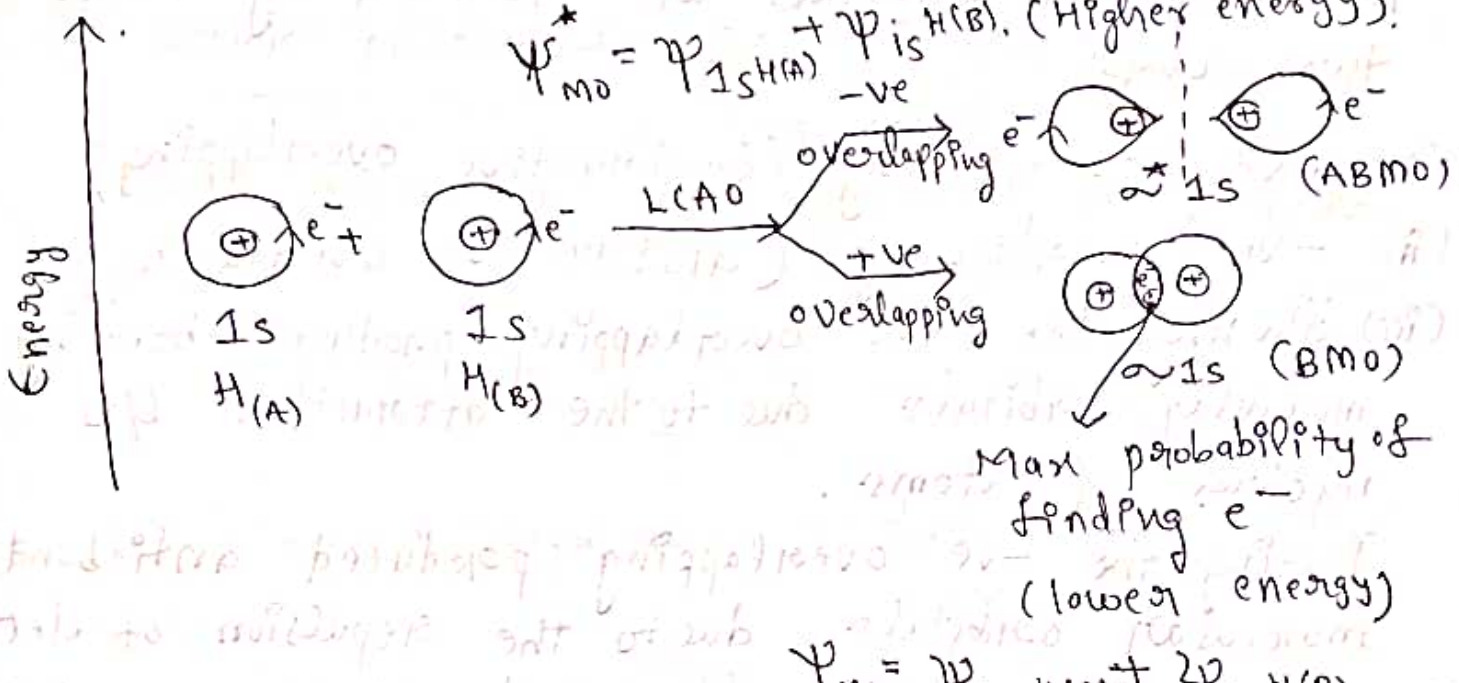
Structure and Bonding Models

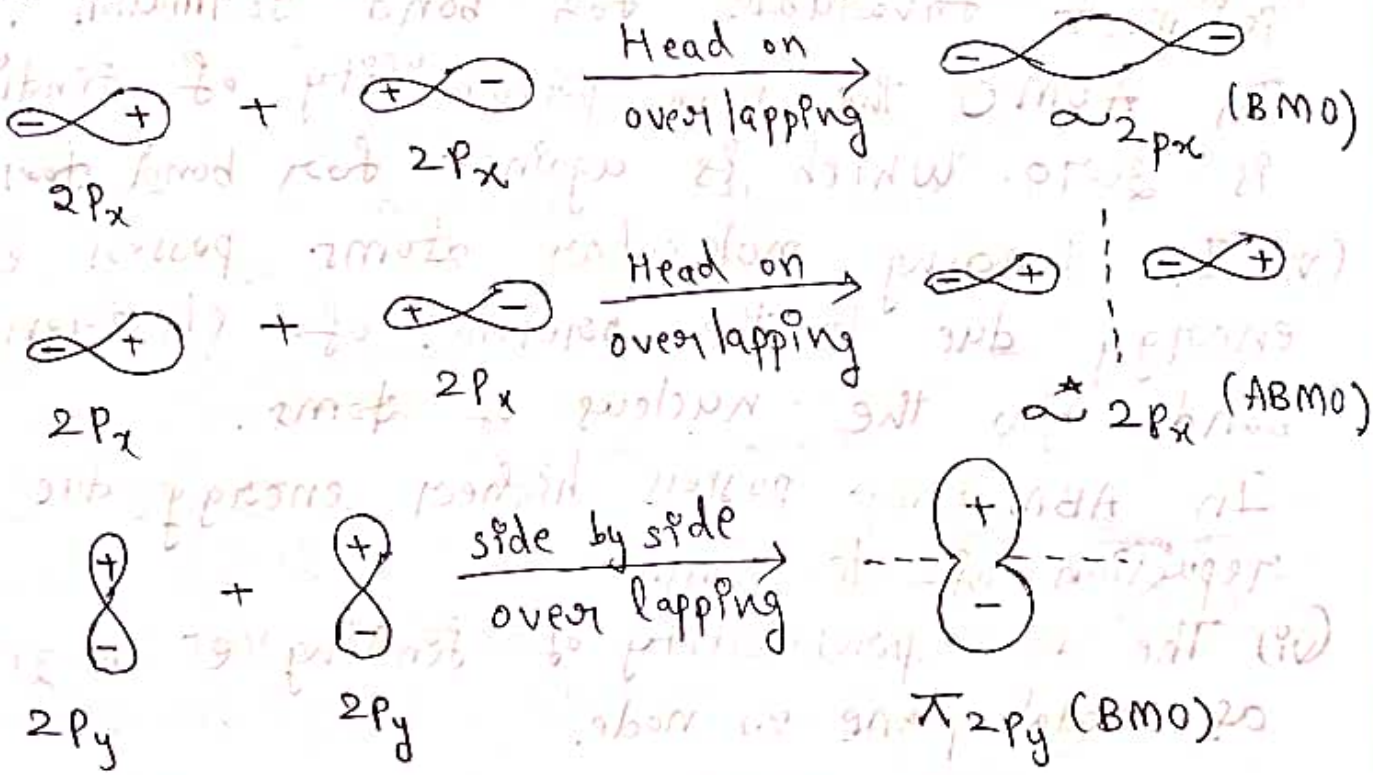
MOT = Molecular Orbital Theory.

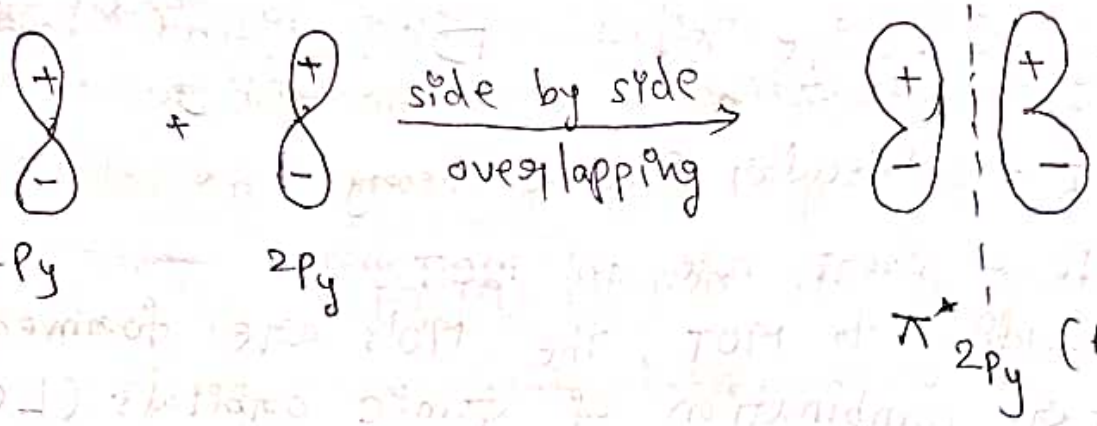
Q. Write a short note on MOT?

