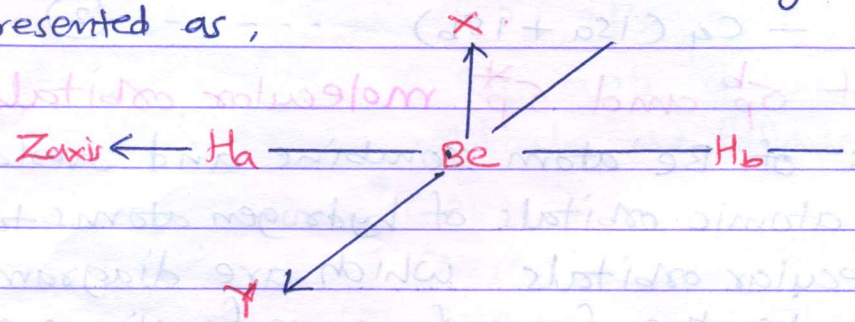
Linear Triatomic molecule – BeH_2 molecule

BeH_2 is linear triatomic molecule. Consider Z axis as the molecular axis the 3 co-ordinate system for BeH_2 molecule represented as,

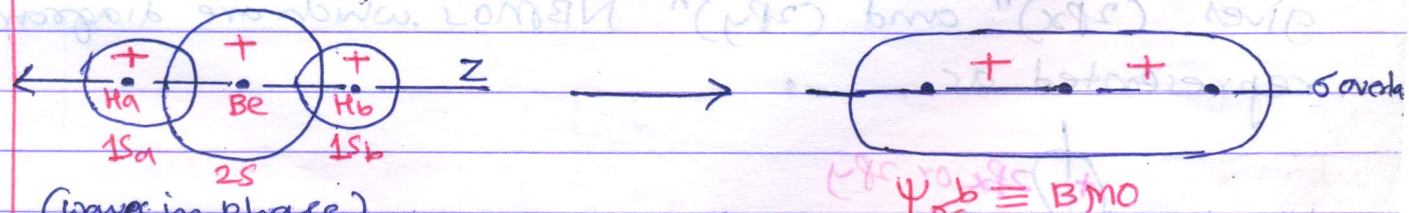


The electronic configns of atoms in BeH_2 molecule is given as

* Be (Z=4) – $1s^2, 2s^2$
* Ha (Z=1) – $1s_a^1$
* Hb (Z=1) – $1s_b^1$

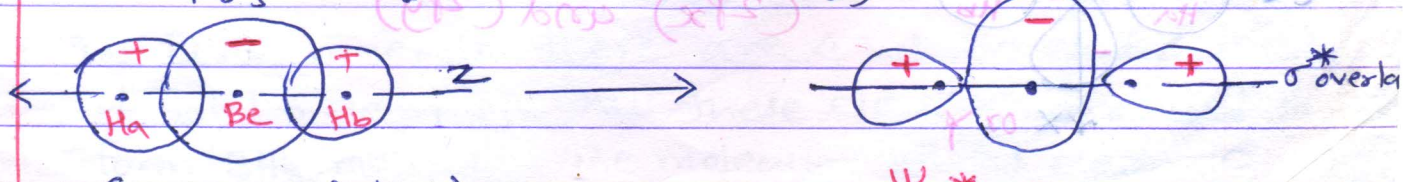
For the formation of BeH_2 molecule, only 2s & $2p_z$ valence atomic orbitals of Be involved in bonding, while $2p_x$ & $2p_y$ atomic orbitals of Be atom have π character and zero overlap with $1s_a$ & $1s_b$ atomic orbitals hydrogen atoms hence cannot play any role in bonding of BeH_2 molecule and remains as non-bonding.

(A) Formation of σ_s^b σ_s^* molecular orbitals – 2s atomic orbital of Be overlap and combine with two $1s_a$ and $1s_b$ atomic orbitals of the hydrogen atoms to form σ_s^b (BMO) and σ_s^* (ABMO) which are represented diagrammatically and in the form of wave function as follows.



$\Psi_{\sigma_s^b} \equiv$ BMO

$$\Psi_{\sigma_s^b} = C_1 2s + C_2 (1s_a + 1s_b) \quad \text{---------} (1)$$

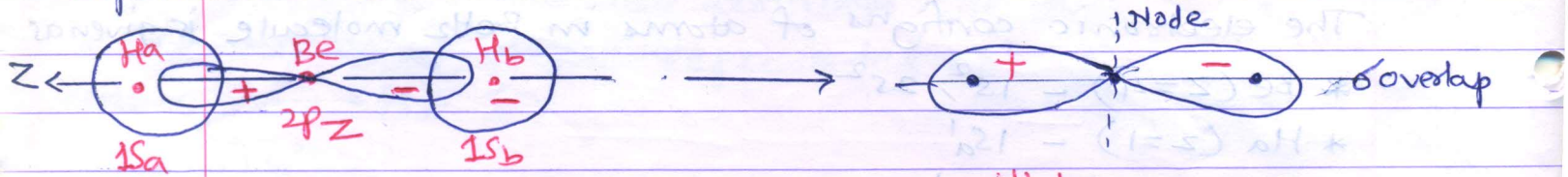


$\Psi_{\sigma_s^*} \equiv$ ABMO

$$\psi_{\sigma_s^*} = C_3\,2s - C_4(1s_a + 1s_b) \quad \text{-------(2)}$$

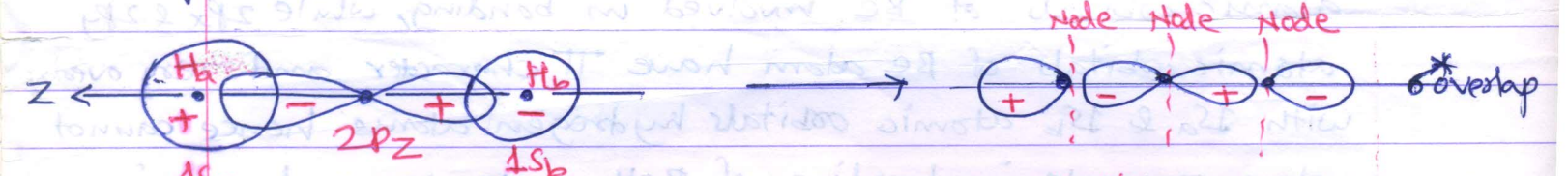
(B) Formation of σ_p^b and σ_p^* molecular orbitals —

The $2p_z$ orbitals of Be atom combine and overlap with two $1s_a$ & $1s_b$ atomic orbitals of hydrogen atoms to give σ_p^b and σ_p^* molecular orbitals which are diagramatically represented and in the form of wave functions as follows



$\psi_{\sigma_p^b} \equiv$ BMO

$$\psi_{\sigma_p^b} = C_5\,2p_z + C_6(1s_a + 1s_b) \quad \text{-------(3)}$$

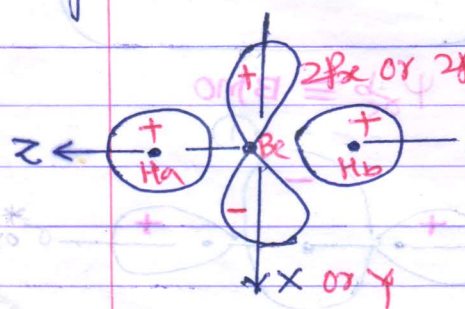


$\psi_{\sigma_p^*} \equiv$ ABMO

$$\psi_{\sigma_p^*} = C_7\,2p_z - C_8(1s_a - 1s_b) \quad \text{-------(4)}$$

(C) Formation of two non bonding molecular orbitals (NBMO)-

The $2p_x$ & $2p_y$ atomic orbitals of Be atom overlap & combine with two $1s_a$ & $1s_b$ atomic orbitals of hydrogen atoms gives $(2p_x)^n$ and $(2p_y)^n$ NBMO's which are diagramatically represented as,



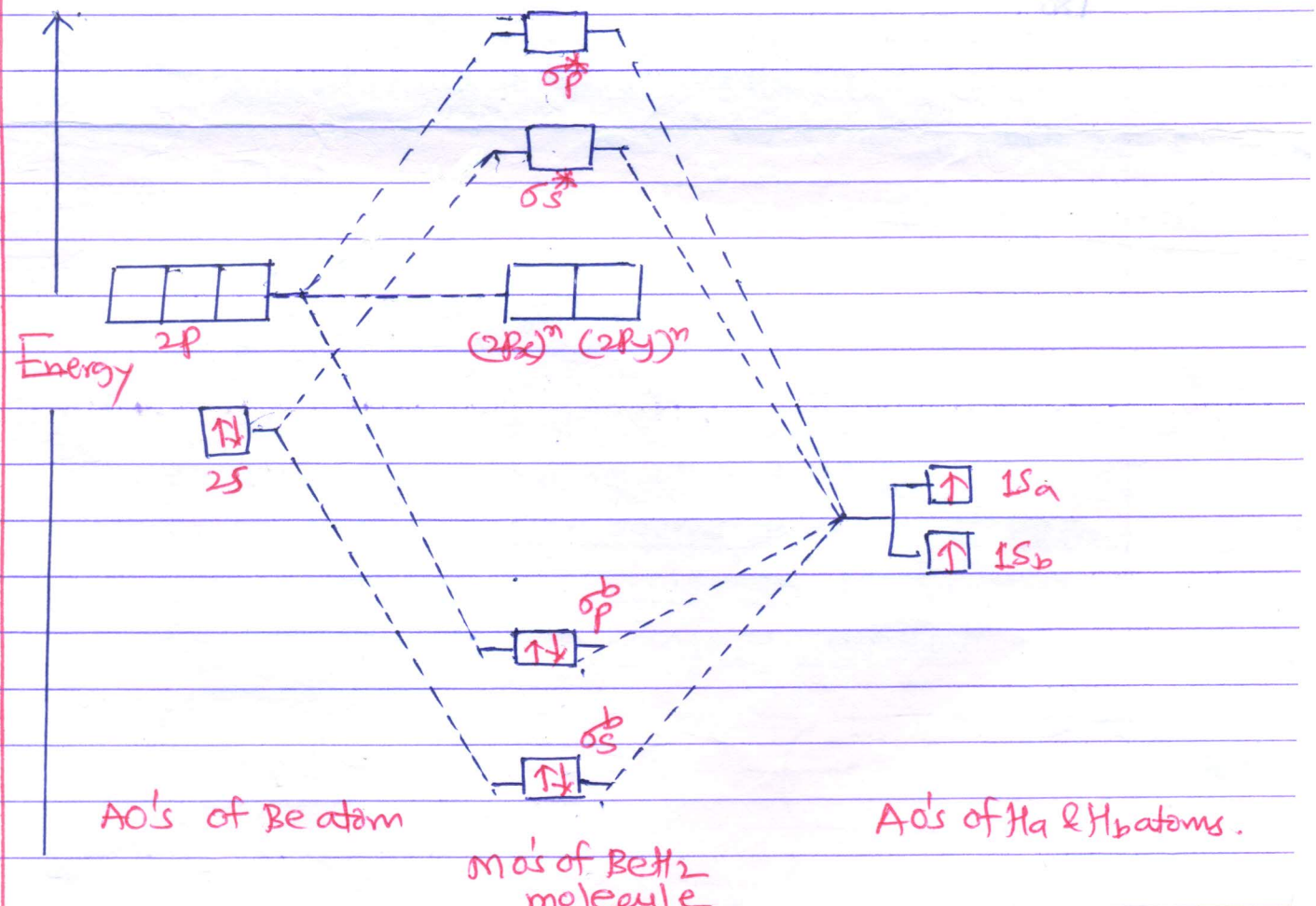
$(2p_x)^n$ and $(2p_y)^n$

Molecular orbital energy level diagram –

The molecular orbitals formed due to overlap and combination of ~~ao's of~~ 2s, 2px, 2py, 2pz ao's of Be atom with $1s_a$ & $1s_b$ ao's of hydrogen atoms. gives six molecular orbitals as follows.

1) σ_s^b (BMO) & σ_s^* (ABMO)
2) σ_p^b (BMO) & σ_p^* (ABMO)
3) $(2p_x)^n$ & $(2p_y)^n$ (NBMO)

Thus two BMO (σ_s^b, σ_p^b), ABMO (σ_s^*, σ_p^*), NBMO ($2p_x^n$, $2p_y^n$) are arranged according to increasing order of energy as σ_s^b, σ_p^b, ~~$(2p_x)^n$~~ $(2p_y)^n$, σ_s^*, σ_p^* in following molecular orbital energy level diagram as.



In BeH_2 molecule, there are 4 valence electrons out of total 6 electrons. Thus these electrons are used to form BeH_2 molecule. The molecular orbital electronic

config of BeH_2 molecule given as.

BeH_2 $[K(\sigma_s^b)^2(\sigma_p^b)^2]$

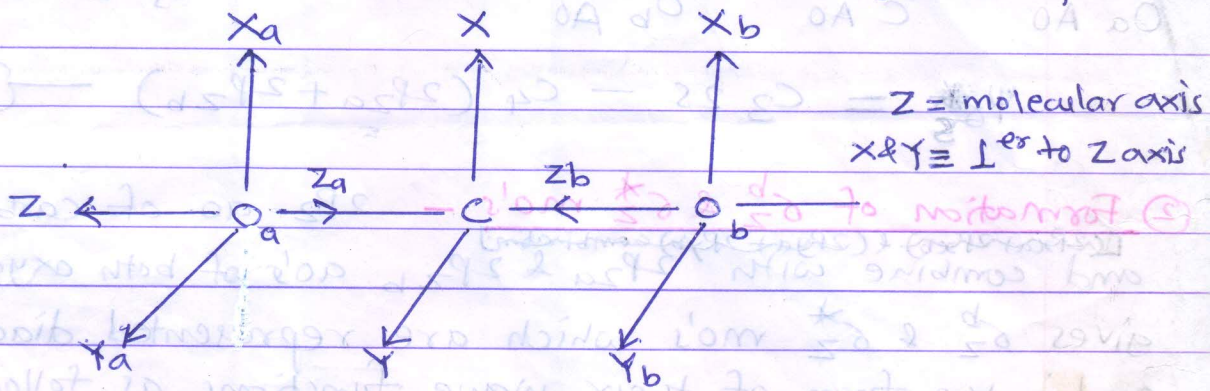
The four valence electrons (2 electrons in 2s atomic orbital of Be and two electrons in $1s_a$ & $1s_b$ atomic orbitals of both hydrogen atoms) occupy $(\sigma_s^b)^2$ & $(\sigma_p^b)^2$ BMO's. So that these two electron pairs form two σ bonds. The total bond order of BeH_2 molecule is two, i.e. there are two equivalent Be–H_a as well as Be–H_b single σ covalent bonds making angle 180°. confirms the BeH_2 triatomic molecule is ~~se~~ linear represented as

H_a — Be — H_b

180°.

