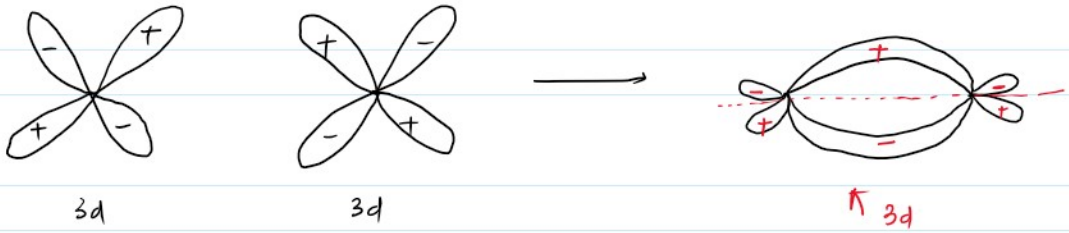
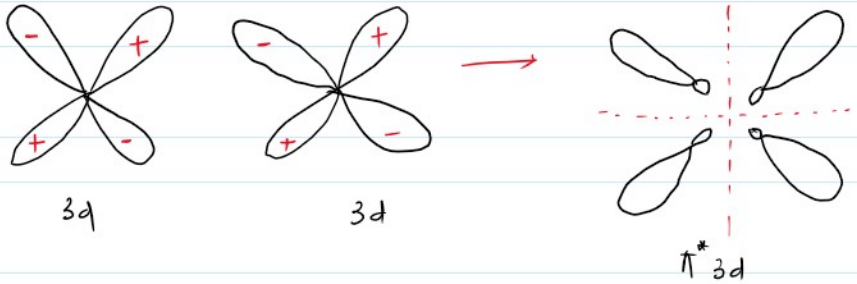


Fig. 2.10. Changes in the energy levels of the MOs and the ground state electronic configurations of homonuclear diatomic molecules involving first-row *p*-block elements



① BMO
② Node = 1
③ cos x
④ Ungerade.

④ π^*_{3d}

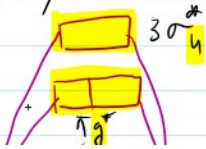


① ABMO
② Node = ②
③ cos ✓
④ Gerade

	MO's	Nodes	cos	Gerade/Ungerade
①	σ	0	✓	Gerade
②	σ^* / π	1	x	Unegrade
③	π^* / δ	②	✓	Gerade
④	δ^*	③	x	Ungerade.

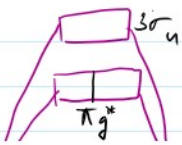
Homonuclear Diatomic M.O Diagram → sp mixing: H_2, Be_2, C_2, B_2, N_2 | No sp mixing: O_2, F_2