Sol: According to MOT, the MO's are formed by linear combination of atomic orbitals (LCAO).



P-P Overlapping:-





The molecular orbitals are formed by LCAO in two ways,

(i) +ve overlapping (constructive overlapping)

(ii) -ve overlapping (distructive overlapping)

(iii) During the +ve overlapping produced bonding molecular orbitals due to the attraction b/w nucleus of atoms.

During the -ve overlapping produced anti bonding molecular orbitals due to the repulsion of electrons.

(iv) In bonding molecular orbitals the max probability of finding electron b/w neucleaus of atoms which is the most favarable for bond formation.

In ABMO the max probability of finding e⁻ is zero. which is against for bond formation.

(v) In bonding molecular atoms possess lower energy due to the presence of electrons in bond b/w the nucleus of atoms.

In ABM atoms posses higher energy due to the repulsion of electrons.

(vi) The max probability of finding e⁻ is zero known as nodal plane or node.

(vii) In quantum mechanics the atomic orbitals are described as wave function, which is denoted by 'ψ' and the max probability of finding e^- is denoted by ψ^2.

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(8). Write the energy level diagrams bond order and magnetic properties of diatomic molecules.

Sol: Bond Order :- The number of chemical bonds b/w the atoms in a molecule is known as Bond order.

$$BO = \frac{(\text{No of } e^- \text{ in BMO} - \text{No of } e^- \text{ in ABMO})}{2}$$

⇒ Bond order = 1, represents 1 chemical bond in a molecule

Bond order = 2, represents 2 chemical bonds in a molecule.

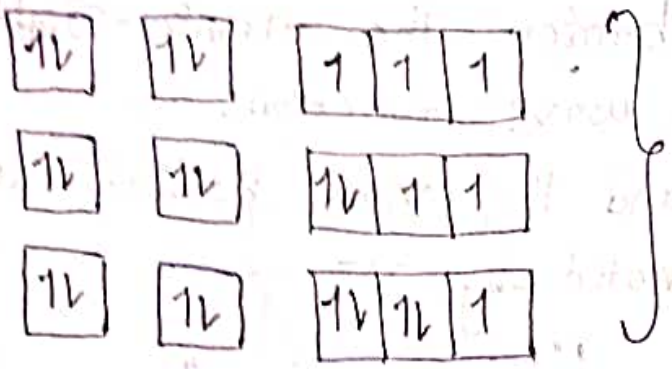
Bond order = 3 represents 3 chemical bonds in a molecule.

Bond order = 0 represents no chemical bonds present in a molecule (or the molecule can't be exist.

Magnetic Character :-

Para-Magnetic :-

If the orbitals contains at least one single electron (lone pair of e^-) then the molecule posses paramagnetic character.

ex:-  para-magnetic character.

Dia-Magnetic:-

If the orbitals contains all the pair of electrons then the molecule possess diamagnetic character.

ex:- 

⇒ The electrons are filled in the orbitals by the following rules.

(i) Aufbau Rule:-

The electrons are filled in lower energy orbital later the electrons are filled in next highest energy orbitals.

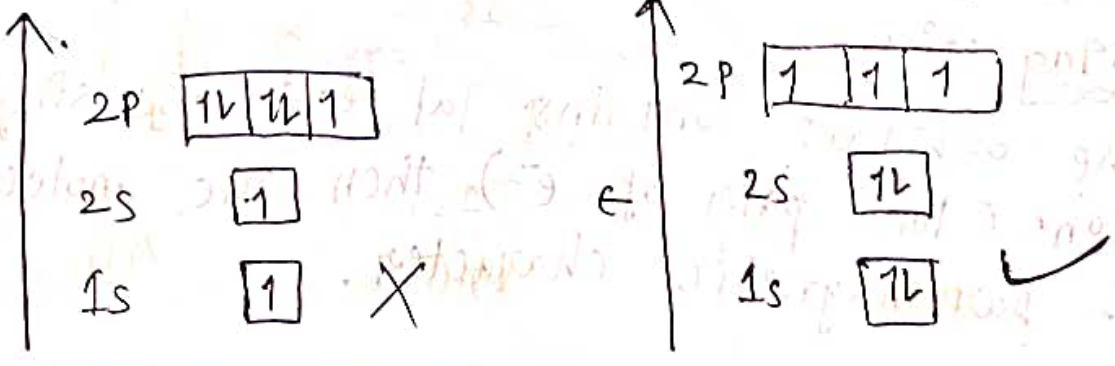
(ii) Hunds Rule:-

In degenerate orbitals first each orbital is filled with single electron later the electrons are paired.

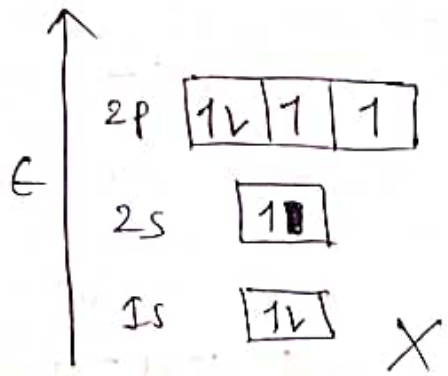
(iii) Poulis Principles

No two electoons have same spin values.

ex:- Aufbau rules → Number of $e^- = 7$



Hund's rule :-



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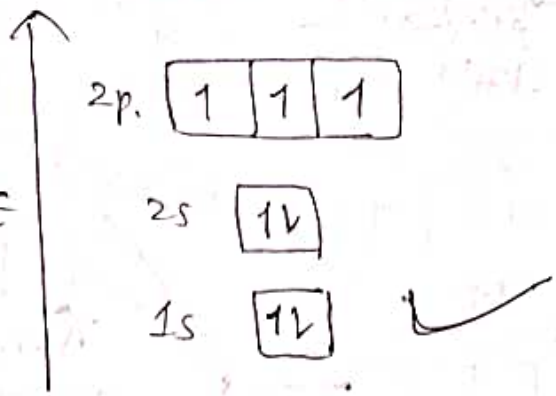
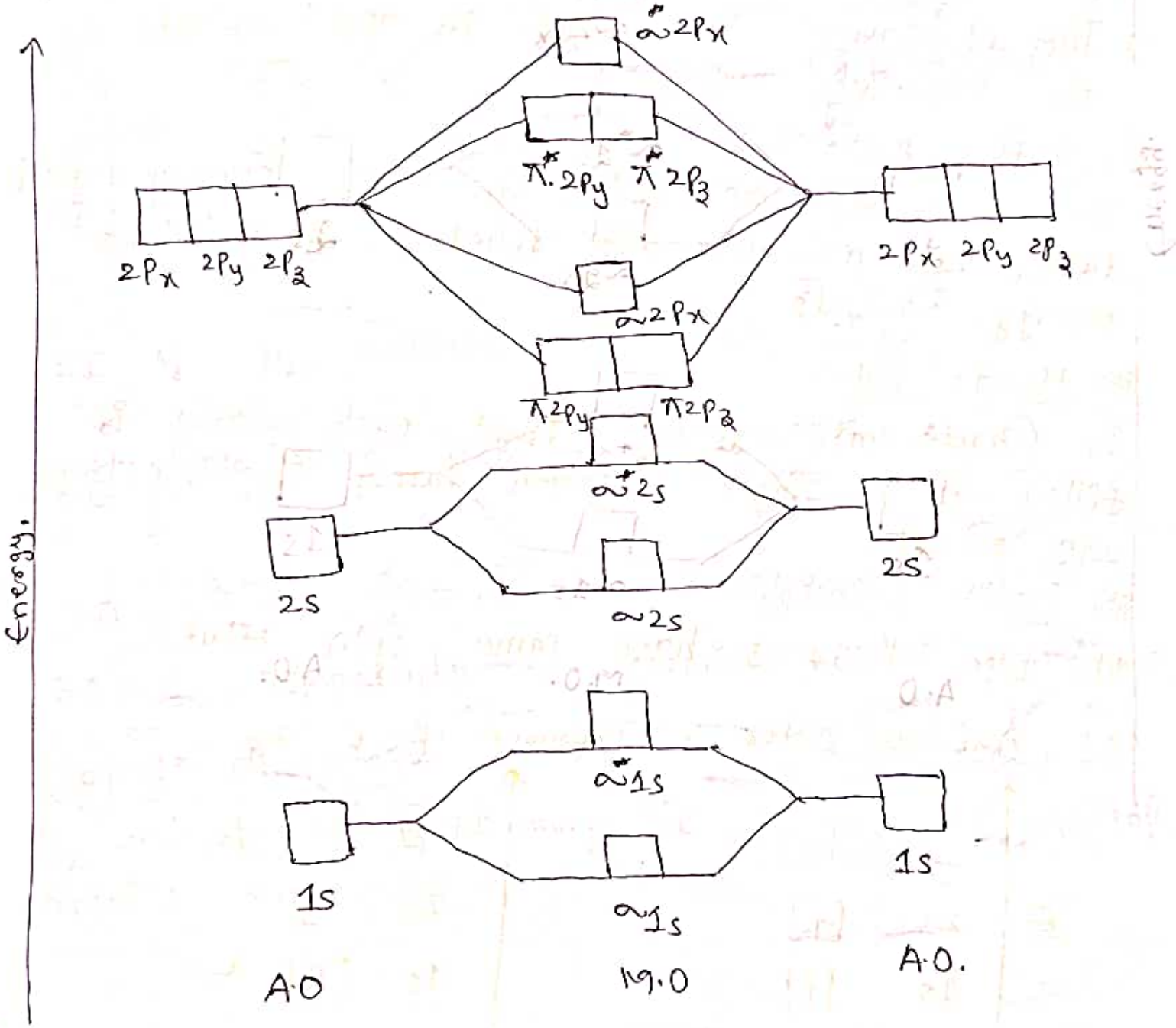
Pauli's rule :-