Linear triatomic molecule with π bonds : CO_2 molecule

The CO_2 molecule is an example of linear triatomic molecule. The CO_2 molecule in co-ordinate system represented



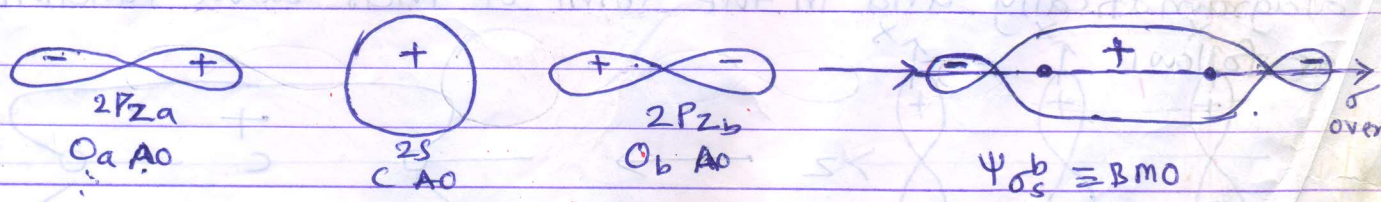
The electronic configuration of atoms in CO_2 molecule is given as

* Carbon (Z=6) – $1s^2, 2s^2, 2p^2$
* Oxygen (a) (Z=8) – $1s_a^2, 2s_a^2, 2p_a^4$
* Oxygen (b) (Z=8) – $1s_b^2, 2s_b^2, 2p_b^4$

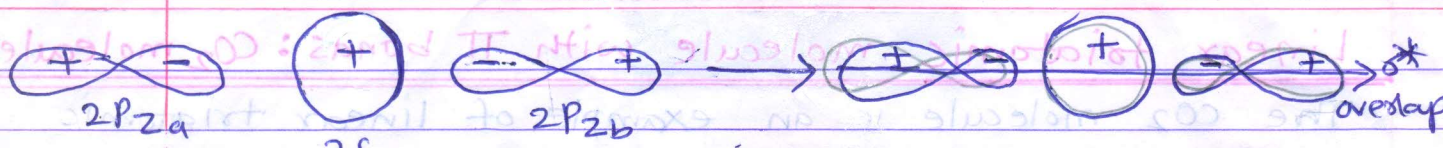
Formation of Molecular orbitals – According to LCAO princip σ, π and non-bonding molecular orbitals formed in the CO_2 molecule

(A) Formation of σ mo's – 2s and $2p_z$ ao's of carbon combine and overlap with $2p_z$ orbitals of O_a and O_b give σ mo's as follows.

(1) Formation of σ_s^b and σ_s^* mo's – 2s ao of carbon overlap and combine with $2p_{za}$ and $2p_{z_b}$ ao's of both oxygen atoms gives σ_s^b (BMO) and σ_s^* (ABMO) which are represented diagramatically and in the form of their wave functions as follows.



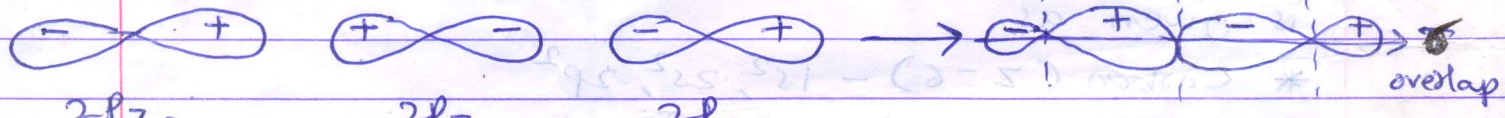
$$\Psi_{\sigma_s^b} = c_1 2s + c_2 (2p_{za} + 2p_{zb}) \quad \text{—— (1)}$$



Oa AO C AO Ob AO $\psi_{\sigma_s^*} \equiv$ ABMO

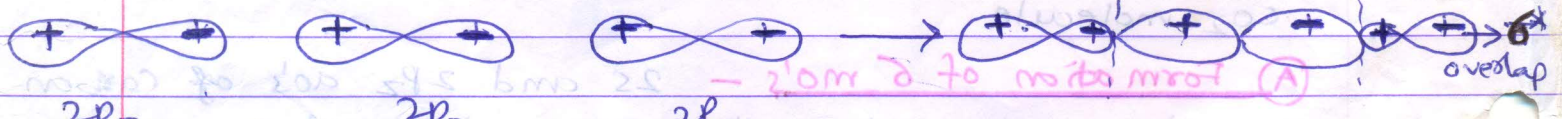
$$\psi_{\sigma_s^*} = c_3\, 2S - c_4 (2p_{z_a} + 2p_{z_b}) \quad \text{---(2)}$$

(2) Formation of σ_z^b & σ_z^* mo's — 2Pz ao of carbon overlap and combine with $2p_{z_a}$ & $2p_{z_b}$ ao's of both oxygen atoms gives σ_z^b & σ_z^* mo's which are represented diagramatically and in the form of their wave functions as follows.



Oa AO C AO C AO $\psi_{\sigma_z^b} \equiv$ BMO

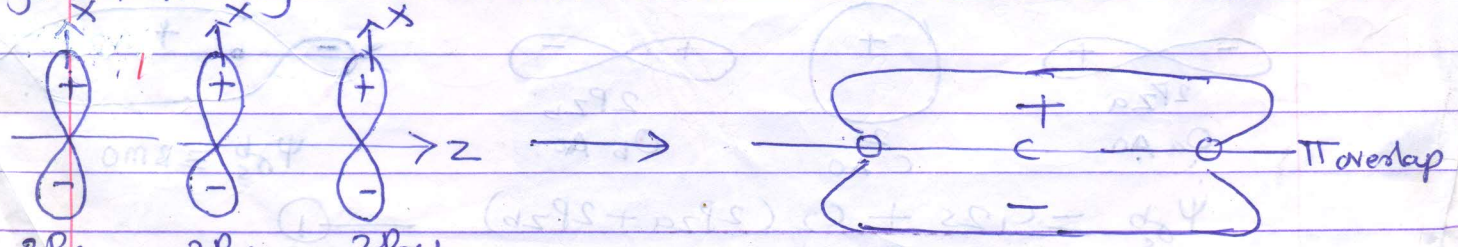
$$\psi_{\sigma_z^b} = c_5 2p_z + c_6 (2p_{z_a} - 2p_{z_b}) \quad \text{---(3)}$$



Oa AO C AO Ob AO' $\psi_{\sigma_z^*} \equiv$ ABMO

$$\psi_{\sigma_z^*} = c_7 2p_z + c_8 (2p_{z_a} + 2p_{z_b}) \quad \text{---(4)}$$

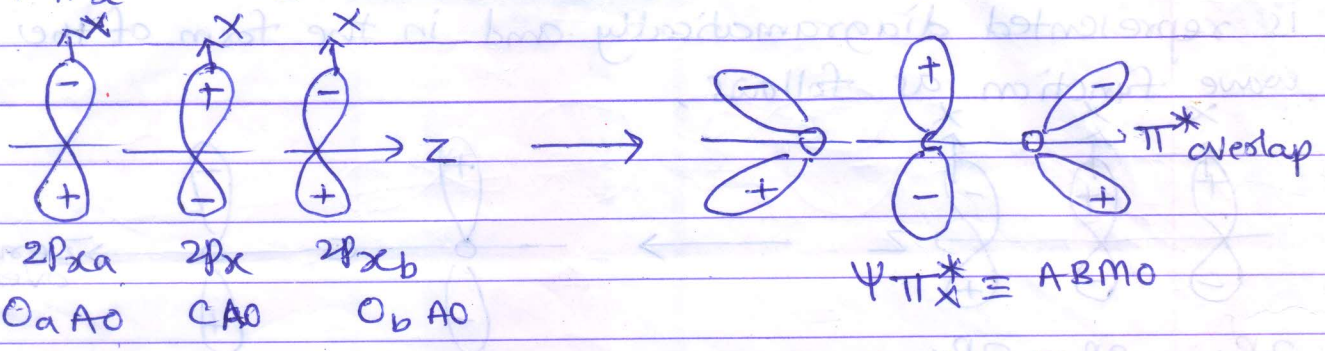
(B) Formation of π mo's — 2Px ao of carbon overlap and combine with 2Pxa and 2Pxb ao's of both oxygen atoms gives π_x^b (BMO) and π_x^* (ABMO) which are represented diagramatically and in the form of their wave functions as



2Pxa 2Px 2Pxb

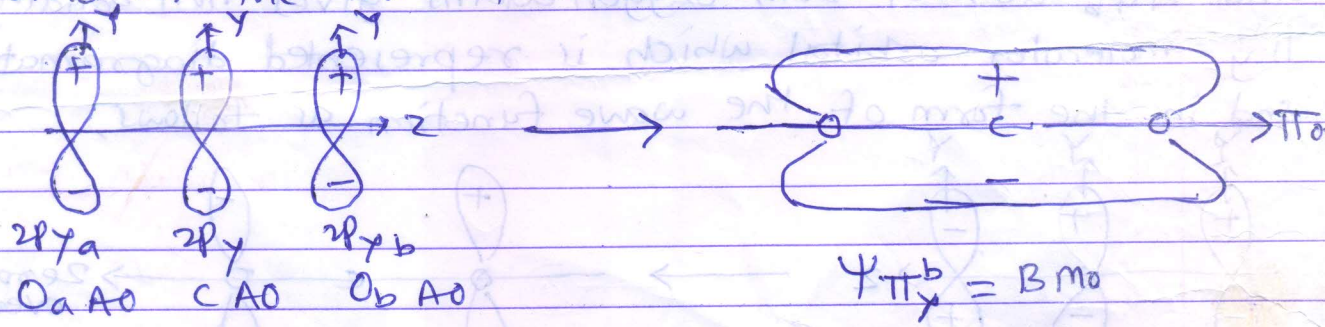
Oa AO's C AO Ob AO's $\psi_{\pi_x^b} \equiv$ BMO

$$\psi_{\pi^b_x} = c_9\, 2p_x + c_{10}(2p_{xa} + 2p_{xb}) \quad \text{—(5)}$$

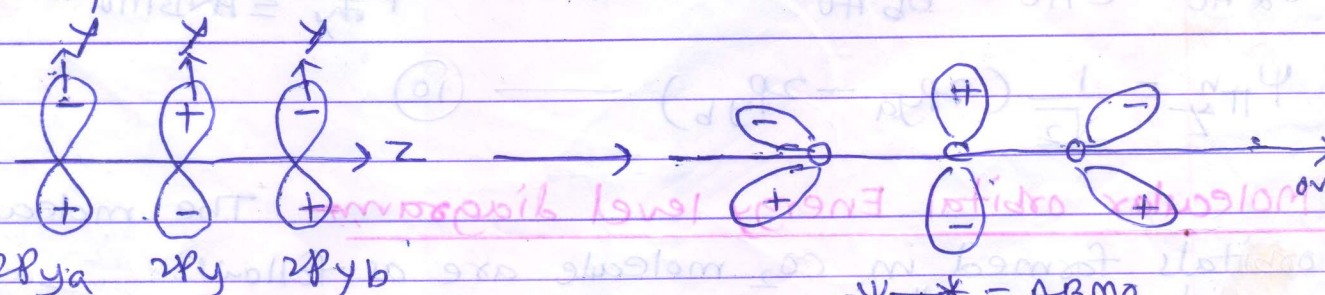


$$\psi_{\pi^*_x} = c_{11}\, 2p_x - c_{12}(2p_{xa} + 2p_{xb}) \quad \text{—(6)}$$

Similary $2p_y$ ao of carbon overlap and combine with $2p_{ya}$ and $2p_{yb}$ ao's of both oxygen atoms gives π^b_y (BMO) and π^*_y (ABMO) which are represented diagramatically and in the form of their wave functions as follows



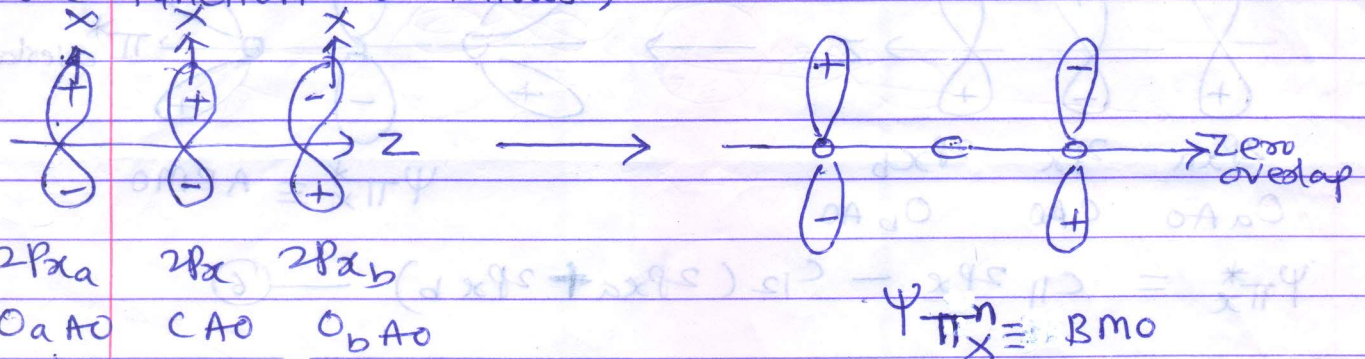
$$\psi_{\pi^b_y} = c_{13}\, 2p_y + c_{14}(2p_{ya} + 2p_{yb}) \quad \text{—(7)}$$



$$\psi_{\pi^*_y} = c_{15}\, 2p_y - c_{16}(2p_{ya} + 2p_{yb}) \quad \text{—(8)}$$

(c) Formation of Non-bonding molecular orbitals - [$(2p_{xa} - 2p_{xb})$ and $(2p_{ya} - 2p_{yb})$ combinations] - The $2p_x$ ao of carbon combine and overlap with $2p_{xa}$ and $2p_{xb}$ of both

oxygen atom gives nonbanding π^n_x molecular orbital which is represented diagramatically and in the form of the wave function as follows,