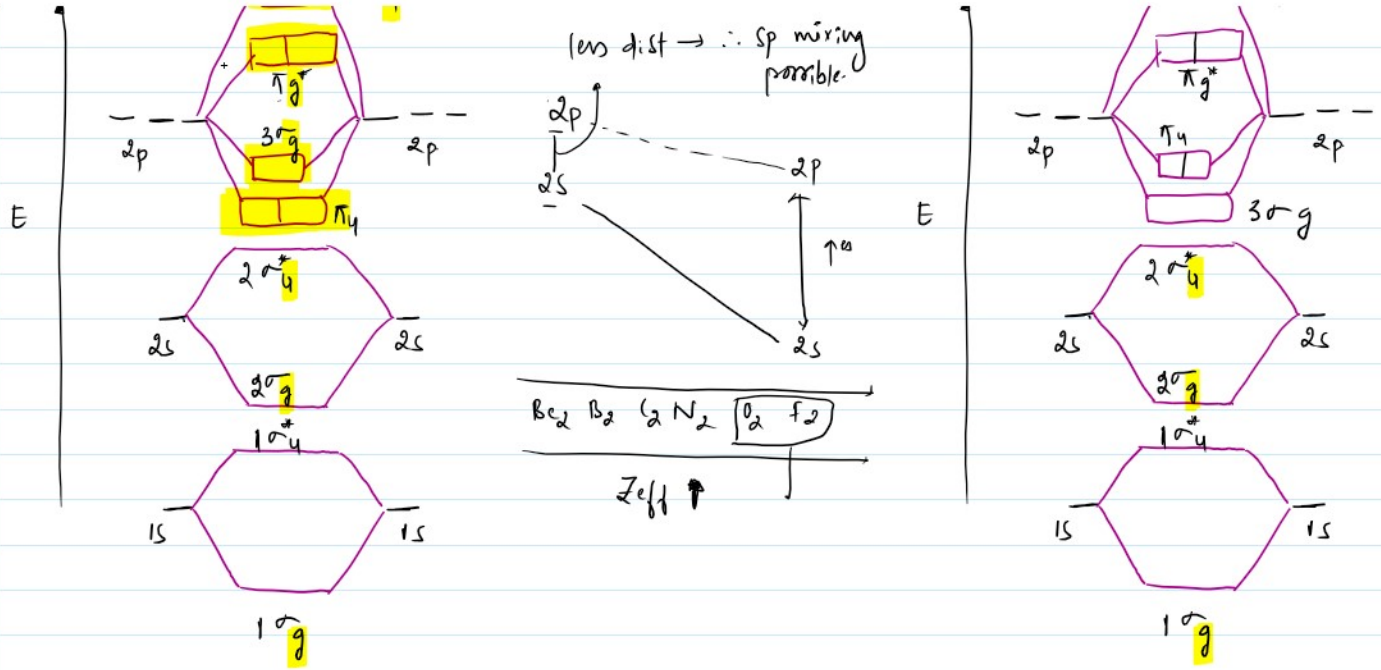
(2121) Unsymmetrical M.O
14 e⁰ / less than 14 e⁰



less dist → ∴ sp mixing possible.

Symmetrical m.O (1221)
If e⁰ more than 14 e⁰

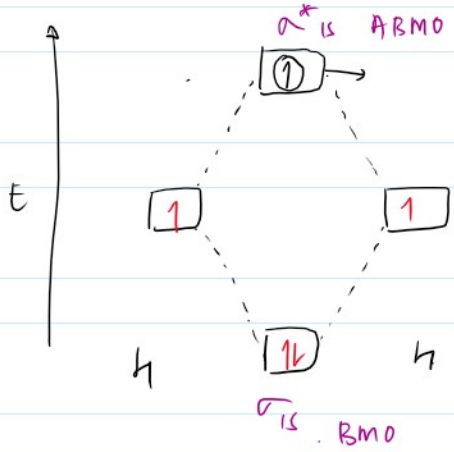




① H_2

$H \rightarrow 1s^1$

$H \rightarrow 1s^1$



① E.C

$\sigma_{1s}^2 < \sigma^*_{2s}$

② B.O = $\frac{\text{No. of } e^\ominus \text{ in BMO} - \text{No. of } e^\ominus \text{ in ABMO}}{2}$

$= \frac{2-0}{2} = \frac{2}{2} = 1$

③ ESR active | ESR inactive

($e^\ominus$ paired → ESR inactive

$e^\ominus$ unpaired → ESR active)

② $H_2^\oplus \rightarrow 1e^\ominus \rightarrow$ B.O = $\frac{1}{2}[1-0] = 0.5$

③ $H_2^\ominus \rightarrow 3e^\ominus \rightarrow$ B.O = $\frac{1}{2}[2-1] = \frac{1}{2} = 0.5$