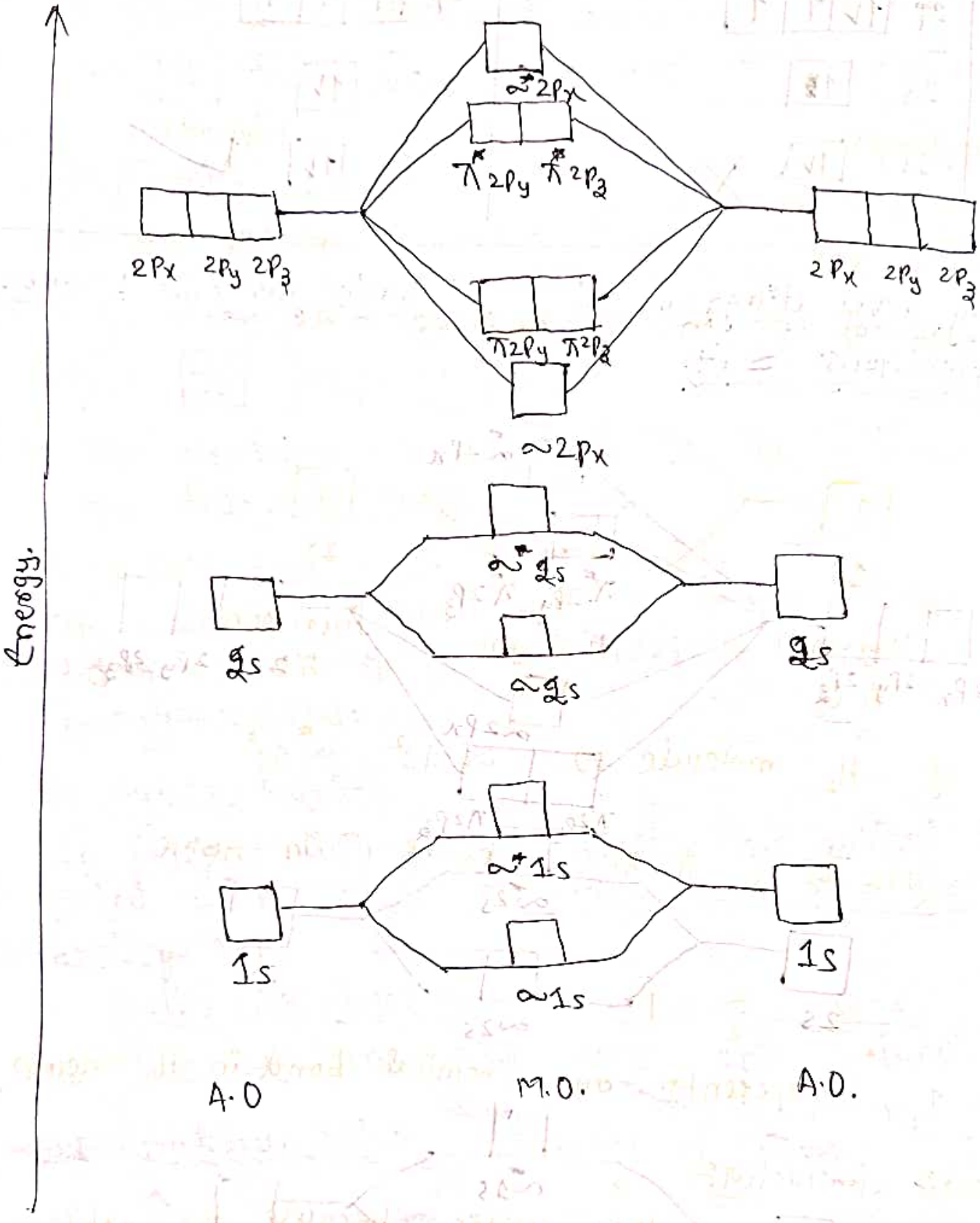


✓

Energy level diagram for diatomic molecule : Number of electrons ≤ 14.



Energy level diagram for diatomic molecules : Numb
of electrons >14



Q. Write the energy level ~~diagram~~ molecular orbital diagrams of the following diatomic molecules.

(i) H_2 (ii) He_2 (iii) N_2 (iv) O_2.

Sol: Energy level diagram for H_2 molecule:

Hydrogen

No of $e^- = 1$

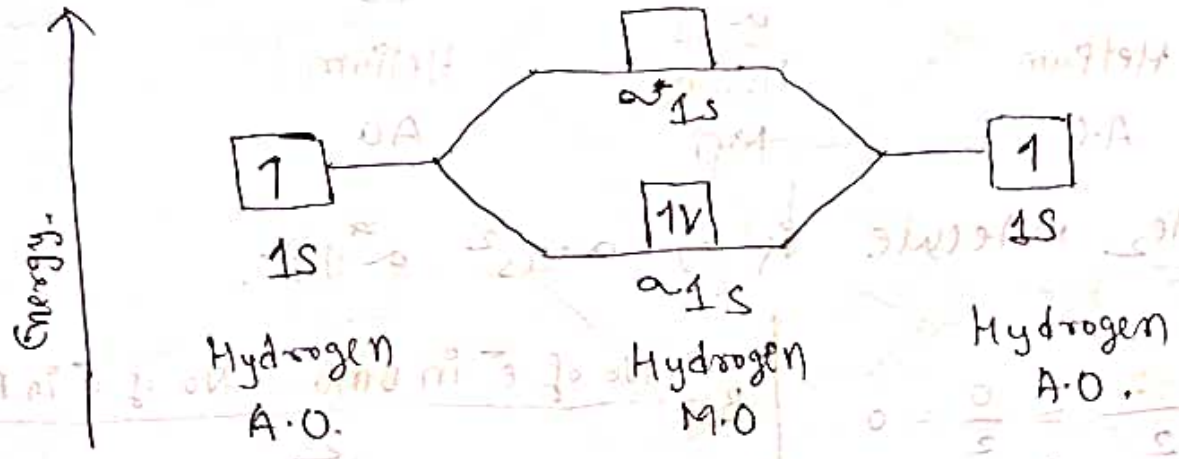
E.C is $1s^1$

Hydrogen

No of $e^- = 1$

EC is $1s^1$

No of e^- in H_2 molecule $= 2e^-$



E.C of H_2 molecule $\Rightarrow$ $\sigma 1s^2$ $\sigma^* 1s^0$.

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

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

B.O = 1, represents one chemical bond in H_2 molecule.