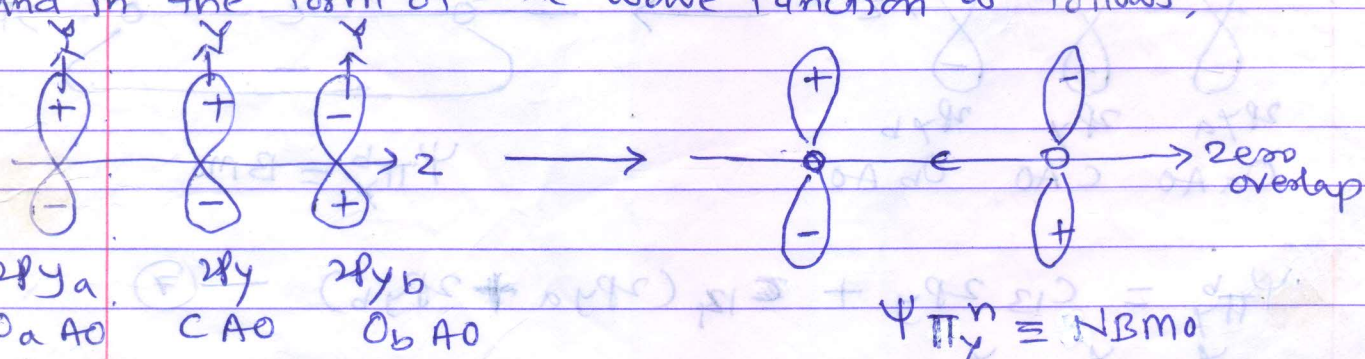


$2p_{xa}$ $2p_x$ $2p_{xb}$
O_a AO CAO O_b AO

$\psi_{\pi^n_x} \equiv$ BMO

$$\psi_{\pi^n_x} = \frac{1}{\sqrt{2}}(2p_{xa} - 2p_{xb}) \quad \text{——} (9)$$

Similarly, 2py ao of carbon overlap and combine with $2p_{y_a}$ and $2p_{y_b}$ ao's of both oxygen atoms gives non bonding π^n_y molecular orbital which is represented diagramatically and in the form of the wave function as follows,



$2p_{y_a}$ $2p_y$ $2p_{y_b}$
O_a AO CAO O_b AO

$\psi_{\pi^n_y} \equiv$ NBMO

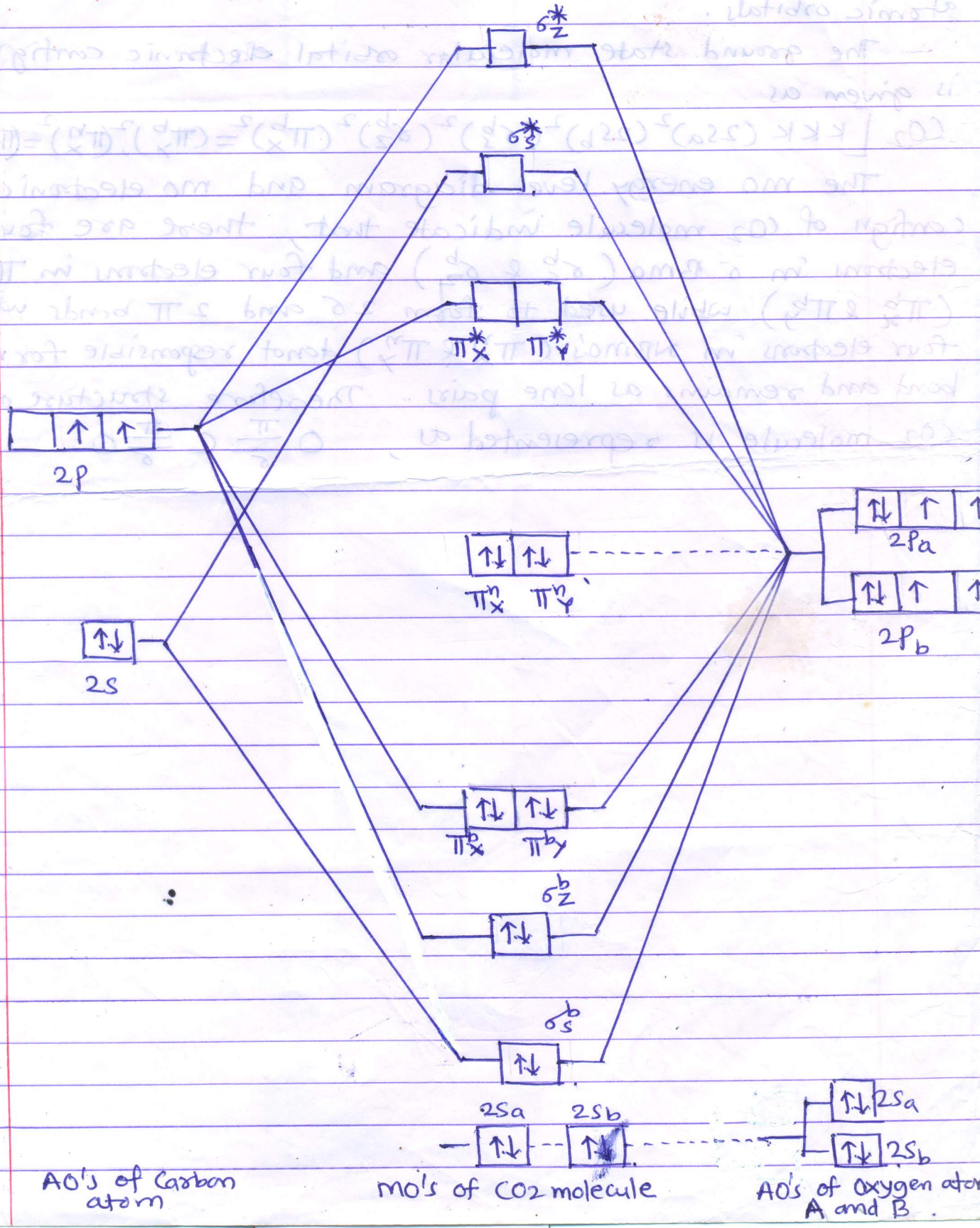
$$\psi_{\pi^n_y} = \frac{1}{\sqrt{2}}(2p_{y_a} - 2p_{y_b}) \quad \text{——} (10)$$

Molecular orbital Energy level diagram — The molecular orbitals formed in CO_2 molecule are as follows.

① σ^b_s (BMO) & σ^*_s (ABMO) ⟶ 2 mo's
② σ^b_z (BMO) & σ^*_z (ABMO) ⟶ 2 mo's
③ π^b_x (BMO) & π^*_x (ABMO) ⟶ 2 mo's
④ π^b_y (BMO) & π^*_y (ABMO) ⟶ 2 mo's
⑤ π^n_x and π^n_y (NBMO's) ⟶ 2 mo's

Total Ten mo's formed

These ten molecular orbitals formed arranged according to increasing order of energy in the following molecular orbital energy level diagram as follows.



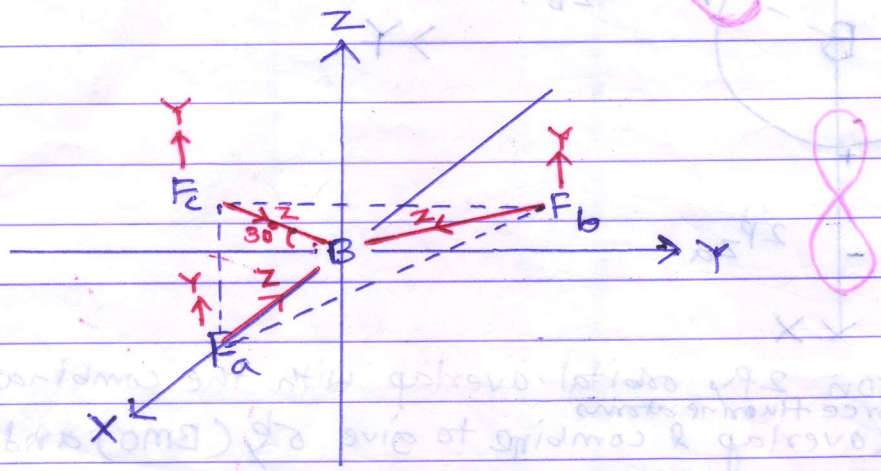
The 2s orbitals of O_a & O_b are of too low energy hence they are not involved in molecular orbital formation. The oxygen orbitals are more stable than carbon atomic orbitals.

The ground state molecular orbital electronic confign is given as.

CO_2 $\left[KKK\,(2s_a)^2(2s_b)^2(\sigma^b_s)^2(\sigma^b_z)^2(\pi^b_x)^2=(\pi^b_y)^2,(\pi^n_x)^2=(\pi^n_y)^2\right]$

The mo energy level diagram and mo electronic confign of CO_2 molecule indicate that, there are four electrons in σ BMO (σ^b_s & σ^b_z) and four electrons in π BMOs (π^b_x & π^b_y) are used to form 2σ and 2π bonds while four electrons in NBMOs (π^n_x & π^n_y) donot responsible for making bond and remains as lone pairs. Therefore structure of CO_2 molecule is represented as, $O \underset{\sigma}{\overset{\pi}{=}} C \underset{\sigma}{\overset{\pi}{=}} O$.

Trigonal planar molecule : BF_3 molecule — Boron trifluo has trigonal planar structure with all F–B–F bond angles 120°. The BF_3 molecule represent in co-ordinate system as



Fa coincides with X-axis, Fb & Fc make angle 30° with +Y and −Y axis. Fa, Fb and Fc alongwith Boron are in one plane.

The electronic config^n of B, Fa, Fb & Fc in the BF_3 molecule is represented as,

Boron (Z=5) – $1s^2, 2s^2, 2p^1$

Fluorine a (Z=9) – $1s_a^2, 2s_a^2, 2p_a^5$

Fluorine b (Z=9) – $1s_b^2, 2s_b^2, 2p_b^5$

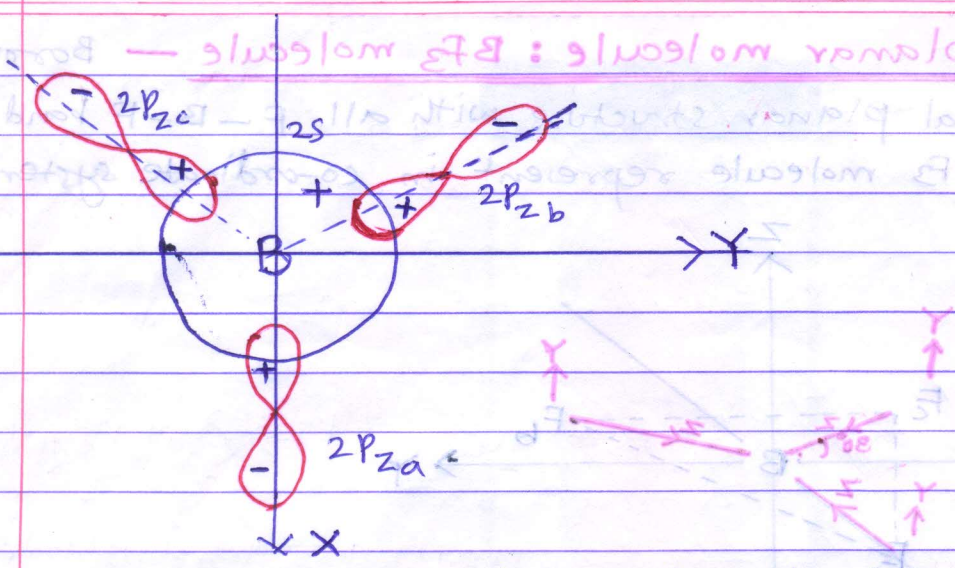
Fluorine c (Z=9) – $1s_c^2, 2s_c^2, 2p_c^5$

Formation of molecular orbital in BF_3 molecule – The mo's formed by linear combination of appropriate ao's of Boron & three Fluorine atoms given as follows.