	H_2	$H_2^\oplus$	$H_2^\ominus$
No. of $e^\ominus$ →	2	1	3
B.O =	1	0.5	0.5

B.α = $H_2 < H_2^\oplus < H_2^\ominus$

① B.O $\propto \frac{1}{B.\alpha}$

② B.α $\propto$ no. of $e^\ominus$

B.O = H_2 < $H_2^{\oplus}$ < $H_2^{\ominus}$

$H_2^{\oplus}$ → $1e^{\ominus}$; $H_2^{\ominus}$ → $3e^{\ominus}$

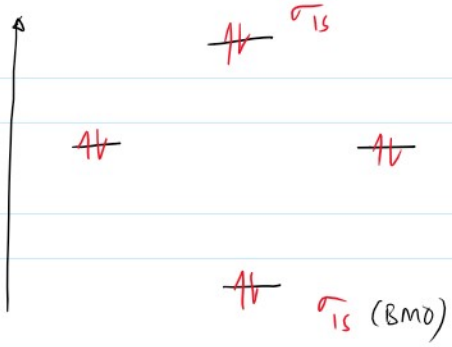
(2) He_2 → Non existence of molecule B.O = 0

He_2

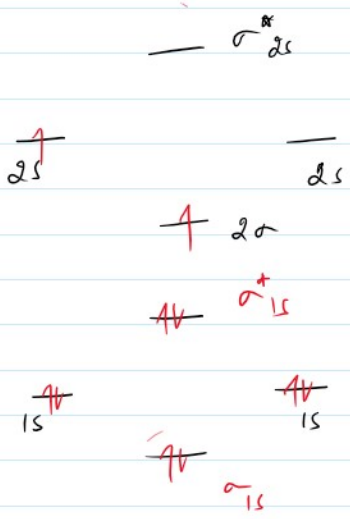
He : $1s^2$ → $4e^{\ominus}$

He : $1s^2$

B.O = $\frac{1}{2}(2-2) = 0$



$He_2^{\ominus}$



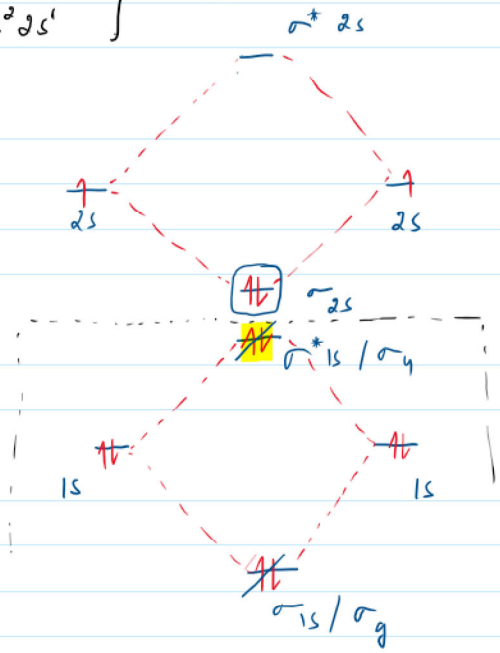
B.O = $\frac{1}{2}$ (BMO − ABMO)

= $\frac{1}{2}[3-2] = \frac{1}{2} = 0.5$

B.O = $\frac{1}{2}[1-0] = \frac{1}{2} = 0.5$

Thank you ☺

Li_2 : $Li \rightarrow 1s^2 2s^1$, $Li \rightarrow 1s^2 2s^1$ } = 6 $e^\ominus$



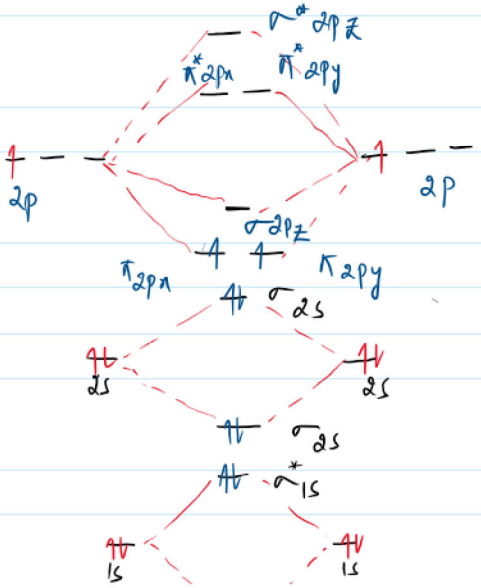
① : $1\sigma_g^2 < 1\sigma$
$\sigma_{1s}^2 < \sigma^*_2$

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

* Be_2 → 8 $e^\ominus$ B.O = 0 → Non existence.