Magnetic character:

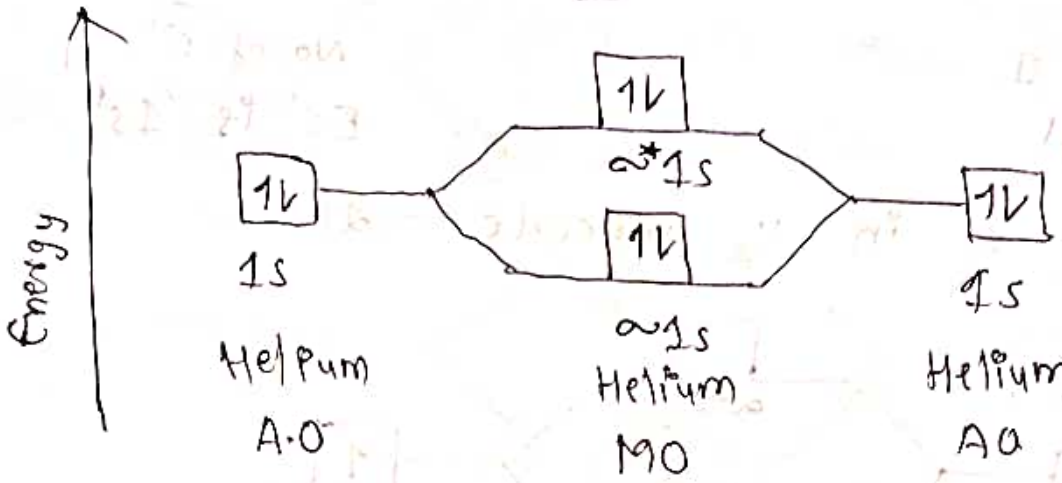
H_2 molecule is a diamagnetic, because the orbitol contains only pair of electrons.

Energy level diagram for He_2 molecule:-

Helium
No of e^- = 2
EC is $1s^2$

Helium
No of e^- = 2
EC is $1s^2$

No of e^- in He_2 molecule = $4e^-$



EC of He_2 molecule is $\Rightarrow \sigma 1s^2 \ \sigma^* 1s^2$.

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

$$B = \frac{(\text{No of } e^- \text{ in BMO} - \text{No of } e^- \text{ in ABMO})}{2}$$

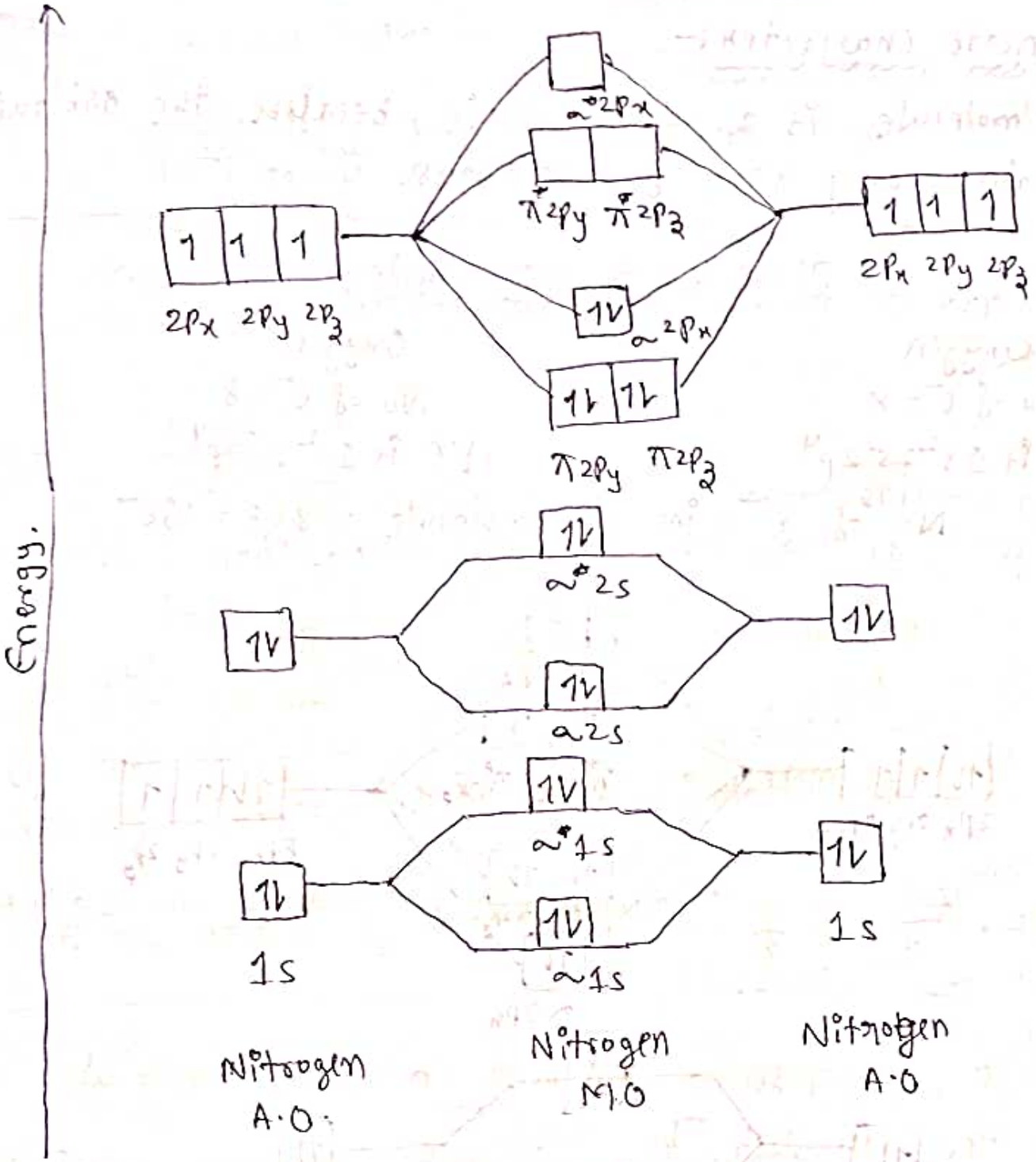
B.O = 0, represents no bond in the He_2 molecule (or) He_2 can not be exist.

Energy level diagram for N_2 molecule:-

Nitrogen
No of e^- = 7
EC is $1s^2 2s^2 2p^3$

Nitrogen
No of e^- = 7
EC is $1s^2 2s^2 2p^3$.

No of e^- in N_2 molecule is = 7+7 = $14e^-$.



EC of N_2 molecule is.

$\Rightarrow \sigma_{1s}^2 \; \sigma^*_{1s}{}^2 \; \sigma_{2s}{}^2 \; \sigma^*_{2s}{}^2 \left(\pi^2_{2py} = \pi^2_{2pz}\right) \sigma^2_{2px}.$

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

$$B.O = \frac{10-4}{2} = \frac{6}{2} = 3.$$

BO = 3, represents three chemical bonds in N_2 molecule ($N \equiv N$).