(A) Formation of σ MO's – ① 2s ao of Boron and ($2p_{za} + 2p_{zb} + 2p_{zc}$) ao's of three fluorine atoms combine & overlap to gi σ_s^b (BMO) and σ_s^* (ABMO) which are represented diagramma and in the form of wave functions as follows:

$$\psi_{\sigma_s^b} = c_1 2s + c_2 (2p_{za} + 2p_{zb} + 2p_{zc}) \quad \text{——①}$$

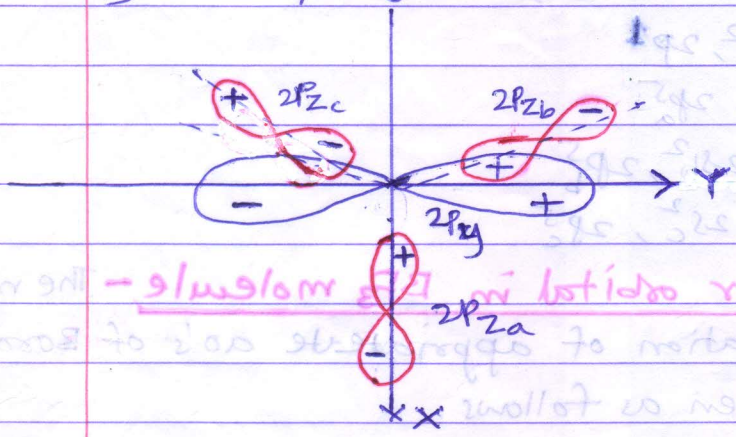
$$\psi_{\sigma_s^*} = c_3 2s - c_4 (2p_{za} + 2p_{zb} + 2p_{zc}) \quad \text{——②}$$



② Similarly Boron 2Py orbital overlap with the combination of $(2P_{z_b} - 2P_{z_c})$ of three fluorine atoms overlap & combine to give σ^b_y (BMO) and σ^*_y (ABMO) which are represented diagramatically & in the form of their wave functions as follows

$$\psi_{\sigma^b_y} = c_5 2P_y + c_6 (2P_{z_b} - 2P_{z_c}) \quad \text{——— (3)}$$

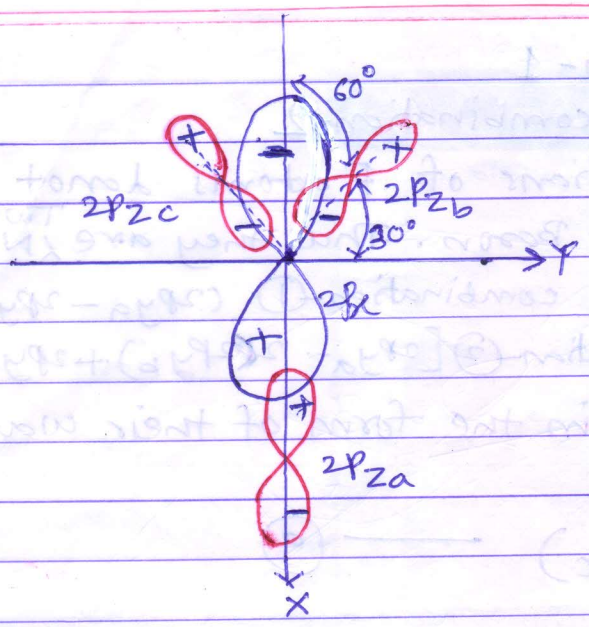
$$\psi_{\sigma^*_y} = c_7 2P_y - c_8 (2P_{z_b} - 2P_{z_c}) \quad \text{——— (4)}$$



③ Similarly, 2Px orbital of Boron overlap with the combination of $(2P_{z_a} - \frac{1}{2}2P_{z_b} - \frac{1}{2}2P_{z_c})$ ~~give~~ of three fluorine atoms to give σ^b_x (BMO) and σ^*_x (ABMO) which are represented diagramatically & in the form of their wave functions as follows,

$$\psi_{\sigma^b_x} = c_9 2P_x + c_{10}(2P_{z_a} - \tfrac{1}{2}2P_{z_b} - \tfrac{1}{2}2P_{z_c}) \quad \text{——— (5)}$$

$$\psi_{\sigma^*_x} = c_{11} 2P_x - c_{12}(2P_{z_a} - \tfrac{1}{2}2P_{z_b} - \tfrac{1}{2}2P_{z_c}) \quad \text{——— (6)}$$

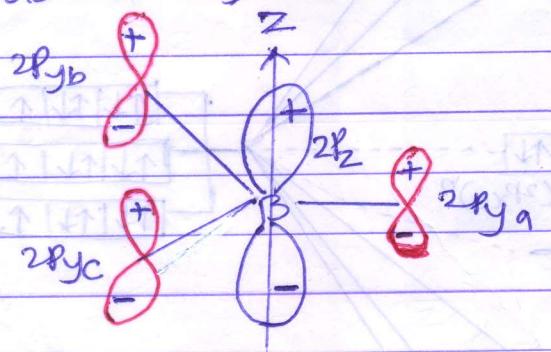


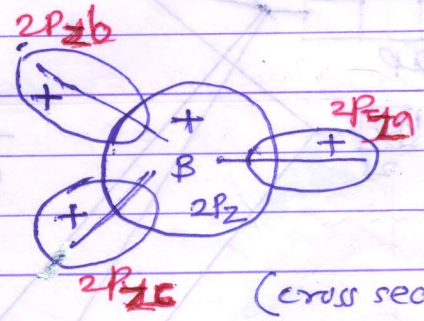
The overlap of three F ao's $2p_{za}$, $2p_{zb}$, $2p_{zc}$ with $2p_x$ ao of boron are not same. $2p_{za}$ ao point directly at the positive lobe of $2p_x$ while $2p_{zb}$ & $2p_{zc}$ ao's are 60° displaced from complete overlap with negative lobe.

$\therefore \cos\theta = \cos 60 = \frac{1}{2}$

Thus $2p_{zb}$ & $2p_{zc}$ have $\frac{1}{2}$ contribution each as compare to $2p_{za}$. Therefore proper combination is $(2p_{za} - \frac{1}{2}2p_{zb} - \frac{1}{2}$

(B) **Formation of π mo's** — $2p_z$ ao of boron overlap combine with $(2p_{ya} + 2p_{yb} + 2p_{yc})$ of three fluorine ato give π_z^b (BMO) and π_z^* (ABMO) which are represent diagramatically and in the form of their wave funct as follows.



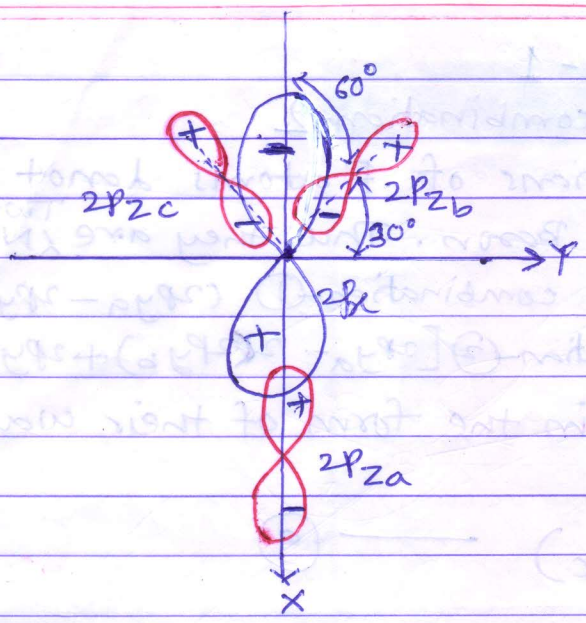


(cross section)

$$\psi_{\pi_z^b} = c_{13}\,2p_z + c_{14}(2p_{ya} + 2p_{yb} + 2p_{yc}) \quad \text{—— (7)}$$

$$\psi_{\pi_z^*} = c_{15}\,2p_z - c_{16}(2p_{ya} + 2p_{yb} + 2p_{yc}) \quad \text{—— (8)}$$

(C) **Formation of NBMO's** — $2p_{ya}$, $2p_{yb}$, $2p_{yc}$ ao's of three F ao's have two independent combinations such as

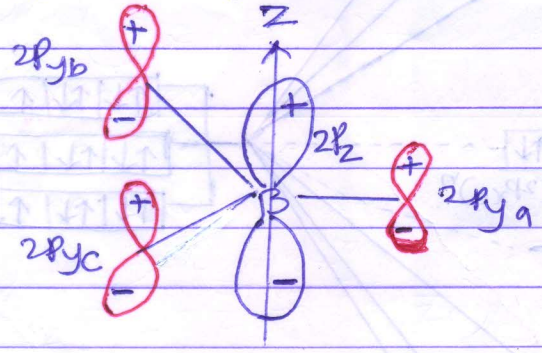


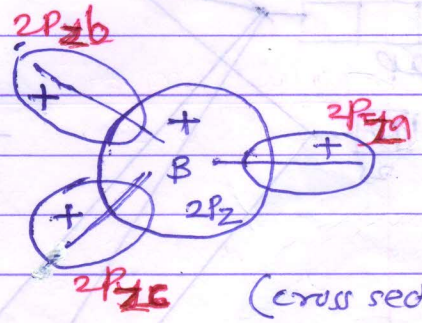
The overlap of three F ao's $2p_{za}$, $2p_{zb}$, $2p_{zc}$ with $2p_x$ ao of boron are not same. $2p_{za}$ ao point directly at the positive lobe of $2p_x$ while $2p_{zb}$ & $2p_{zc}$ ao's are 60° displaced from complete overlap with negative lobe.

$\therefore \cos\theta = \cos 60 = \frac{1}{2}$

Thus $2p_{zb}$ & $2p_{zc}$ have $\frac{1}{2}$ contribution each as compare to $2p_{za}$. Therefore proper combination is $(2p_{za} - \frac{1}{2}2p_{zb} - \frac{1}{2}$

(B) **Formation of π mo's** — $2p_z$ ao of boron overlap a combine with $(2p_{ya} + 2p_{yb} + 2p_{yc})$ of three fluorine atom give π_z^b (BMO) and π_z^* (ABMO) which are represente diagramatically and in the form of their wave functi as follows.





(cross section)

$$\psi_{\pi_z^b} = c_{13}\,2p_z + c_{14}(2p_{ya} + 2p_{yb} + 2p_{yc}) \quad \text{—— (7)}$$

$$\psi_{\pi_z^*} = c_{15}\,2p_z - c_{16}(2p_{ya} + 2p_{yb} + 2p_{yc}) \quad \text{—— (8)}$$

(C) **Formation of NBMO's** — $2p_{ya}$, $2p_{yb}$, $2p_{yc}$ ao's of three F ao's have two independent combinations such as

① $(2p_{y_a} - 2p_{y_c})$ combination-1

② $[2p_{y_a} - 2(2p_{y_b}) + 2p_{y_c}]$ combination-2

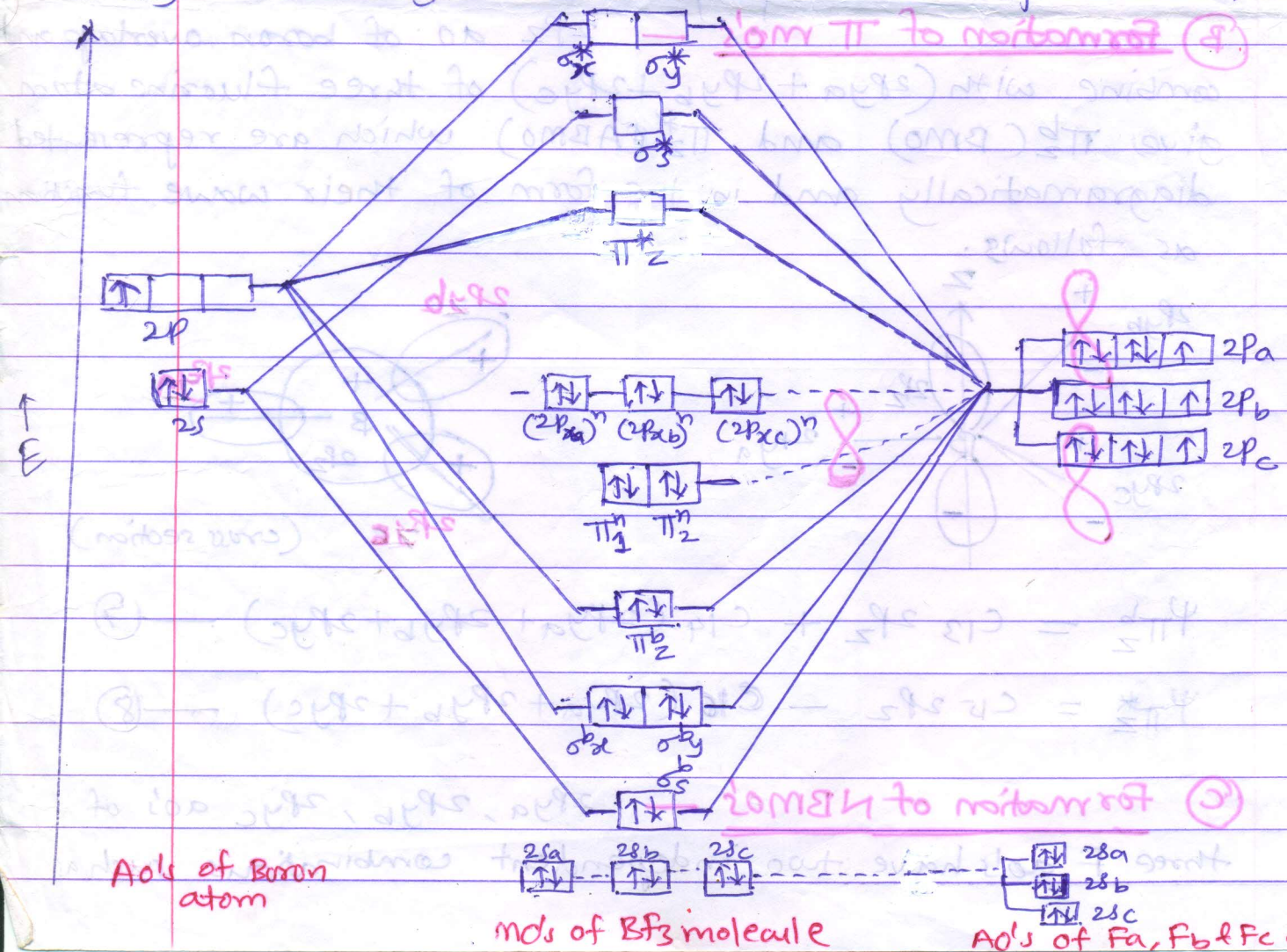
These two orbital combinations of F atoms do not overlap and combine with $2p_z$ ao of Boron. Thus they are Two NBMO in BF_3 as π_1^n (formed due to combination-① $(2p_{y_a} - 2p_{y_c})$) and π_2^n (formed due to combination-② $[2p_{y_a} - 2(2p_{y_b}) + 2p_{y_c}]$

These NBMO's are represent in the form of their wave functions as follows.

$$\psi_{\pi_1^n} = \frac{1}{\sqrt{2}}(2p_{y_a} - 2p_{y_c}) \quad \text{——— (9)}$$

$$\psi_{\pi_2^n} = \frac{1}{\sqrt{6}}(2p_{y_a} - 2(2p_{y_b}) + 2p_{y_c}) \quad \text{——— (10)}$$

MO energy level diagram of BF_3 molecule — The MO energy level diagram of BF_3 molecule is represented as,



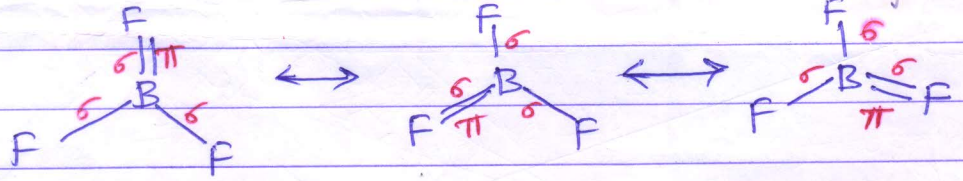
The valence ao's (2s & 2p) of F are more stable than the valence aos (2s & 2p) of B hence electrons in BMo's are more closer to Fluorine nuclei. The σ^b_z & σ^b_y mo's ar degenerate.