He_2 → 2 $e^\ominus$; Be_2 → 8 $e^\ominus$; Ne_2 → 20 $e^\ominus$ → Not exist.

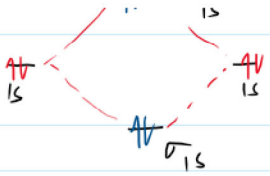
* B_2 : B : $1s^2 2s^2 2p^1$, B : $1s^2 2s^2 2p^1$ } = 10 $e^\ominus$ → less 14 $e^\ominus$ → unsym. (2)



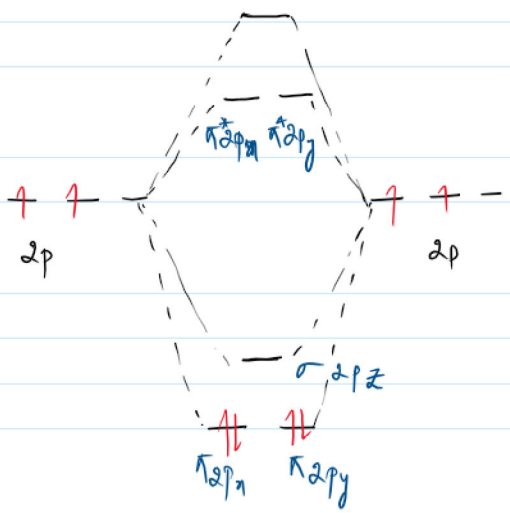
① E.C : $\sigma_{1s}^2 < (\sigma^*_{1s})^2 < \sigma_{2s}^2$ <

② B.O = $\frac{1}{2}[2-0] = \frac{2}{2}$ =

B — B
↳ π Bond (weak)
(∵ at R.T it is unstable)



* C_2 : C : $1s^2\ 2s^2\ 2p^2$ } 12 $e^\ominus$ → less than 14 $e^\ominus$ → Unsym ↑
C : $1s^2\ 2s^2\ 2p^2$ } (2 1 2 1)



B.O = $\frac{1}{2}$ [4 −

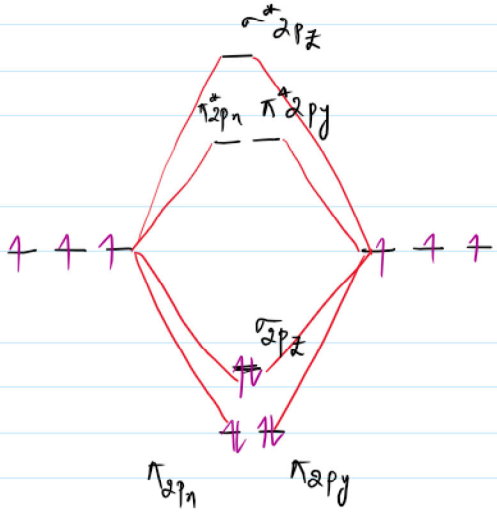
C = C →

Very unst

$H_2C = CH_2$

1σ + 1π

N_2 : N : $1s^2\ 2s^2\ 2p^3$ } 14 → (Unsym MOT)
N : $1s^2\ 2s^2\ 2p^3$ } (2 1 2 1)



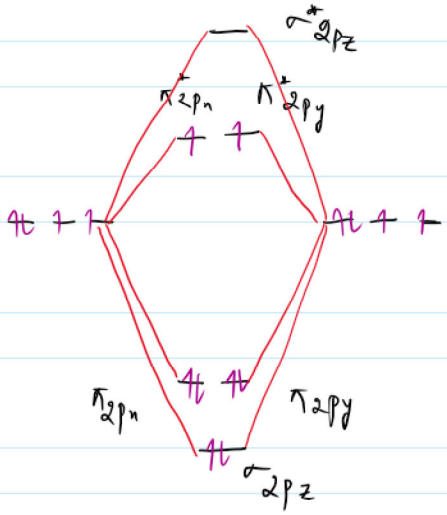
① B.O = $\frac{1}{2}$ [6 − 0

(

N ≡ N

\# O_2 : O : $1s^2\ 2s^2\ 2p^4$ } 16 $e^\ominus$ → No s-p mixing → Symm. M
O : $1s^2\ 2s^2\ 2p^4$ } (1 2 2 1)