Magnetic character:-

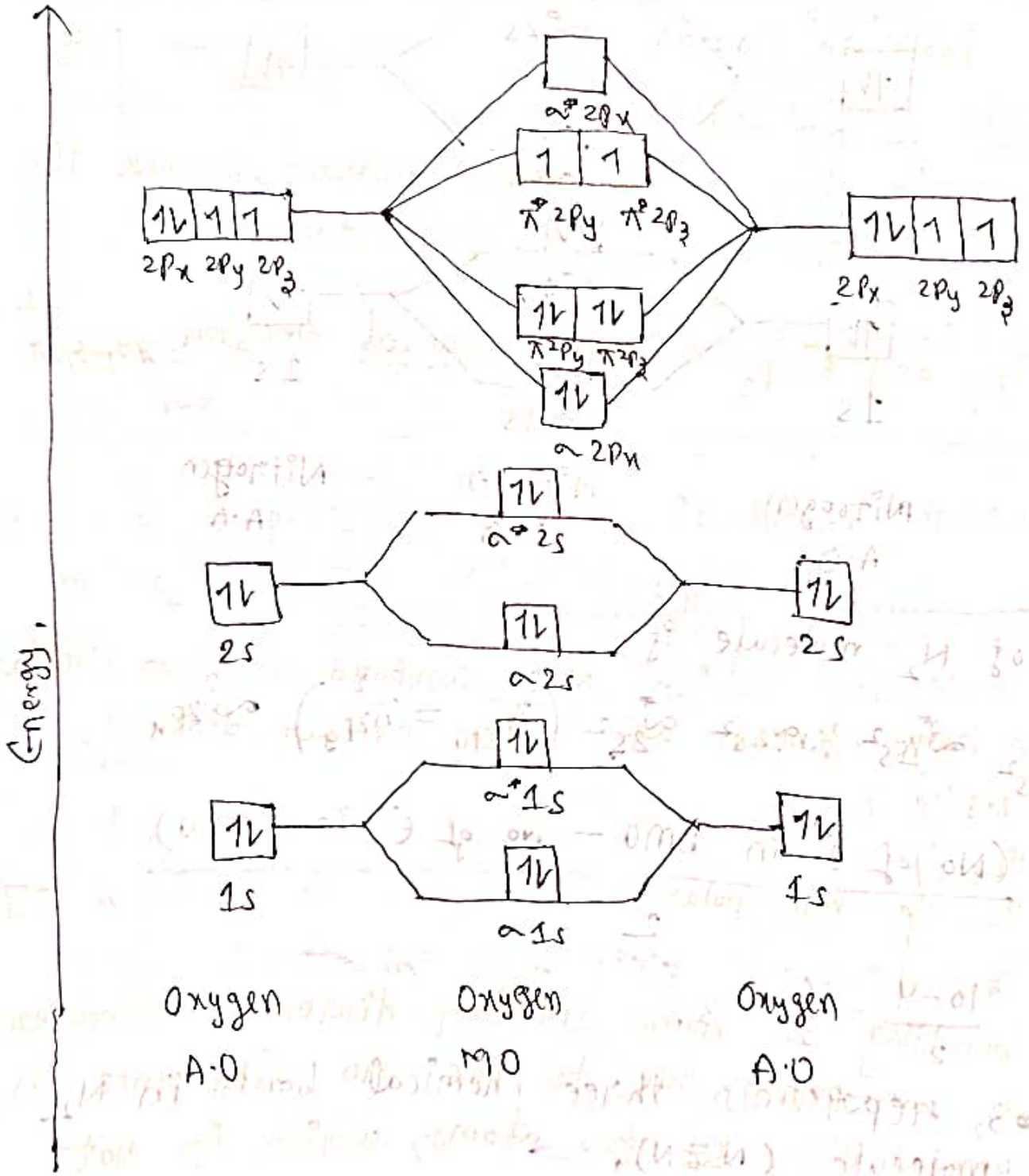
N_2 molecule is a diamagnetic, because the orbital contains only pair of electrons.

Energy level diagram for O_2 molecule:-

Oxygen
No of $e^- = 8$
EC is $1s^2 2s^2 2p^4$

Oxygen
No of $e^- = 8$
EC is $1s^2 2s^2 2p^4$

No of e^- in O_2 molecule $= 8+8 = 16e^-$



EC of O_2 molecule is

$\Rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_x}^2 (\pi_{2p_y}^2 = \pi_{2p_z}^2)(\pi_{2p_y}^{*1} = \pi_{2p_z}^{*1})$.

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

$$B.O = \frac{10-6}{2} = \frac{4}{2} = 2.$$

B.O = 2, represents two chemical bonds in O_2 molecule (O=O).

Magnetic character:-

O_2 molecule has paramagnetic nature, because the orbitals contains lone pair of electrons.

(or)

$\pi^*_{2p_y}$ and $\pi^*_{2p_z}$ contains unpaired electrons. //

Q. Write the bonding in Homo nuclear and Hetero nuclear diatomic molecules.

Sol:- Homo nuclear diatomic molecules:-

The molecules which are composed of two similar atoms are known as "Homo nuclear diatomic molecules".

Ex:- H_2, O_2, N_2 } non-polar.

The bonding in homo nuclear diatomic molecules is a non-polar due to the no difference in electronegativity of two atoms, which is not

effect on the energies of BMO and ABMO.

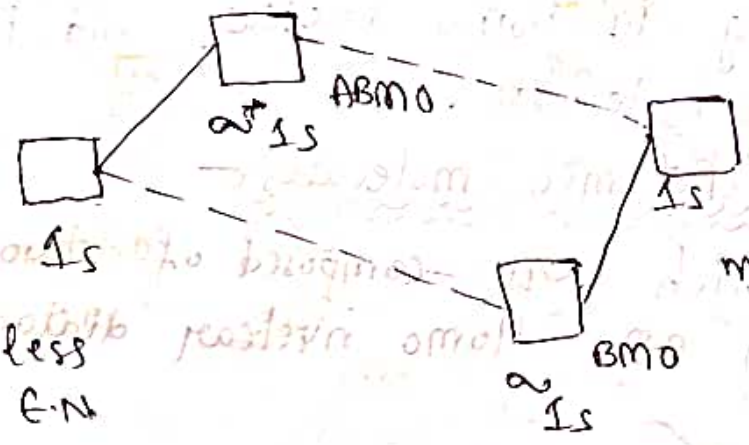
Hetero Nuclear diatomic molecules:-

The molecules which are composed of two different atoms are known as "Hetero nuclear diatomic molecules".

ex:- NO, CO, CN } polar.

The bonding in hetero nuclear diatomic molecules is a polar due to the difference in electro-negativity of two atoms, which is effect on the energies of BMO and ABMO

The more electronegative atoms contributes to BMO. Hence, the more electronegative atoms are closer to BMO. Similarly less electronegative atoms contributes to ABMO. Hence, less electronegative atoms are closer to ABMO.



(Q). Write the energy level MO diagrams of the following diatomic molecules.

(i) NO.

Sol:- Energy level MO diagram of NO:-

Nitrogen

No of $e^- = 7e^-$

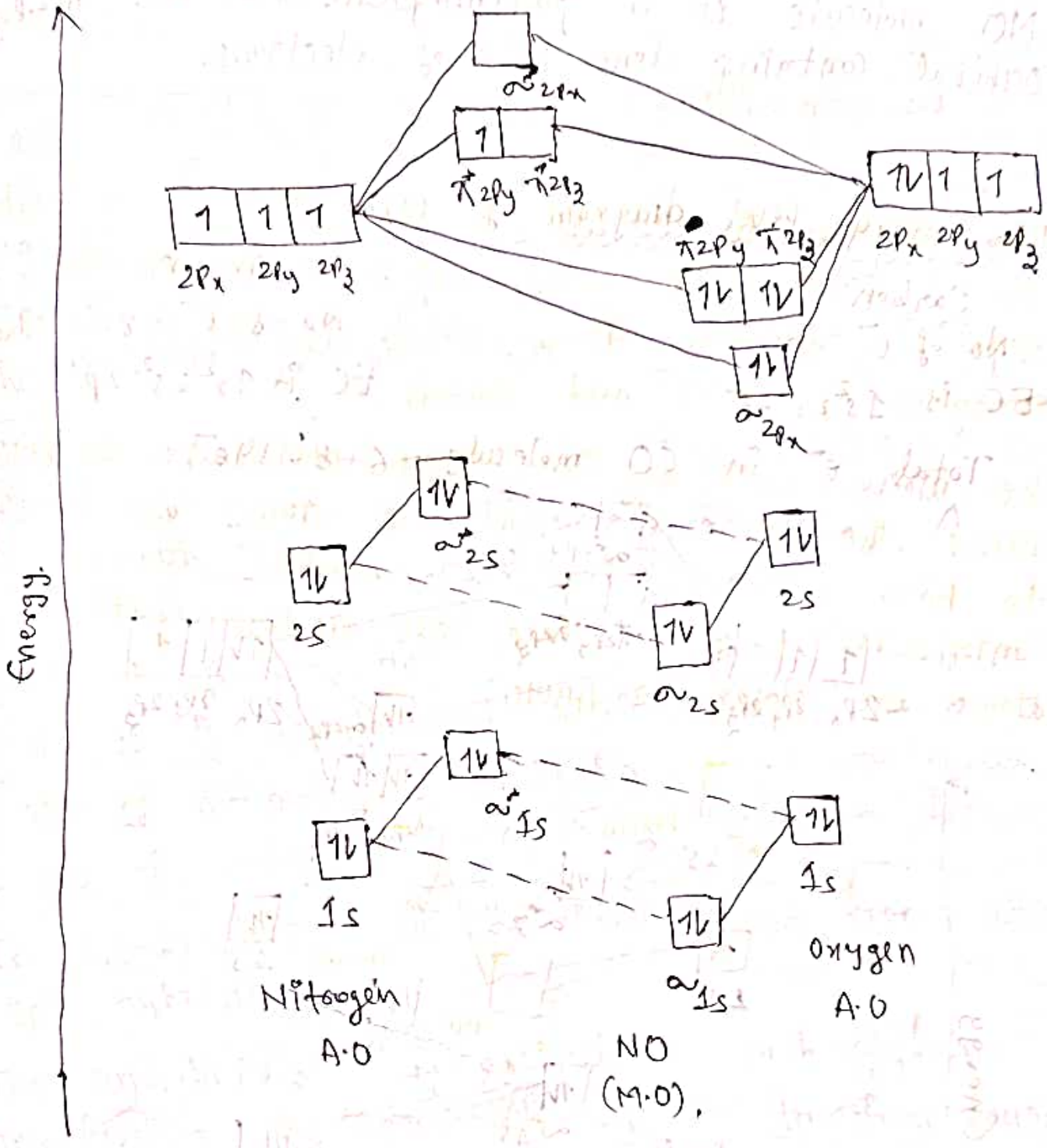
EC is $1s^2 2s^2 2p^3$

Oxygen

No of $e^- = 8e^-$

EC is $1s^2 2s^2 2p^4$

Total e^- in NO molecule = 7+8 = $15e^-$



EC of NO molecule is,

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_x}^2 \left(\pi_{2p_y}^2 = \pi_{2p_z}^2\right) \pi^{*1}_{2p_y}$$

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

$B.O = \frac{10-5}{2} = 2.5$. represents ($N \Rightarrow O$) two chemical bonds and one covalent bond.