There are 24 valence electrons (out of total 32 ele$^-$) in BF_3 molecule. These electr are used to form BF_3 molecule. Thus Mo electronic confi of BF_3 molecule is given as,

BF_3 [KKKK $(2s_a)^2, (2s_b)^2, (2s_c)^2, (\sigma^b_s)^2, (\sigma^b_x)^2 = (\sigma^b_y)^2, (\pi^b_z)^2, (\pi^n_1)^2 = (\pi^n_2)^2$ $(2p^n_{xa}) = (2p^n_{xb})^2 = (2p^n_{xc})^2$]

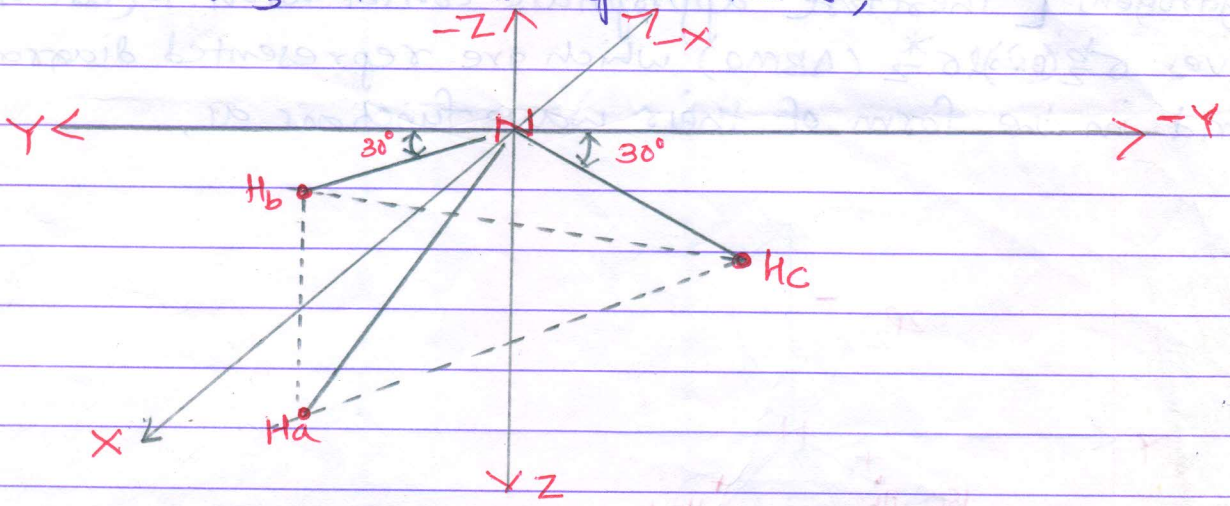
There are six electrons in σ mo's ($\sigma^b_s, \sigma^b_x, \sigma^b_y$) gives three σ bonds in BF_3 molecule, while two electrons in π mo (π^b_z) gives one π bond in BF_3 molecule. The B-F bond length in BF_3 molecule is 1.291 A°.

The structure of BF_3 molecule is represented in resonanc form



Ammonia (NH_3) molecule: Trigonal Pyramidal molecule:

Ammonia molecule has trigonal pyramidal geometry. The co-ordinate system for NH_3 molecule is represented as,



Ammonia has trigonal pyramidal structure in which three hydroge H_a, H_b and H_c are placed out of X, Y plane hence forms the base of trigonal pyramid. Therefore nitrogen observed at the ape Each N—H bond makes angle θ with Z axis. In addn to this, N—H_a is linked up with X axis, while N—H_b and N—H_c makes 30° angle with +Y and −Y axes respectively. Thus NH_3 is trigonal planar molecule. but with three peripheral hydrogen atoms bent down.

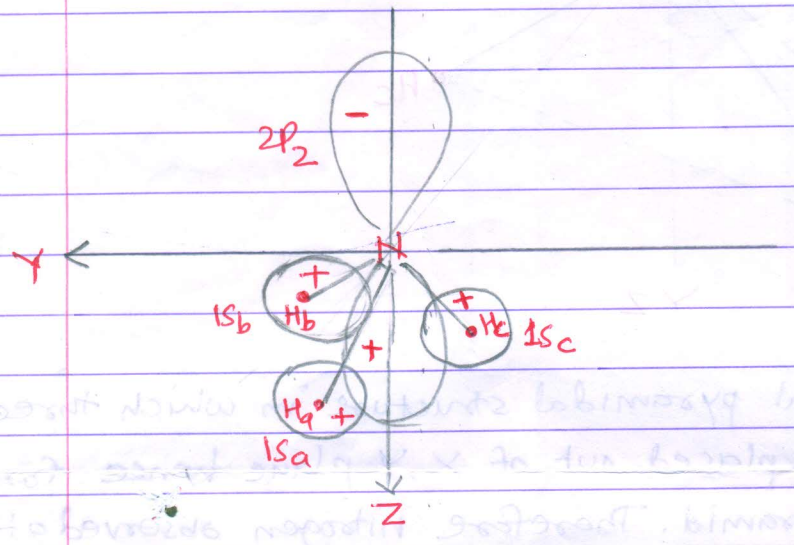
The electronic confign of atoms in NH_3 molecule is given as,

Nitrogen ($Z = 7$) − $1s^2, 2s^2, 2p^3$
Hydrogen (a) ($Z = 1$) − $1s'_a$
Hydrogen (b) ($Z = 1$) − $1s'_b$
Hydrogen (c) ($Z = 1$) − $1s'_c$

Formation of molecular orbitals — The valence orbitals of nitrogen 2s and 2p overlaps & combines with three hydrogen $1s_a$, $1s_b$, $1s_c$ ao's to give σ(BMO), σ^*(ABMO) and σ^n(NBMO in ammonia molecule.

Formation of σ molecular orbitals — In NH_3 molecule various σ BMO, σ^*ABMO & σ^n NBMO's are formed on the basis of LCAO principle as,

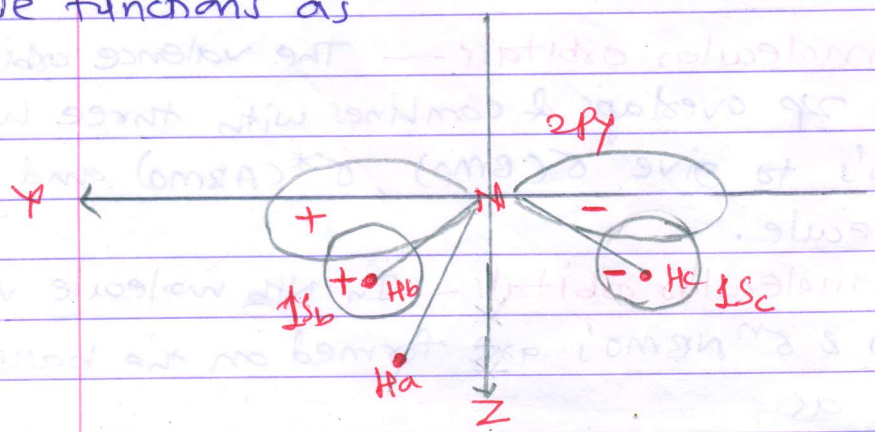
(1) Formation of σ_z^b and σ_z^* mo's — $2p_z$ ao of nitrogen combine and overlap with 1sa, 1sb & 1sc ao's of three hydrogens [Therefore appropriate combination is (1sa+1sb+1sc)] gives σ_z^b (BMO) & σ_z^* (ABMO) which are represented diagramatically and in the form of their wave functions as,



$$\psi_{\sigma_z^b} = c_1 2p_z + c_2 (1sa + 1sb + 1sc) \quad \text{——(1)}$$

$$\psi_{\sigma_z^*} = c_3 2p_z - c_4 (1sa + 1sb + 1sc) \quad \text{——(2)}$$

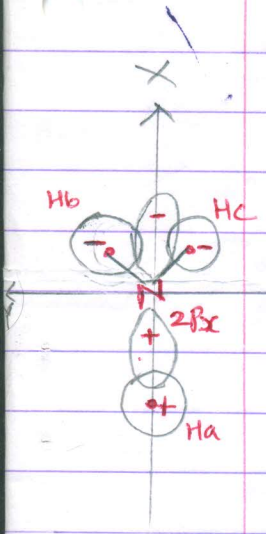
(2) Formation of σ_y^b and σ_y^* mo's — $2p_y$ ao of nitrogen combine and overlap with ~~1sa~~, 1sb & 1sc ao's of two hydrogens [Therefore appropriate combination is (1sb − 1sc)] gives σ_y^b (BMO) and σ_y^* (ABMO) which are represented diagramatically and in the form of their wave functions as



$$\psi_{\sigma_y^b} = c_5\,2p_y + c_6(1s_b - 1s_c) \quad \text{——(3)}$$

$$\psi_{\sigma_y^*} = c_7\,2p_y - c_8(1s_b - 1s_c) \quad \text{——(4)}$$

(3) Formation of σ_x^b and σ_x^* mo's — 2px ao of nitroge combines and overlaps with 1Sa, 1Sb & 1Sc of three hydrogens [Therefore appropriate combination is $(1Sa - \frac{1}{2}1Sb - \frac{1}{2}1Sc$ because 1Sb & 1Sc manke angle 60° with 2px ao hence $\cos\theta = \frac{1}{2}$ hence $\frac{1}{2}$ contribution from 1Sb and 1Sc while (overlap) full contribution from 1Sa] gives σ_x^b (Bmo) and σ_x^* (ABmo which are represented diagramatically and in the form of their wavefunctions as,



$$\psi_{\sigma_x^b} = c_9\,2p_x + c_{10}(1Sa - \tfrac{1}{2}1S_b - \tfrac{1}{2}1Sc) \quad \text{——(5)}$$

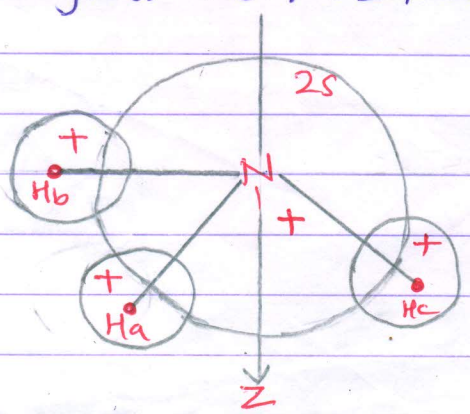
$$\psi_{\sigma_x^*} = c_{11}\,2p_x - c_{12}(1Sa - \tfrac{1}{2}1S_b - \tfrac{1}{2}1Sc) \quad \text{——(6)}$$

are equivalent doubly

since σ_x^b & σ_y^b are degenerate because both mo's have same energy similarly their corresponding σ_x^* & σ_y^* are equivalent and are doubly degenerate because both mo's have identical energy.