σ* 2p



① B.O = $\frac{1}{2}[6-2]$

Trick:

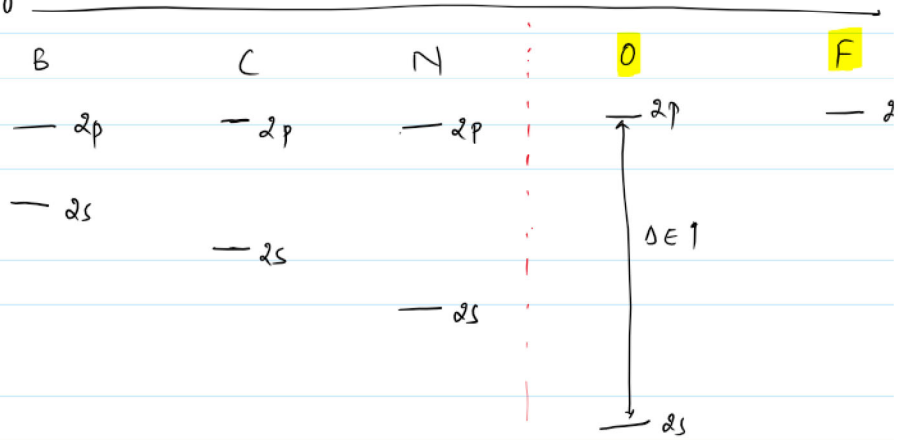
No. of $e^{\ominus}$	8	9	10	11	12	13	14	15	16	17	18
B.O:	0	0.5	1	1.5	2	2.5	3	2.5	2	1.5	1