Magnetic Character:-

NO molecule is a paramagnetic, because $\pi^*_{2p_y}$ orbital contains lone pair of electrons.

(ip) CO.

Sol:- Energy level diagram of CO:-

Carbon

No of $e^- = 6e^-$

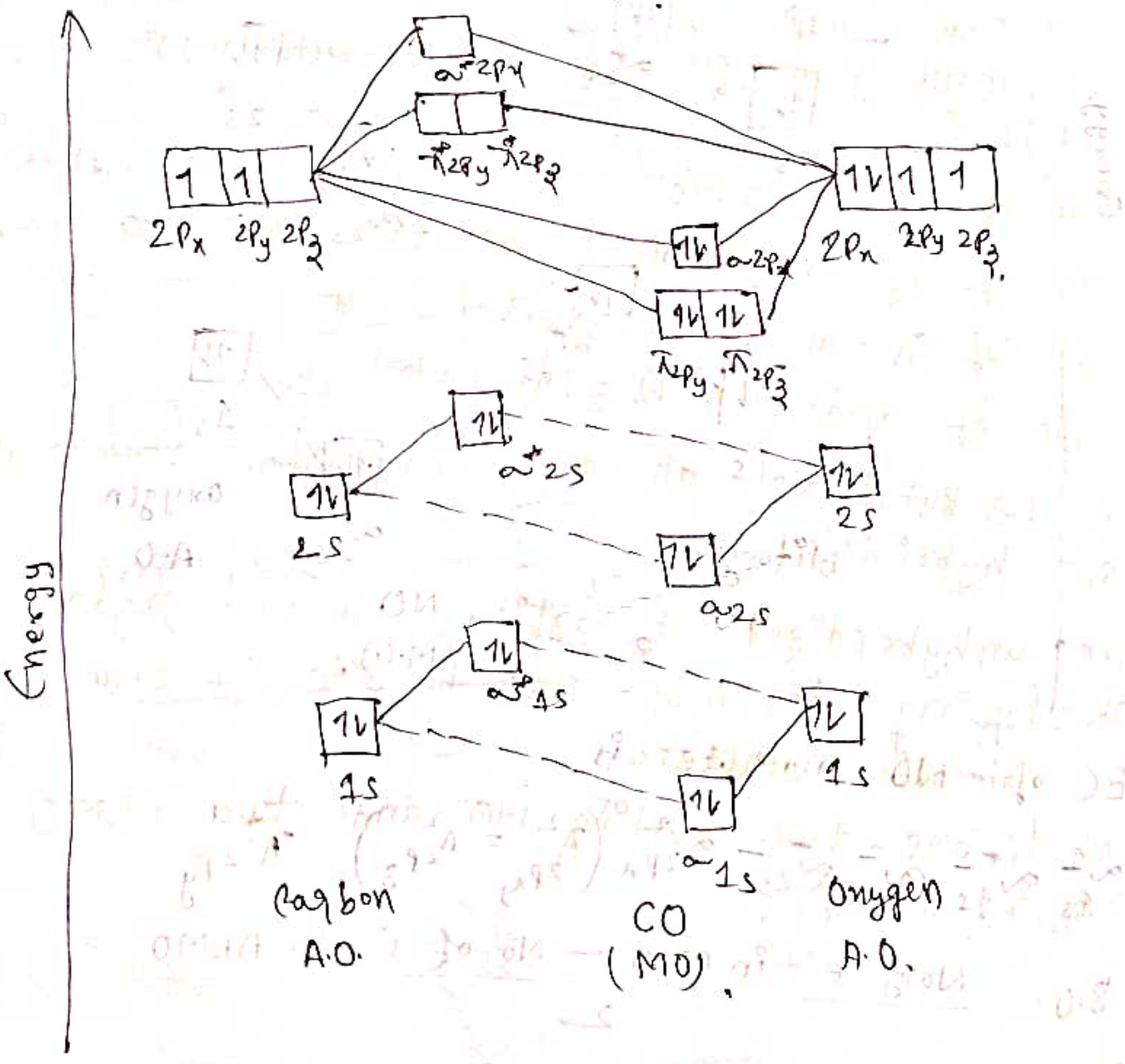
EC is $1s^2 2s^2 2p^2$

Oxygen

No of $e^- = 8e^-$

EC is $1s^2 2s^2 2p^4$

Total e^- in CO molecule $= 6+8 = 14e^-$



EC of CO molecule is,

$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left(\pi_{2p_y}^2 = \pi_{2p_z}^2\right) \sigma_{2p_x}^2$.

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

$B.O = \frac{10-4}{2} = \frac{6}{2} = 3$, represents three chemical bonds in CO molecule.

Magnetic character:-

CO molecule is a diamagnetic, because all the orbitals contains pair of electrons.

Q. Write the π- molecular orbitals of 1,3-Butadiene.

Sol:- $\overset{sp^2}{CH_2}_1 = \overset{sp^2}{CH}_2 - \overset{sp^2}{CH}_3 = \overset{sp^2}{CH_2}_4$ (1,3-Butadiene).

No of π e^- = $4e^-$

No of P_z unhybridized orbitals (n) = 4.

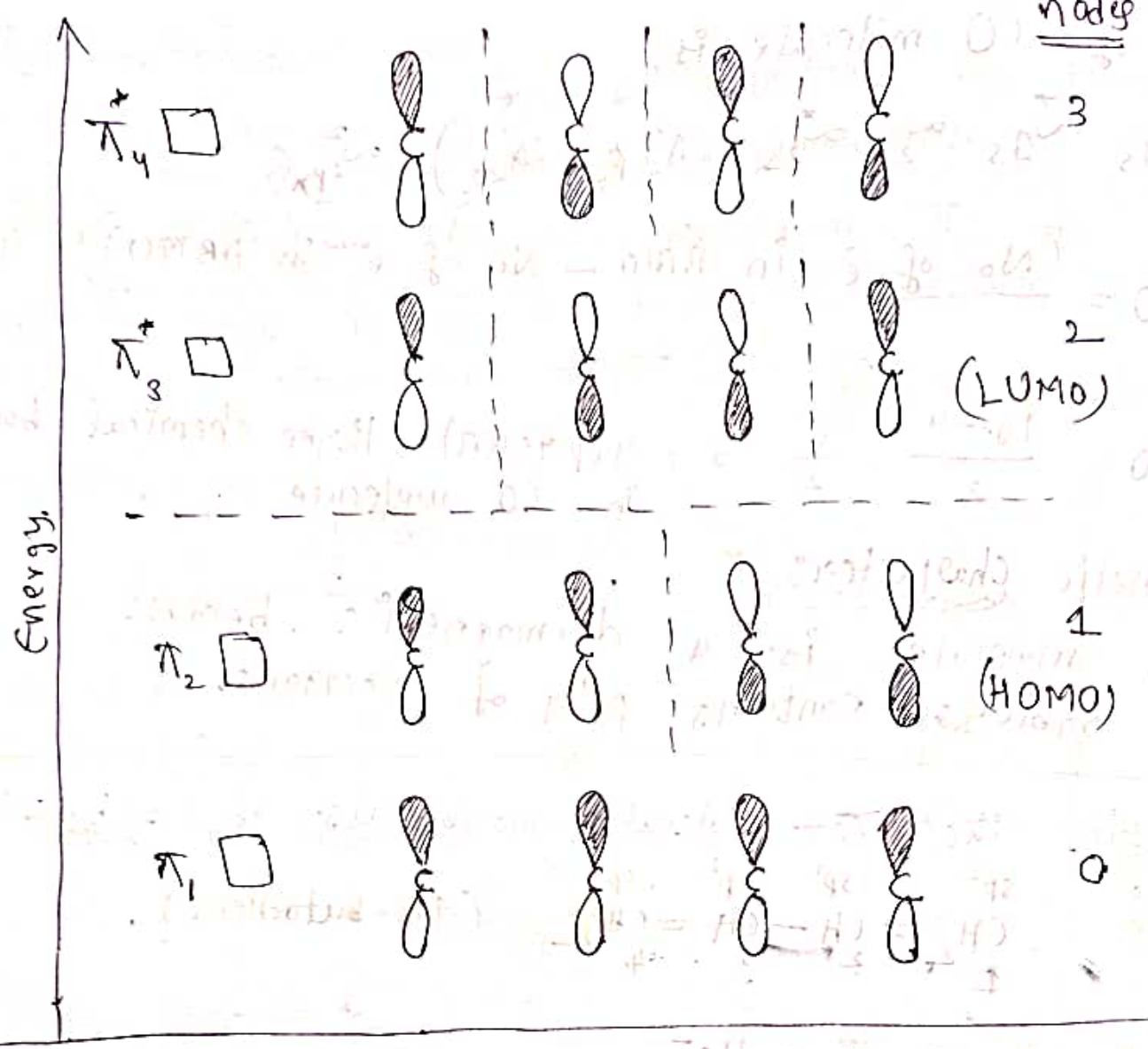
No of π-molecular orbitals = 4.