(4) Formation of σ_s^b and σ_z^n mo's — 2s ao of nitrogen combines and overlaps with 1Sa, 1Sb, 1Sc ao's of three hydrogen [Therefore appropriate combination is $(1Sa+1S_b+1S$ gives σ_s^b mo. This is same combination of $(1Sa+1S_b+1Sc)$ of three hydrog 1Sa, 1Sb & 1Sc ao's to give σ_z^b & σ_z^* mo's] ~~gives σ_s^b mo.~~

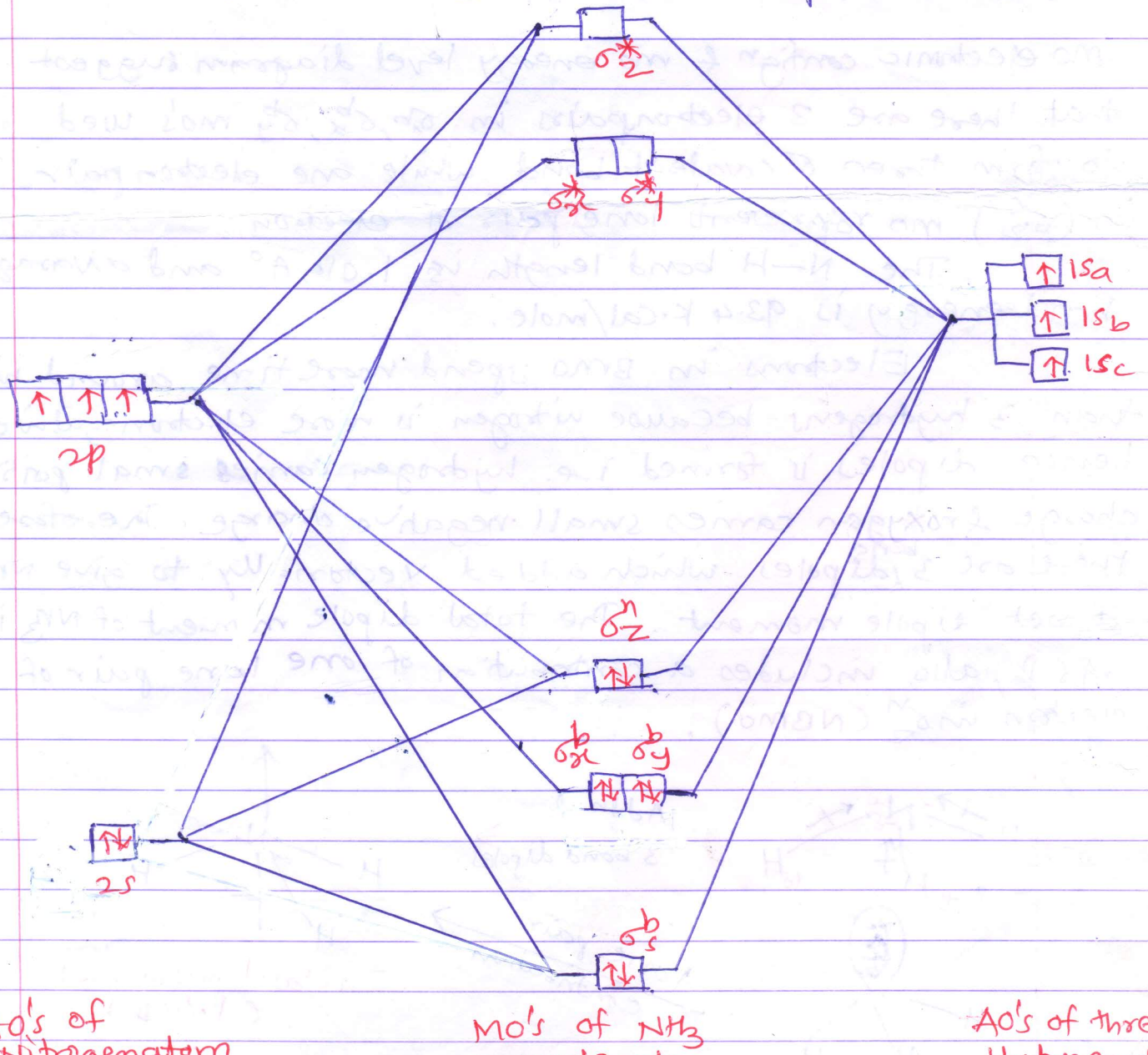
This σ_s^b mo mixes with σ_z^b & σ_z^* molecular orbitals gives σ_s^b, σ_z^n, σ_z^* mo's



The addition of 2s character from nitrogen to the N—H bonding increases the H—N—H bond angle from 90° to 107°.

The actual H—N—H bond angle in NH_3 molecule is 107°. If only 2px, 2py and 2pz orbitals of nitrogen are to be used to form NH_3 molecule then H—N—H bond angl may be 90° but actual bond angle H—N—H is 17° wide due to involvement of 2s ao of nitrogen in the bonding.

Molecular orbital energy level diagram — The mo ener level diagram of NH_3 molecule is represented as,



The ao's of nitrogen (2s & 2p) and ao's of three hydrogens ($1s_a$, $1s_b$, $1s_c$) combine and overlap linearly with each other gives (σ^b_s, σ^b_x, σ^b_y) BMO, (σ^n_z) NBMO, (σ^*_x, σ^*_y and σ^*_z) ABMO molecular orbitals represented in above mo energy level diagram.

These molecular orbitals arranged in increasing order of energy in NH_3 molecule as (σ^b_s), $(\sigma^b_x) = (\sigma^b_y)$, (σ^n_z), $(\sigma^*_x) = (\sigma^*_y)$, (σ^*_z).

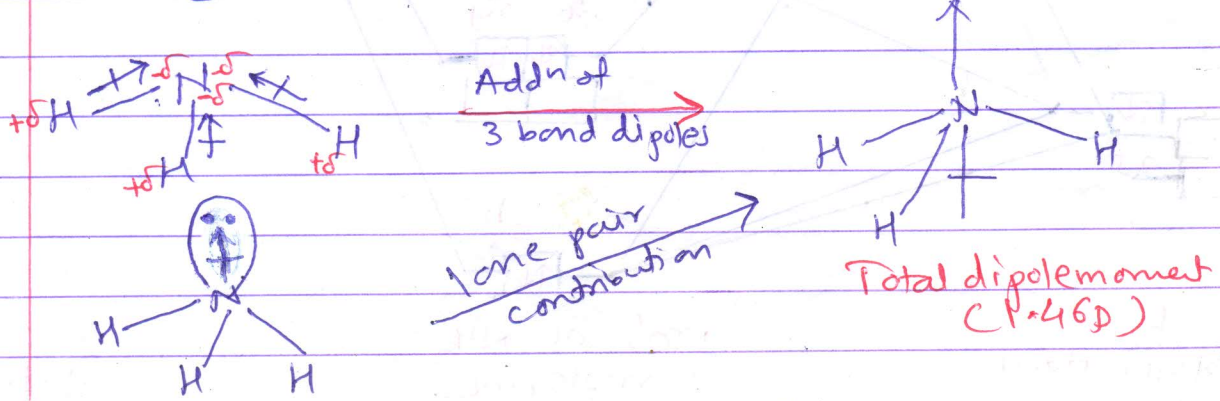
Therefore G.S. mo electronic confign of NH_3 molecule is given as,

$NH_3 \left[K(\sigma^b_s)^2, (\sigma^b_x)^2 = (\sigma^b_y)^2, (\sigma^n_z)^2\right]$

MO electronic confign & mo energy level diagram suggest that there are 3 electronpairs in $\sigma^b_s, \sigma^b_x, \sigma^b_y$ mo's used to form three σ covalent bond while one electron pair in (σ^n_z) mo represents lone pair of electron.

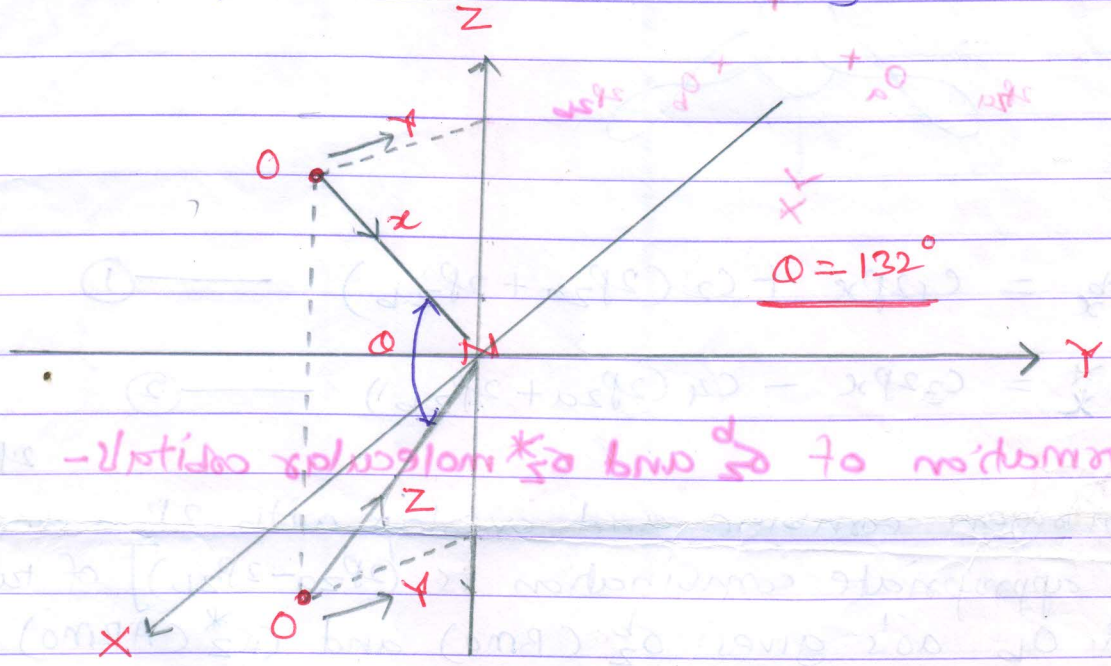
The N—H bond length is 1.014 A° and avarage bond energy is 93.4 K.cal/mole.

Electrons in BMO spend more time around nitrogen than 3 hydrogens because nitrogen is more electronegative hence dipoles is formed i.e. hydrogen carries small positive charge & nitrogen carries small negative charge. Therefore these are 3 bond dipoles which added vectorially to give NH_3 a net dipole moment. The total dipole moment of NH_3 is 1.46 D, also includes a contribution of one lone pair of electron in σ^n_z (NBMO).



Angular Triatomic molecule with π bonding :

NO_2 molecule : NO_2 molecule is an exawple of an angular triatomic molecule with both σ & π bonding In co-ordinate system, Nitrogen of NO_2 is placed at the origin of XYZ as shown in following co-ordinate system,

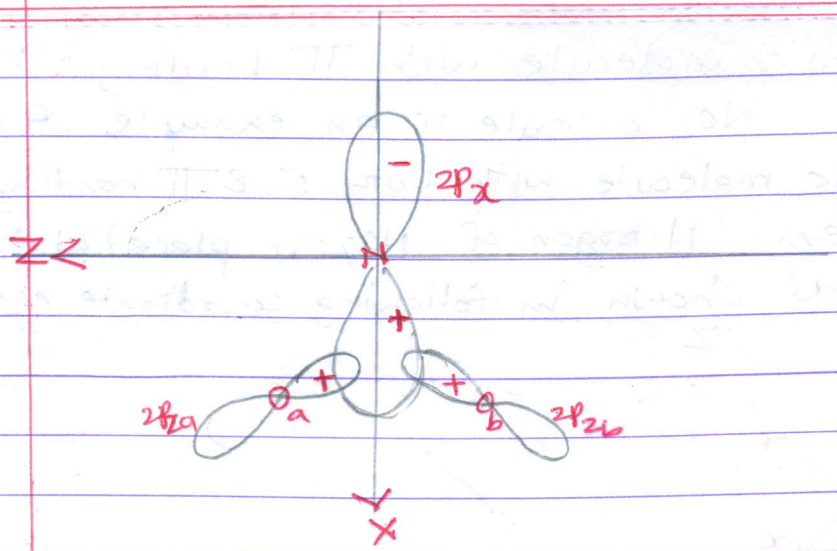


The two oxygen atoms Oa & Ob situated in XZ plane bent away from Z axis. The O – N – O bond angle is θ.

Formation of molecular orbitals – According to LCAO principle σ, π and non bonding mo's are formed in the NO_2 moleaule

(A) Formation of σ molecular orbitals – 2s & 2p$_x$ ao of nitroge overlap and combine with 2p$_{za}$ and 2p$_{zb}$ orbitals of Oa & Ob gives σ mo's as follows.

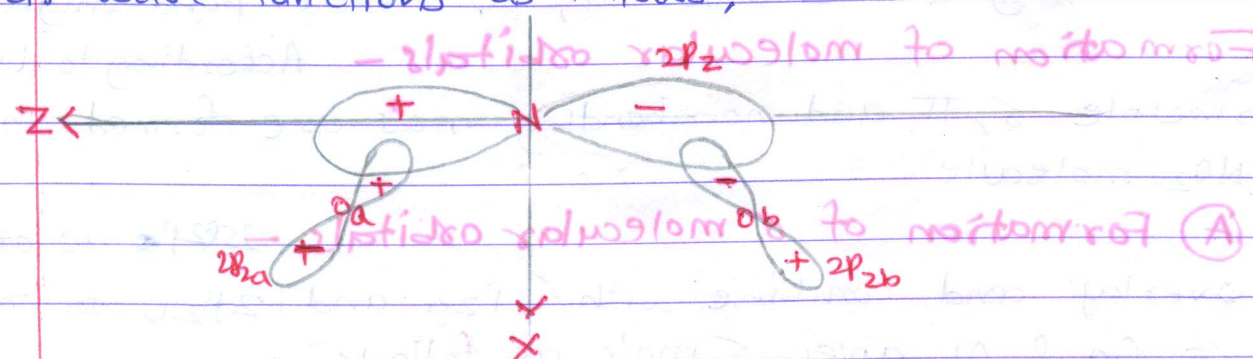
(1) Formation of σ_x^b and σ_x^* mo's – 2p$_x$ ao of the nitrogen overlap and combine with 2p$_{za}$ and 2p$_{zb}$ ao's of two oxygen atoms gives $\sigma_{x_L}^{b\,(BMO)}$ and $\sigma_{x_L}^{*\,(ABMO)}$ mo's. which are represented diagramatically and in the form of their wave functions as follows:



$$\psi_{\sigma_x^b} = c_1 2p_x + c_2(2p_{za} + 2p_{zb}) \quad \text{——— (1)}$$

$$\psi_{\sigma_x^*} = c_3 2p_x - c_4(2p_{za} + 2p_{zb}) \quad \text{——— (2)}$$

(2) Formation of σ_z^b and σ_z^* molecular orbitals – $2p_z$ ao of nitrogen combine and overlap with $2p_z$ a and $2p_{zb}$ [The appropriate combination is $(2p_{za} - 2p_{zb})$] of two O_a and O_b ao's gives σ_z^b (BMO) and σ_z^* (ABMO) which are represented diagramatically and in the form of their wave functions as follows,