Exceptn : $CO^{\oplus}$ → more than

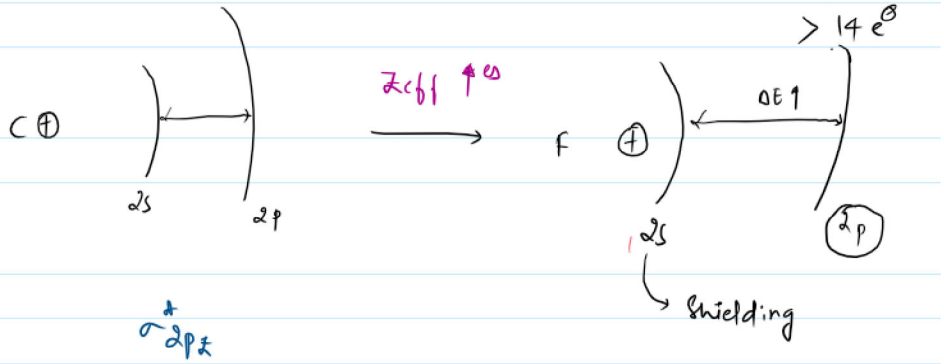
* F_2

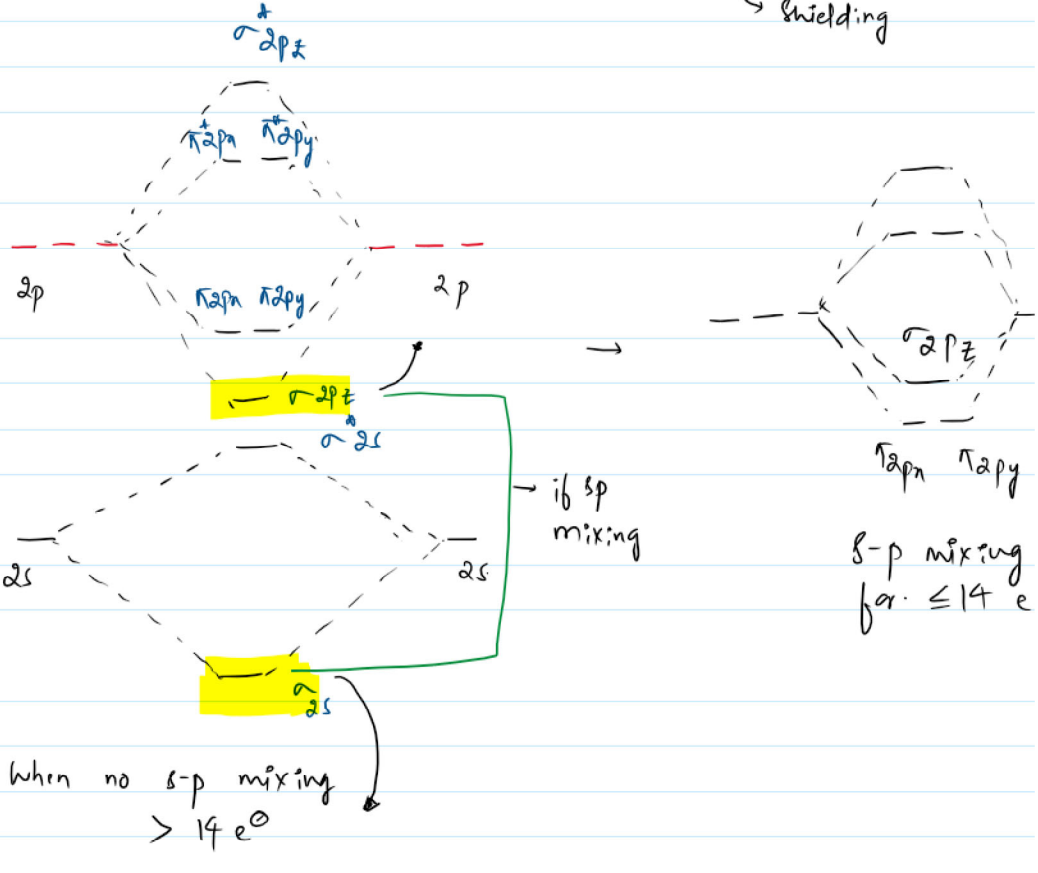
O_2 & F_2 have diff MOT because of no s-p mix

s-p mixing :



NO sp mixi





Heteronuclear diatomic Molecules

[HF, $OH^{\ominus}$, CO, CO^{+}, NO, $CN^{\ominus}$]

→ AB

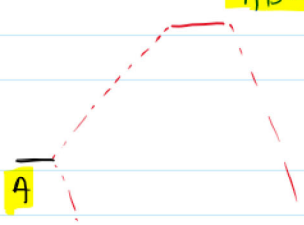
$\chi_B > \chi_A$

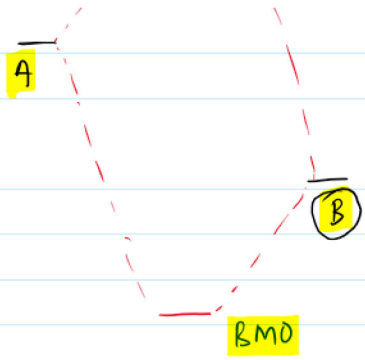
ABMO

(matching) (similar)