No of nodes (n-1) = (4-1) = 3.

(i) In 1,3-Butadiene all the four carbon atoms are sp^2 hybridized.

(ii) The unhybridized P_z orbitals of each carbon overlapping together side by side to form four π-molecular orbitals.

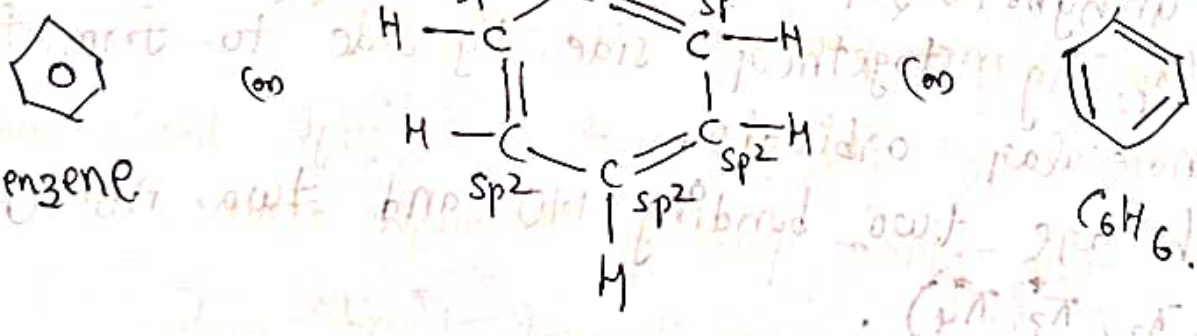
(iii) Which are two bonding MO and two ABMO ($\pi_1, \pi_2, \pi_3^*, \pi_4^*$).



π_1 molecular orbital possess more stability and less energy due to the delocalization and π_4^* molecular orbital possess less stability and more energy due to the non-delocalization.

Q. Write the π-molecular orbitals of benzene (cyclic).

Sol:

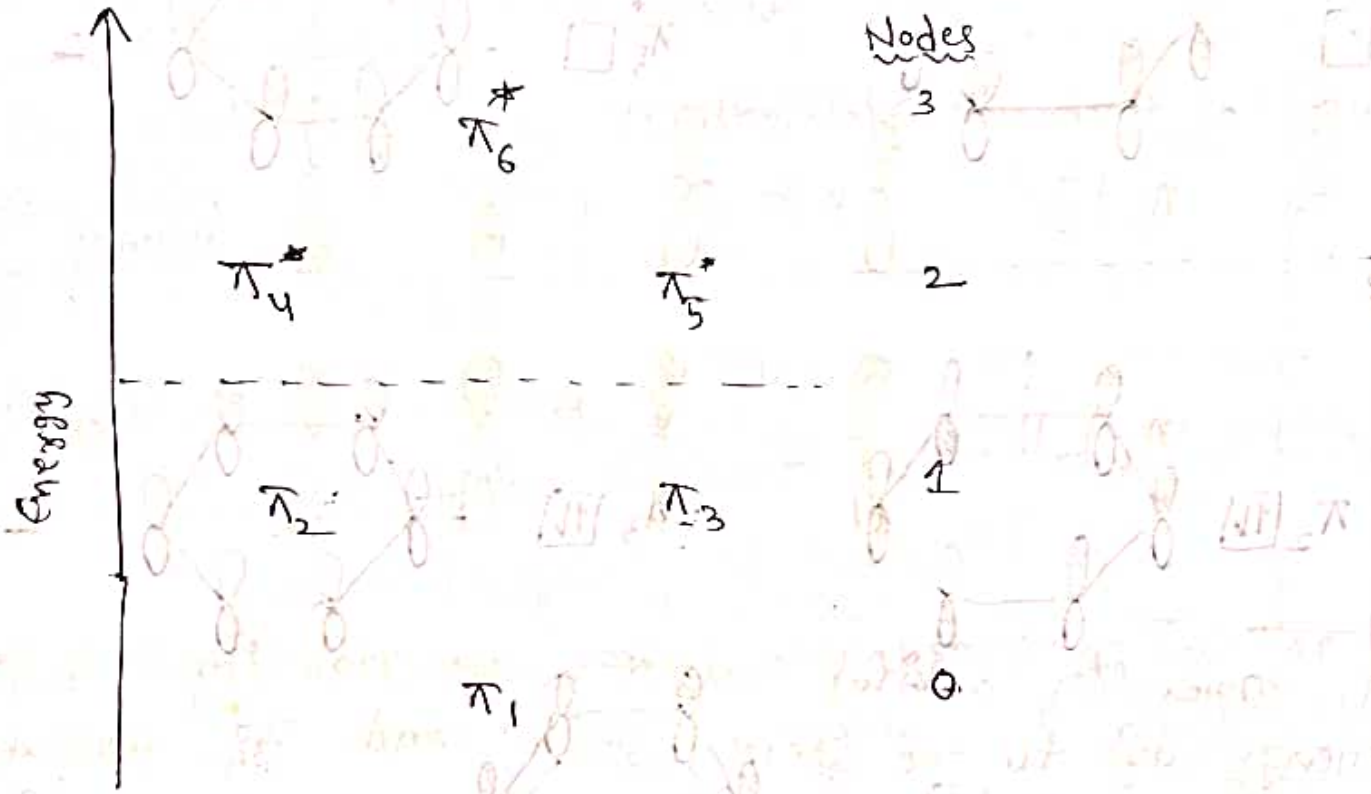


No of π electrons = 6 e^-

No of unhybridized p_z orbitals = 6

No of π molecular orbitals = 6. ($\pi_1, \pi_2, \pi_3, \pi_4^*, \pi_5^*, \pi_6^*$).

No of nodes = 3.



π_1 ⇒ More stability, less energy.