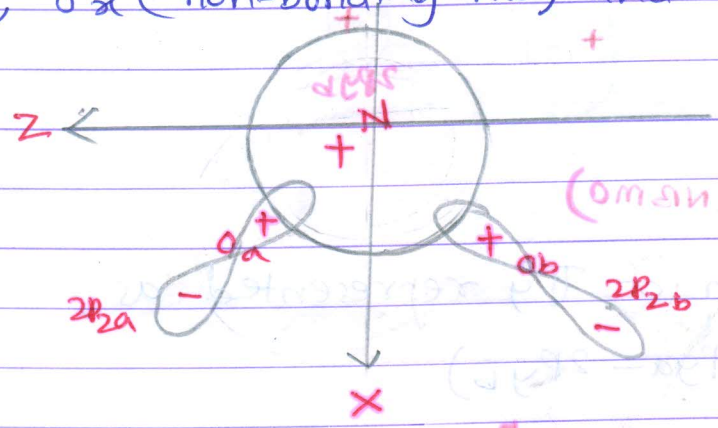


$$\psi_{\sigma_z^b} = c_5 2p_z + c_6(2p_{za} - 2p_{zb}) \quad \text{——— (3)}$$

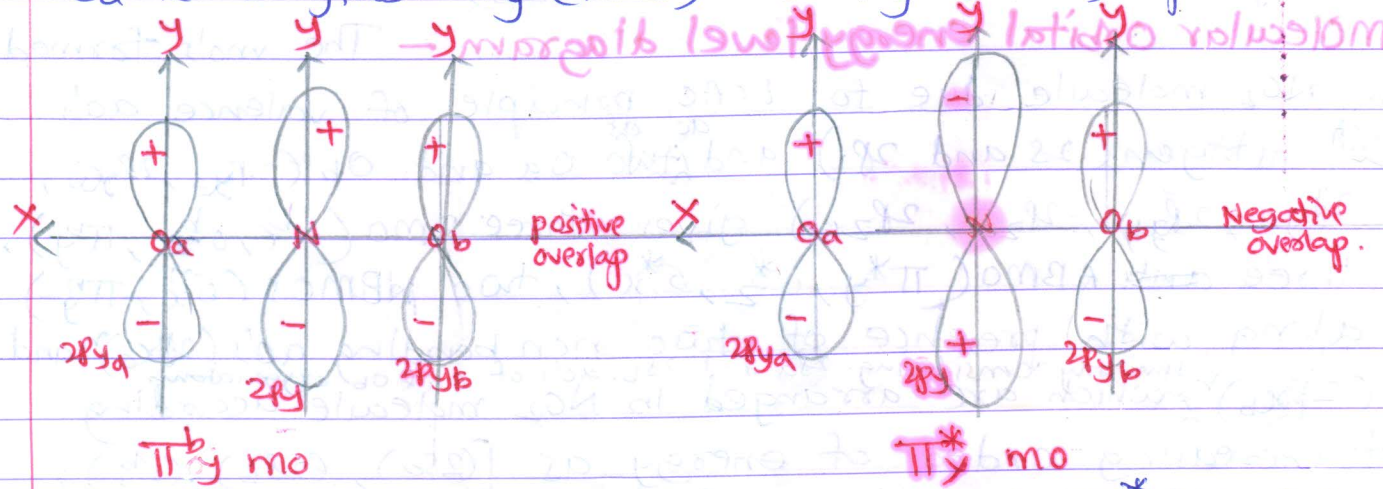
$$\psi_{\sigma_z^*} = c_7 2p_z - c_8(2p_{za} - 2p_{zb}) \quad \text{——— (4)}$$

(3) Formation of σ_s^b σ_z^b, σ_z^* mols – 2s ao of nitrogen overlap with $2p_{za}$ & $2p_{zb}$ [The appropriate combination is $(2p_{za} + 2p_{zb})$] gives σ_s^b (BMO). since the combination $(2p_{za} + 2p_{zb})$

has been used in formation of σ^b_x & σ^*_x mo's. The same $(2p_{2a} + 2p_{2b})$ combination is used for 2s ao combination which gives σ^b_s (BMO) mo. Therefore σ^b_s mo overlaps mixes with The σ^b_x and σ^*_x molecular orbital and gives σ^b_s, (BMO), σ^n_x (non-bonding mo) and σ^*_x (ABMO)



(B) Formation of π molecular orbitals – 2py ao of nitrogen overlap and combines with 2pya & 2pyb ao's of two Oa & Ob gives π^b_y (BMO) and π^*_y (ABMO) represented as



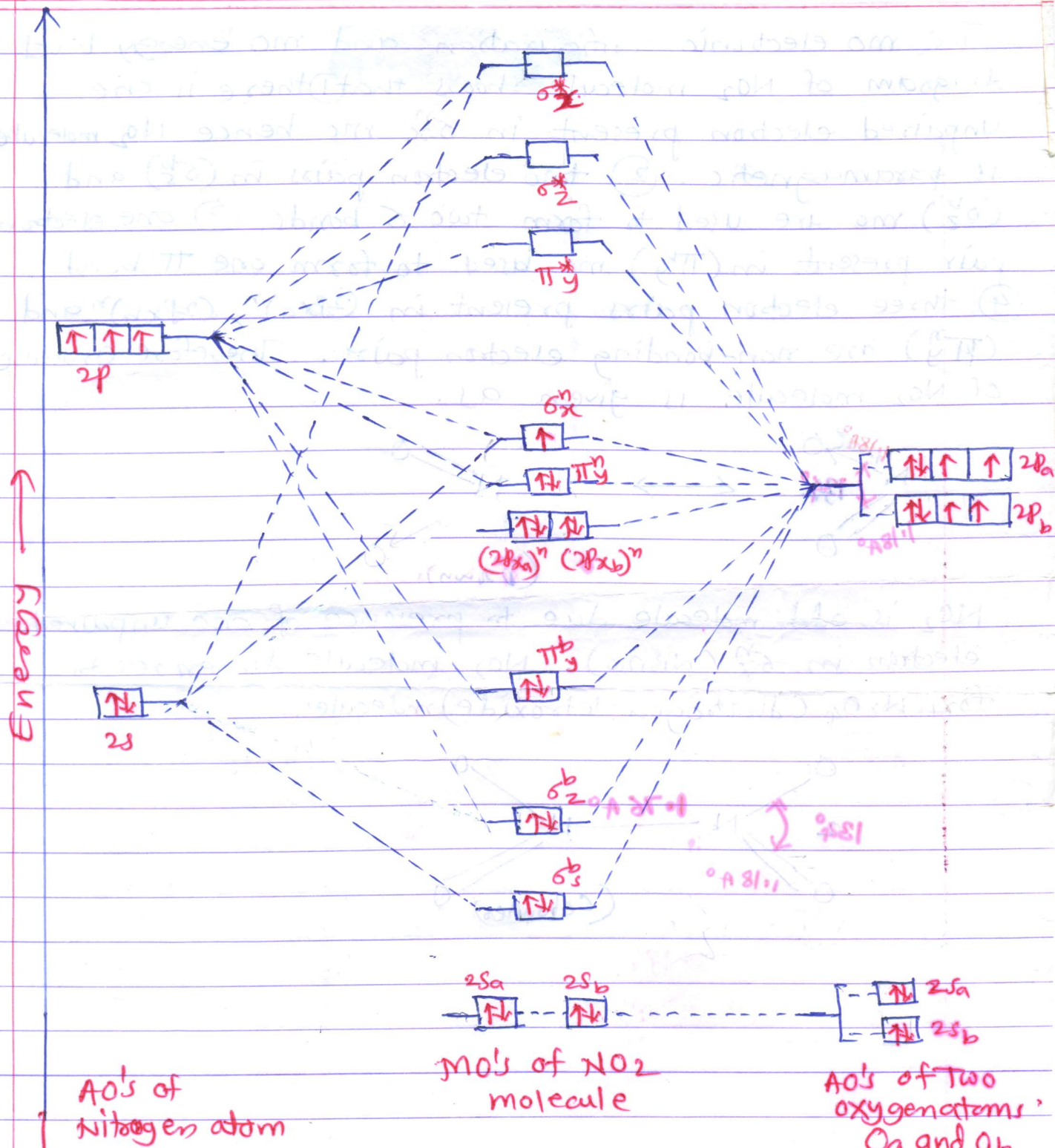
π^b_y mo $\qquad$ π^*_y mo

The wave function for π^b_y (Bmo) and π^*_y (ABMO) given as

$$\psi_{\pi^b_y} = c_9 2p_y + c_{10}(2p_{ya} + 2p_{yb}) \qquad \text{——(5)}$$

$$\psi_{\pi^*_y} = c_{11} 2p_y - c_{12}(2p_{ya} + 2p_{yb}) \qquad \text{——(6)}$$

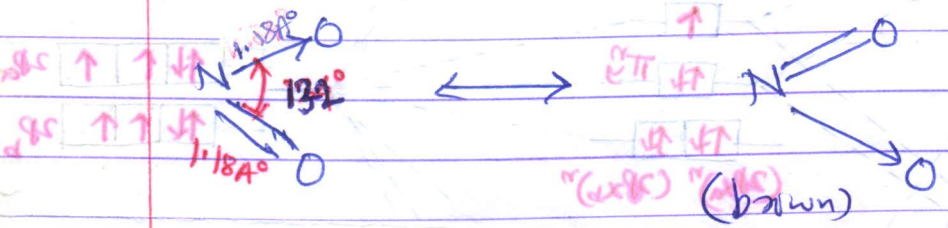
(C) Formation of π^n_y (NBMO) — 2py ao of nitrogen combine and overlaps with 2pya & 2pyb ao's of Oa & Ob gives. π^n_y (NBMO) mo represented diagramatically as,



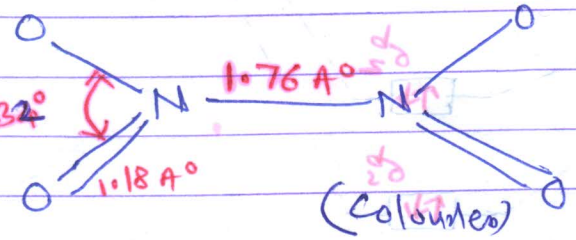
In NO_2 molecule, there are total 23 electron & 17 valence electron. Therefore the ground state electronic configuration of NO_2 molecule is given as.

$NO_2[KKK(2sa)^2, (2s_b)^2, (\sigma^b_s)^2, (\sigma^b_2)^2, (\pi^b_y)^2, (2p_{xa})^2 = (2p_{x_b})^2, (\pi^n_y)^2, (\sigma^n_x)^1]$

The mo electronic configuration and mo energy level diagram of NO_2 molecule shows that ① there is one unpaired electron present in σ^n_x mo hence NO_2 molecule is paramagnetic. ② two electron pairs in (σ^b_s) and (σ^b_z) mo are used to form two σ bonds. ③ one electron pair present in (Π^b_y) mo used to form one π bond ④ three electron pairs present in $(2p_{xa})^n$, $(2p_{xb})^n$ and (Π^n_y) are non-bonding electron pairs. Therefore structure of NO_2 molecule is given as.

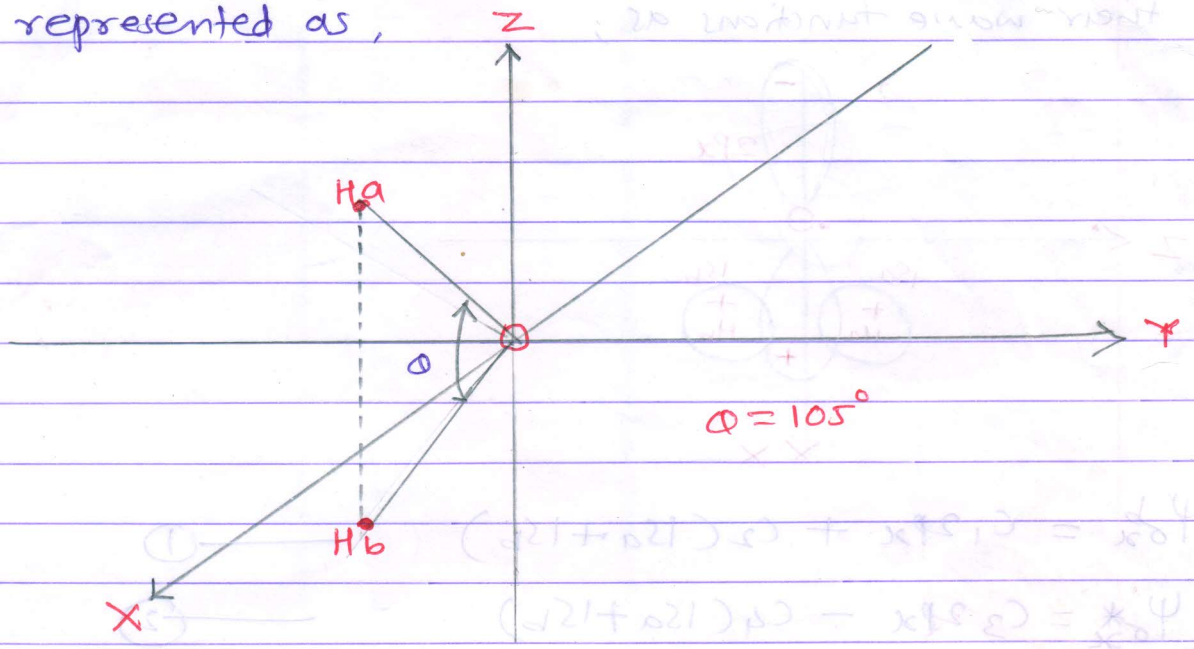


NO_2 is odd molecule due to presence of one unpaired electron in σ^n_x (NBMO). NO_2 molecule dimerizes to for N_2O_4 (dinitrogen tetroxide) molecule.



Angular Triatomic moleaule : water molecule (H_2O):

water moleule is angular triatomic molecule with H—O—H bond angle 105°. The co-ordinate system for H_2O molecule is represented as,



The two hydrogens are placed in the XZ plane. Consider H—O—H along Z-axis and bending the two hydrogens towards the X-axis until the H—O—H angle Φ corresponds to observed 105°. The two hydrogens are bend to the same amount from Z-axis hence X-axis bisects the Φ.