BMO will resemble more with more

ABMO will resemble more with less

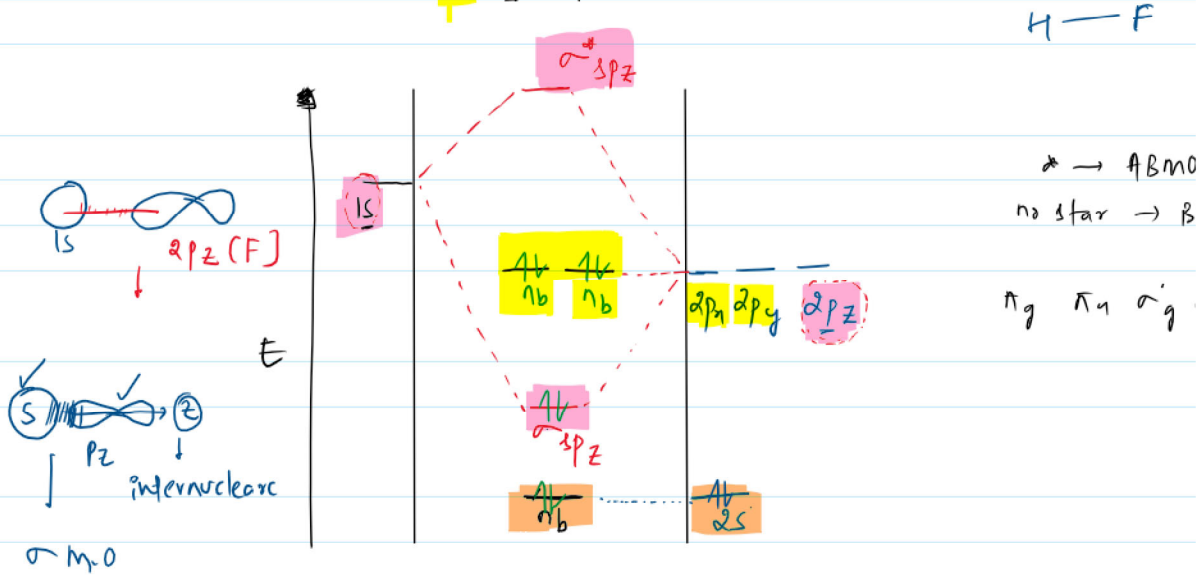




① HF : $H \rightarrow 1s^1$
$F \rightarrow 1s^2 2s^2 2p^5$

E.N : $\chi_F >>> \chi_H$

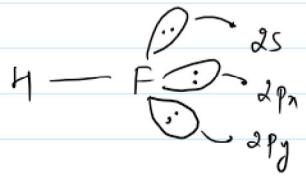
H — F



① HOMO (Highest occupied M.O) : Non Bondinding [π_x, π_y]

② LUMO : (Lowest unoccupied M.O] : σ^*_{1pz} [antibonding]

③ B.O : $\frac{1}{2}[n_b - n_a] = \frac{1}{2}[2-0] = \frac{2}{2} =$ ①

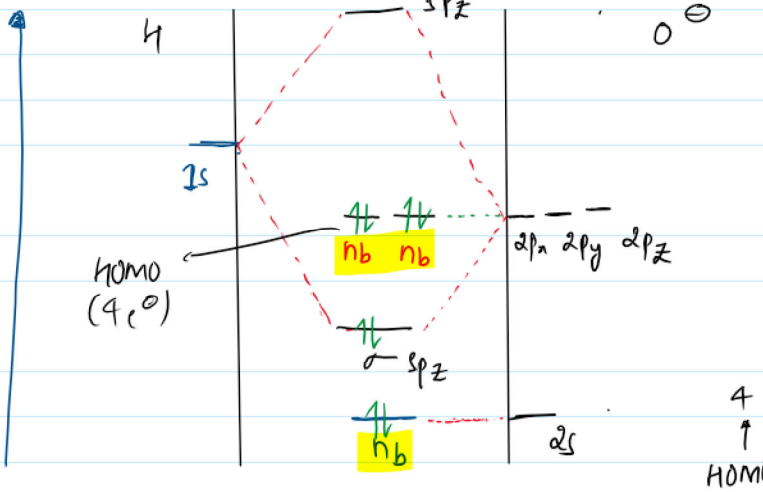


② $O^{\ominus} \rightarrow H \rightarrow 1s^1$
$O^{\ominus} \rightarrow 1s^2 2s^2 2p^5 \rightarrow$ (F)