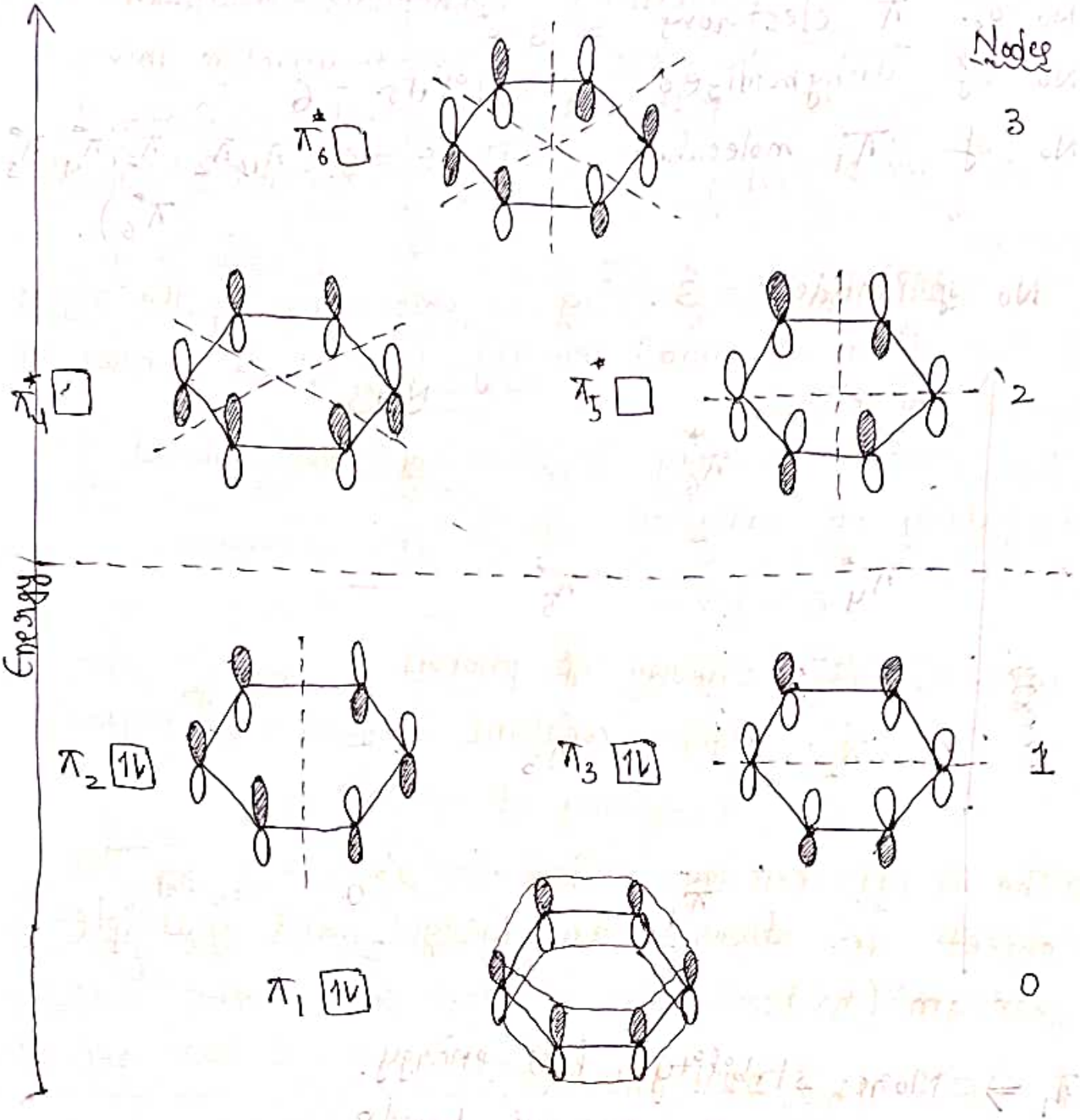
π_2 ⇒ plane passing through bonds

π_3 ⇒ plane passing through atoms.

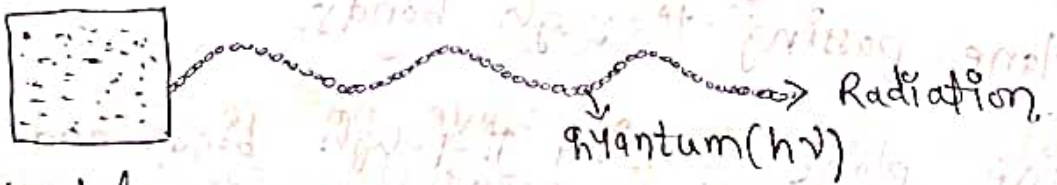
π_4^* ⇒ plane passing through bonds.

π_5^* ⇒ one plane passing through bonds and one plane passing through atoms.

π_6^* → plane passing through bonds only.



Plank's Quantum Theory:-



(i) The heated object emits radiation (light) of various wavelengths and various frequencies in the form of wave nature.

(ii) To explain these radiations max plank proposed a theory of radiation known as planks quantum theory.

(iii). Planks quantum theory state that the radiation is emiting (or) observing by the object is non-continuous process.

(iv) the radiation is emiting (or) observing by the object in the form of small energy pockets is known as quanta (or) photons.

(v) The photon energy is directely proportional to frequency of radiation $E \propto \nu$

$$\epsilon = h\nu$$

where, E = Energy of photon

h = planks constant (6.625×10^{-27} ergsec).

ν = frequency of radiation.

(vi) The total energy emited (or) observed by the object is always an integer and multiple of quantum ($h\nu$).

ex:- $E = 1h\nu, 2h\nu, 3h\nu, 4h\nu, \ldots\ldots$

$E = nh\nu$.

---

(3). Explain the dual nature of matter (or) Write the de-Broglie's concept?

Sol:- The radiation behaves as wave nature and partide nature. Hence the radiation possess dual nature. So that the matter also should possess dual nature which was proved by de-Broglie's concept.

de-Broglie's Equations

de-Broglie concept states that the matter particles like electrons, protons etc have the dual nature. It means when the matter is moving it shows the wave properties and when the matter in the state of rest it shows particle properties. The wavelength of matter particle (electron) in motion is given by $\lambda = \frac{h}{mv} = \frac{h}{p}$.

where, $p = mv$.

where, λ = wave length of e^-

m = mass of the e^-

h = plank's constant

v = velocity of e^-

p = momentum.

The above equation is known as de-Broglie's equation. de-Broglies concept is significant for microscopic particles like e^- only, for macroscopic particles the wavelength is so short and wave properties can not be observed.

Q. Write the schrodinger wave equation.

Sol:- The mathematical form of the probability of finding electron positions in various locations around to the nucleus as a wave motion in three dimensional space (x,y,z - coordinates) is known as schrodinger wave equation.

The wave function of a wave moving in a three dimensional space, with velocity(v), frequency (ν) and

wavelength (λ).

The ψ can be represented mathematically,

$$\psi = A \sin \frac{2\pi x}{\lambda} \rightarrow (1)$$

$$\frac{\partial \psi}{\partial x} = A \cos\left(\frac{2\pi x}{\lambda}\right) \cdot \left(\frac{2\pi}{\lambda}\right).$$

$$\frac{\partial \psi}{\partial x} = A \cdot \frac{2\pi}{\lambda} \cdot \cos\left(\frac{2\pi x}{\lambda}\right).$$

$$\frac{\partial^2 \psi}{\partial x^2} = A\left(\frac{2\pi}{\lambda}\right) \cdot \left(-\sin\left(\frac{2\pi x}{\lambda}\right)\right) \cdot \left(\frac{2\pi}{\lambda}\right).$$

$$\frac{\partial^2 \psi}{\partial x^2} = -A \cdot \left(\frac{2\pi}{\lambda}\right)^2 \sin\left(\frac{2\pi x}{\lambda}\right) \rightarrow (2).$$

Sub eqn (1) in (2),

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad \downarrow \text{ from eqn (1)}$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \psi = 0 \longrightarrow (3).$$

de-Broglie equation $\lambda = \frac{h}{mv}$.

Sub λ in eqn (3),

$$\frac{\partial^2 \psi}{\partial x^2} + 4\pi^2 \left(\frac{m^2 v^2}{h^2}\right) \psi = 0 \longrightarrow (4)$$

Total energy $E = PE + KE$

$$E = V + \frac{1}{2} m v^2$$

$$\frac{1}{2} m v^2 = E - V$$

$$v^2 = \frac{2(E - V)}{m}.$$

sub v^2 in eq^n (4),

$$\frac{\partial^2\psi}{\partial x^2} + 4\pi^2 \cdot \frac{m^2 2(\epsilon - V)}{m \times h^2} \cdot \psi = 0$$

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

∴ The above equation is schrodinger eq's for x-dimension.

The schrodinger's wave eq's for three dimensions is $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m(\epsilon - V)\psi}{h^2} = 0.$

Laplace operator, $\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

$$\Rightarrow \nabla^2\psi + \frac{8\pi^2 m}{h^2}(\epsilon - V)\psi = 0.$$

where,

m = mass of e^-

E = total energy

h = plank's constant.

V = potential energy

x, y, z = coordinates in three dimensional space