The electronic config^n of atoms in the H_2O molecul is represented as,

Oxygen (Z=8) — $1s^2, 2s^2, 2p^4$

Hydrogen (a) (Z=1) — $1s_a^1$

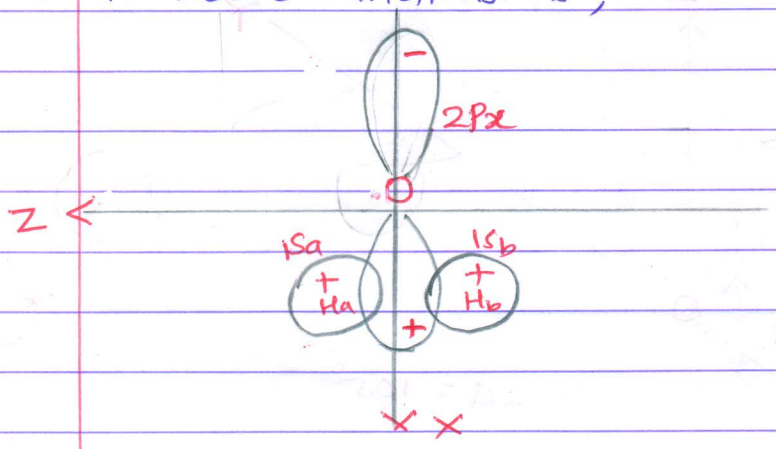
Hydrogen (b) (Z=1) — $1s_b^1$

Formation of molecular orbitals — The valence orbitals of oxygen 2s & 2p overlaps and combine with two hydroge 1Sa & $1S_b$ ao's to give σ(BMO) and σ*(ABMO) (also σ^n(NBMO)) in the H_2O molecule.

(A) **Formation of σ mo's** - In H_2O molecule various σ(BMO) and σ*(ABMO) are formed on the basis of LCAO principle as,

(1) **Formation of σ_x^b and σ_x^* mo's** — The $2p_x$ ao' of oxygen combine and overlap with 1Sa & $1S_b$ ao's of two hydrogen (There

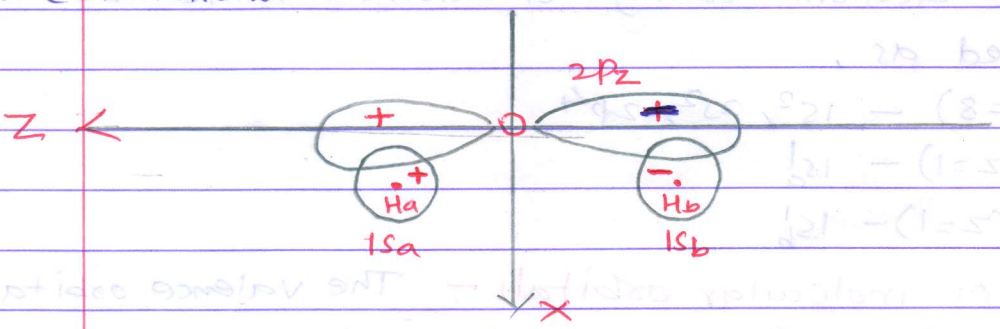
appropriate combination is $(1s_a + 1s_b)$] gives σ_x^b & σ_x^* mo's which are represented diagramatically and in the form of their wave functions as,



$$\psi_{\sigma_x^b} = c_1 2p_x + c_2(1s_a + 1s_b) \quad \text{——— (1)}$$

$$\psi_{\sigma_x^*} = c_3 2p_x - c_4(1s_a + 1s_b) \quad \text{——— (2)}$$

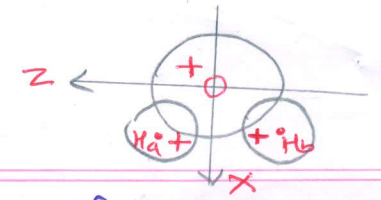
(2) Formation of σ_z^b and σ_z^* mo's — The $2p_z$ ao of oxygen combine and overlap with $1s_a$ & $1s_b$ ao's of two hydrogens [Therefore appropriate combination is $(1s_a - 1s_b)$] gives σ_z^b & σ_z^* mo's which are represented diagramatically and in the form of their wave functions as.



$$\psi_{\sigma_z^b} = c_5 2p_z + c_6(1s_a - 1s_b) \quad \text{——— (3)}$$

$$\psi_{\sigma_z^*} = c_7 2p_z - c_8(1s_a - 1s_b) \quad \text{——— (4)}$$

(3) Formation of σ_s^b, σ_x^n mo's — The 2py ao of oxygen has no overlap with either $1s_a$ & $1s_b$ ao's of two hydrogen, remains nonbonding as $(2p_y)^n$



The 2s ao of oxygen overlap and combine with 1sa & 1sb ao's of two hydrogens (Therefore appropriate combination is (1sa+1sb) which has used in σ_x^b mo's hence it correct for 2s ao]. This indicates that formation of σ_s^b mo. This σ_s^b mo mixes with σ_x^{b*} mo [because in the formation of both mo's the appropriate combination of two hydrogen ao's 1sa & 1sb is (1sa+1sb)]

Then σ_s^b mixes with σ_x^b & σ_x^* result in the formation of σ_s^b, σ_x^n & σ_x^* mo's.

Therefore in H2O molecule σ_s^b, σ_z^b, σ_x^n, σ_x^*, σ_z^* mo's form while 2py orbital of oxygen is non-bonding.

Molecular orbital energy level diagram - The mo's form due to LCAO principle of valence oxygen ao's (2s, 2p) and two hydrogen ao's (1sa & 1sb) gives two BMO (σ_s^b, σ_z^b), two ABMO (σ_x^*, σ_z^*), one NBMO (σ_x^n). The mo's arrang in H2O molecule according to increasing order of energy (including non-banding $(2p_y)^n$ ao of oxygen) as, (σ_s^b), (σ_z^b) (σ_x^n), $(2p_y)^n$, (σ_z^*) (σ_x^*).

The ao's of oxygen and ao's of two hydrogens with their mo's represented in following mo energy level diagram as follow.

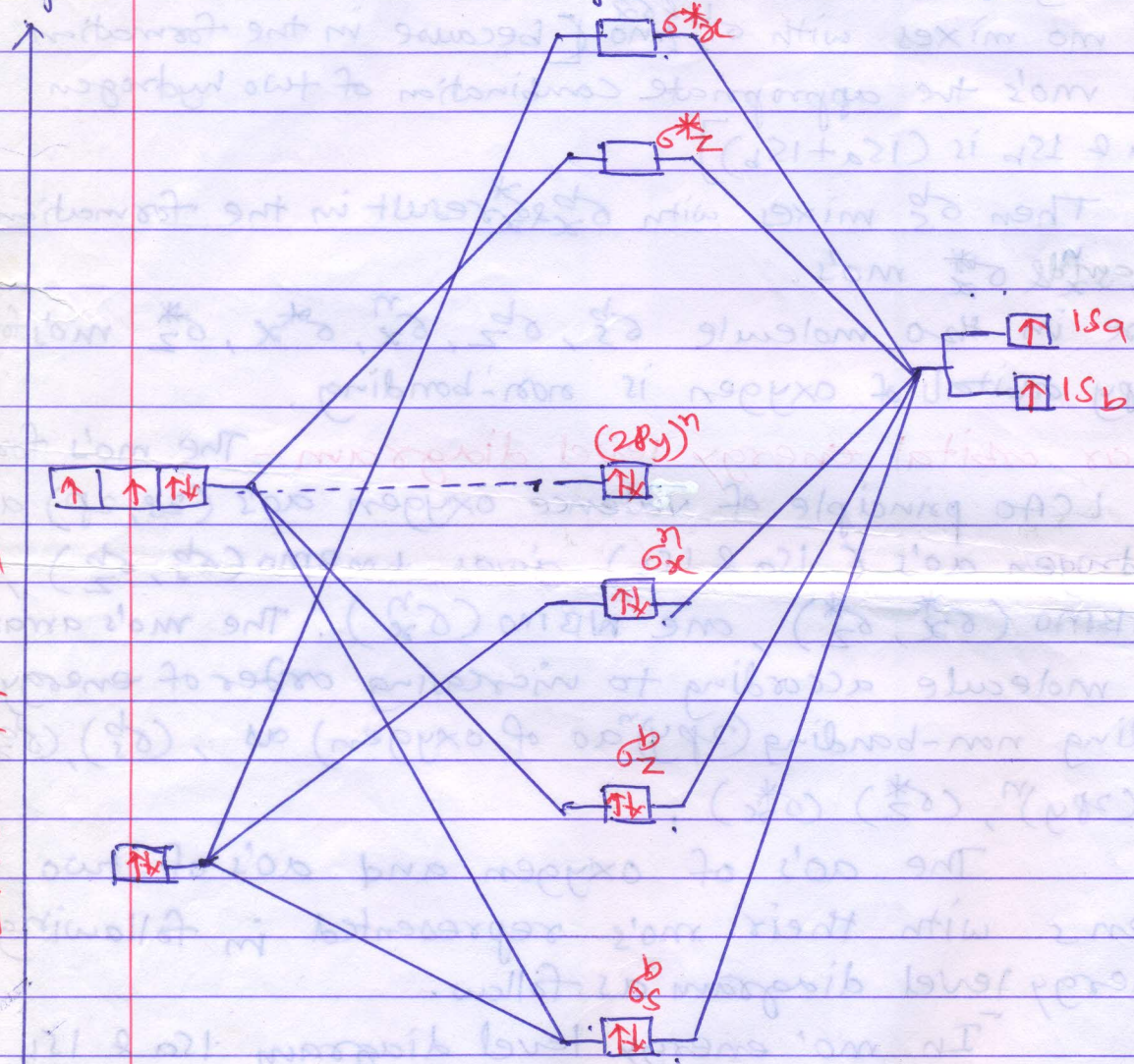
In mo' energy level diagram 1sa & 1sb hydrogen ao's are placed above the 2s & 2p valence ao's of oxygen due to electronegativity difference.

The G.S. electronic config of H2O molecule is given as,

$H_2O\left[K\,(\sigma_s^b)^2, (\sigma_z^b)^2, (\sigma_x^n)^2, (2p_y^n)^2\right]$

The mo'energy level diagram & mo electronic config of H2O molecule give idea about the magnetic propertie Thus all electrons in mo's are paired hence H2O molec is diamagnetic.

There are two electron pairs present in 2 BMO (σ_s^b, σ_z^b mo's) and 2 electron pair in non bonding form in (σ_x^n) and $(2p_y)^n$ called as two lone pairs in the H_2O molecule. Thus due to presence of 2 electronpairs in 2 BMO gives two σ bonds

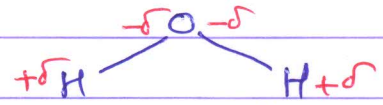


AO's of oxygen atom | MO's of H_2O molecule | AO's of Two hydrogen atoms

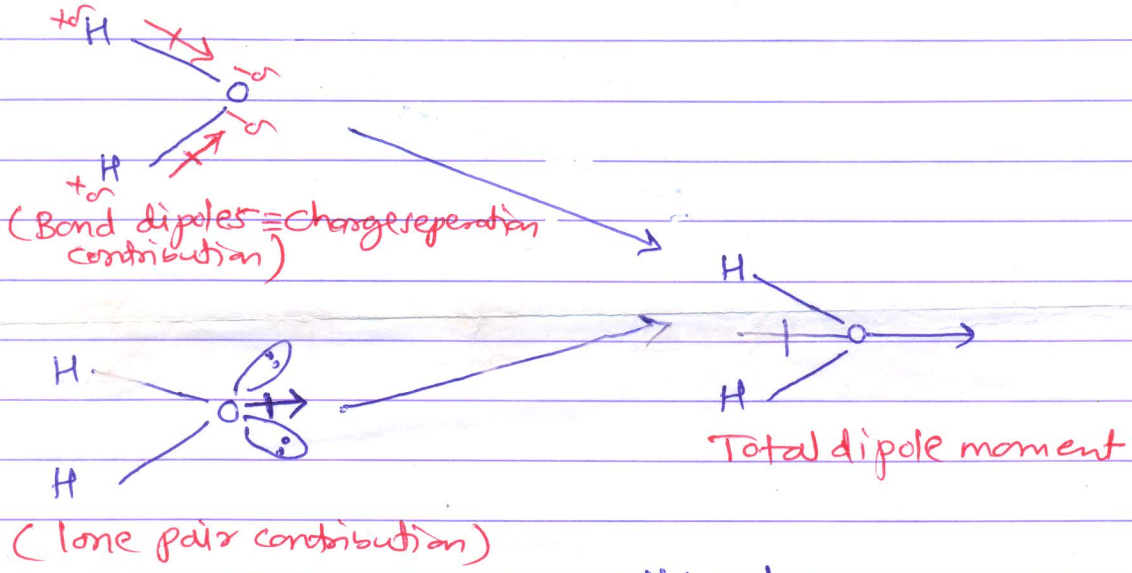
If pure $2p_x$ & $2p_y$ ao's of oxygen are wed in σ bonding then the expected angle θ for H—O—H is 90°. But possibility of 2s orbitals of oxygen being involved in bonding cause 15° deviation of H—O—H angle from 90° to 105°.

The electron in σ BMO (σ_s^b & σ_z^b) also non bonding electrons in σ_x^n & $(2p_y)^n$ spend more

time near oxygen atom than hydrogens due to larger electronegativity of oxygen hence dipoles is formed i.e. hydrogen carries small positive charge and oxygen carries small negative charge



Therefore H2O molecule is polar and has dipole moment 1·844 D. hence dipole moment in H2O molecule is due to charge seperation as well as due to two lone pairs.



Each H2O molecule has small bond dipole moment resulting from the charge seperation. Since H2O molecule is angular, these bond moments added together to give resultant dipole moment. along with dipole moment obtained by two lone pair of electrons present in σ_x^n mo & (2py^n) ao.