LUMO = 0 $e^{\ominus}$

σ^*_{1pz}

$O^{\ominus} \rightarrow 1s^2 2s^2 2p^6 \rightarrow (F)$



① B.O = $\frac{1}{2}$ (

= $\frac{1}{2}$ [a -

+10

(

4 + 0 = 4

↑ ↑

HOMO + LUMO

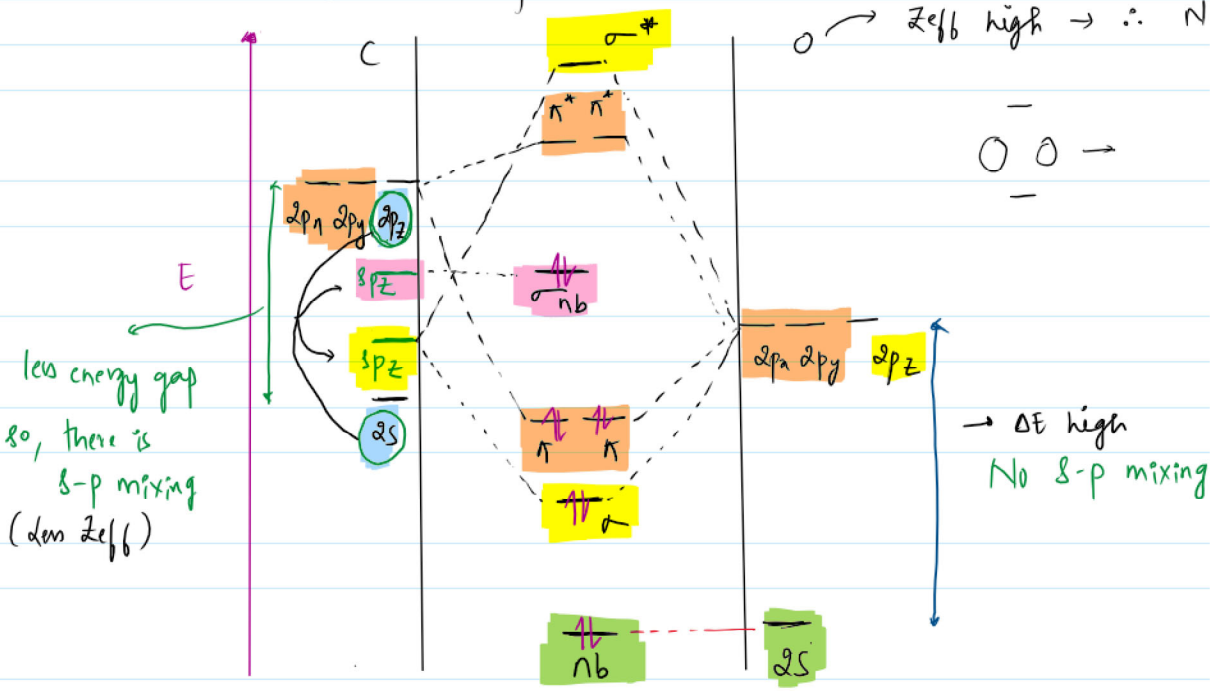
Q How many $e^{\ominus}$ are present in the frontier orbitals of

(a) 2 (b) 6 (c) 4 (d) 0

Q How many $e^{\ominus}$ nb M.O of HF → (6) $e^{\ominus}$ ✓

③ CO: C → $2s^2 2p^2$

O → $2s^2 2p^4$



O → Zeff high → ∴ N

O O →

Characteristics of CO MO Diagram

① HOMO : σ_{nB} [with some antibonding character]

① HOMO : σ_{nB} [with some antibonding character]

② LUMO : π^* [ABMO]

③ B.O of CO $= \frac{1}{2}[n_B - n_A] = \frac{1}{2}[6-0] = \frac{6}{2} = 3$

④ B.O of $CO^{\oplus}$ =

$$CO \xrightarrow{-e^{\ominus}} CO^{\oplus}$$

B.O of $CO^{\oplus} > 3 \simeq 3.5$

B.O of $CO^{\oplus}$ is greater than CO, $e^{\ominus}$ is removing which has some antibonding.

⑤ B.O of $CO^{\ominus}$: $\frac{1}{2}[n_B - n_A]$

$= \frac{1}{2}[6-1] = 2.5$

B.O comparision for : $CO^{\oplus} > CO > CO^{\ominus}$

$\simeq 3.5 \quad 3 \quad 2.5$

Thank you :)

Q