

Molecular Orbital Theory (MOT):

Hund & Mulliken proposed the MOT. According to this theory all the atomic orbitals of the participating atoms gets mixed up to give equal no. of new orbitals called molecular orbitals (MO)

Linear combination of atomic orbitals [LCAO]:

Molecular orbitals of a molecules are obtained by the linear combination of atomic orbitals of bonded atoms. (According to LCAO method, the LCAO can take place either by adding (constructive) or subtracting (destructive).)

(The wave function of the atomic orbitals include involve.) If two identical waves are added they combine constructively to produce wave with double the amplitude and same wave length.)

(If they combine destructively to produce the wave with zero amplitude.)



Result in wave with double the amplitude & same wave length



Resulting wave with zero amplitude

The molecular orbital formed as a result of constructive interface is known as Bond Molecular orbital [BMO] and the molecular orbital formed as a result of destructive interface is known as Anti-Bonding molecular orbital [ABMO].

Characteristics of BMO & ABMO:

BMO

- 1) The probability of finding e^- in the inter nuclear region is greater than that of combining atomic orbitals.
- 2) The electrons present in the BMO result in the attraction b/w the two atoms.
- 3) The BMO has a lower energy as a result of attraction & hence has greater stability than that of the combining atomic orbitals.
- 4) They are formed by the additive effect of atomic orbitals so that the amplitude of the new wave is given by $\Psi = \Psi_A + \Psi_B$.
- 5) They are represented by σ , π etc.

ABMO.

- 1) The probability of finding e^- in the inter nuclear region decreases.
- 2) The electrons present in ABMO result in repulsion b/w the two atoms.
- 3) The ABMO have higher energy because of repulsive forces & lower stability.
- 4) They are formed by the subtractive effect of atomic orbitals the amplitude of the new wave is given by $\Psi = \Psi_A - \Psi_B$.
- 5) They are represented as σ^* , π^* etc.

* Salient features of molecular orbital Theory :

1) The no. of molecules produced is equal to the no. of atomic orbitals combined.

2) When two atomic orbitals combine they form two molecular orbitals one of which is called Bonding molecular orbital, and the other is called Antibonding molecular orbital.

3) These are formed by addition & subtraction of wave function respectively.

3) Bonding molecular orbitals have energy lower than the combining atomic orbitals, while Antibonding molecular orbitals have higher energy than combining atomic orbitals.

4) Each molecular orbital accommodates a maximum of two electrons obeying Pauli exclusion principle.

5) Electrons enter in the molecular orbitals of identical energies singly before they pair up obeying Hund's rule.

6) Molecular orbitals are filled to increase energies starting with the orbital of minimum energy obeying Aufbau principle.

7) Shapes of molecular orbitals formed depend on the type of combining orbitals.

* Energy level diagram for molecular orbital:

The energy of molecular orbital depends on the following facts.

→ The energy of σ_{2s} and σ^*_{2s} and molecular orbitals formed by the combination of ~~two~~ two $2s$ orbitals will be higher than the molecular orbitals of σ_{1s} and σ^*_{1s} is formed by the combination of two $1s$ orbitals.

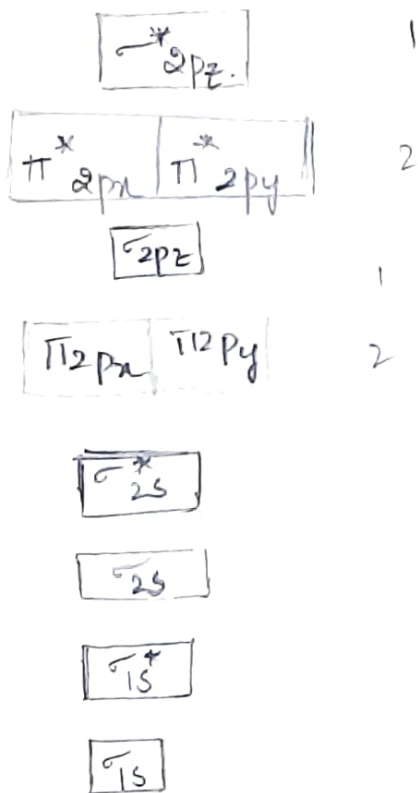
→ The molecular orbitals formed by the combination of two p orbitals will have higher energy than those formed by two s orbitals.

→ The energy of these molecular orbitals have been determined experimentally by spectroscopic method. π_{2p_x} , π_{2p_y} are degenerate orbitals. Similarly $\pi^*_{2p_x}$, $\pi^*_{2p_y}$ are degenerate orbitals.

→ $2p_z$ have max energy among six $2p$ molecular orbitals. The energy of σ_{2p_z} is not definite. When the energy difference between $2s$ and $2p$ is smaller σ_{2p_z} molecular orbital lies at higher energy than π_{2p_x} , π_{2p_y} . Thus the energy for σ_{2p_z} is higher.

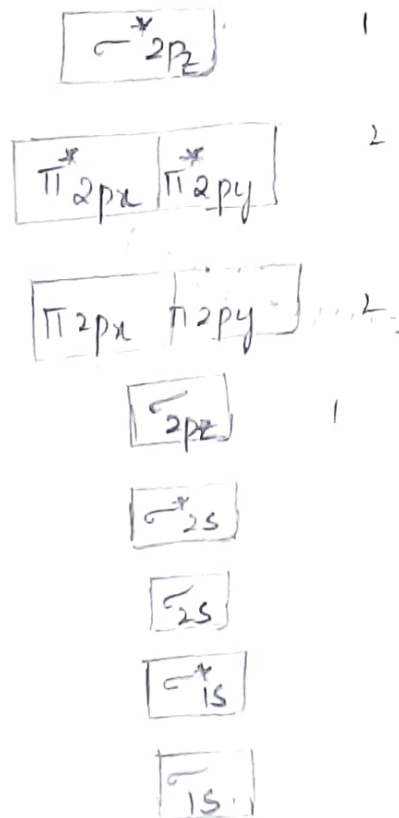
≤ 14

EX: H_2, C_2, B_2



> 14

EX: Cl_2, O_2, F_2

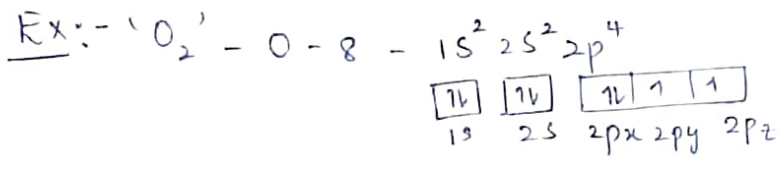


$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$

Bond Order:

Bond order is defined as half the difference b/w Num of e^- present in bonding and antibonding orbitals.

Mathematically Bond order = $\frac{1}{2} [N_b - N_a]$
 [half \times no. of e^- in Bonding - no. of e^- in Antibonding]
 = $\frac{1}{2} [N_b - N_a]$



$$\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2p_z}^2 < \pi_{2p_x}^2 = \pi_{2p_y}^2 < \pi_{2p_x}^{*1} = \pi_{2p_y}^{*1} < \sigma_{2p_z}^{*0}$$

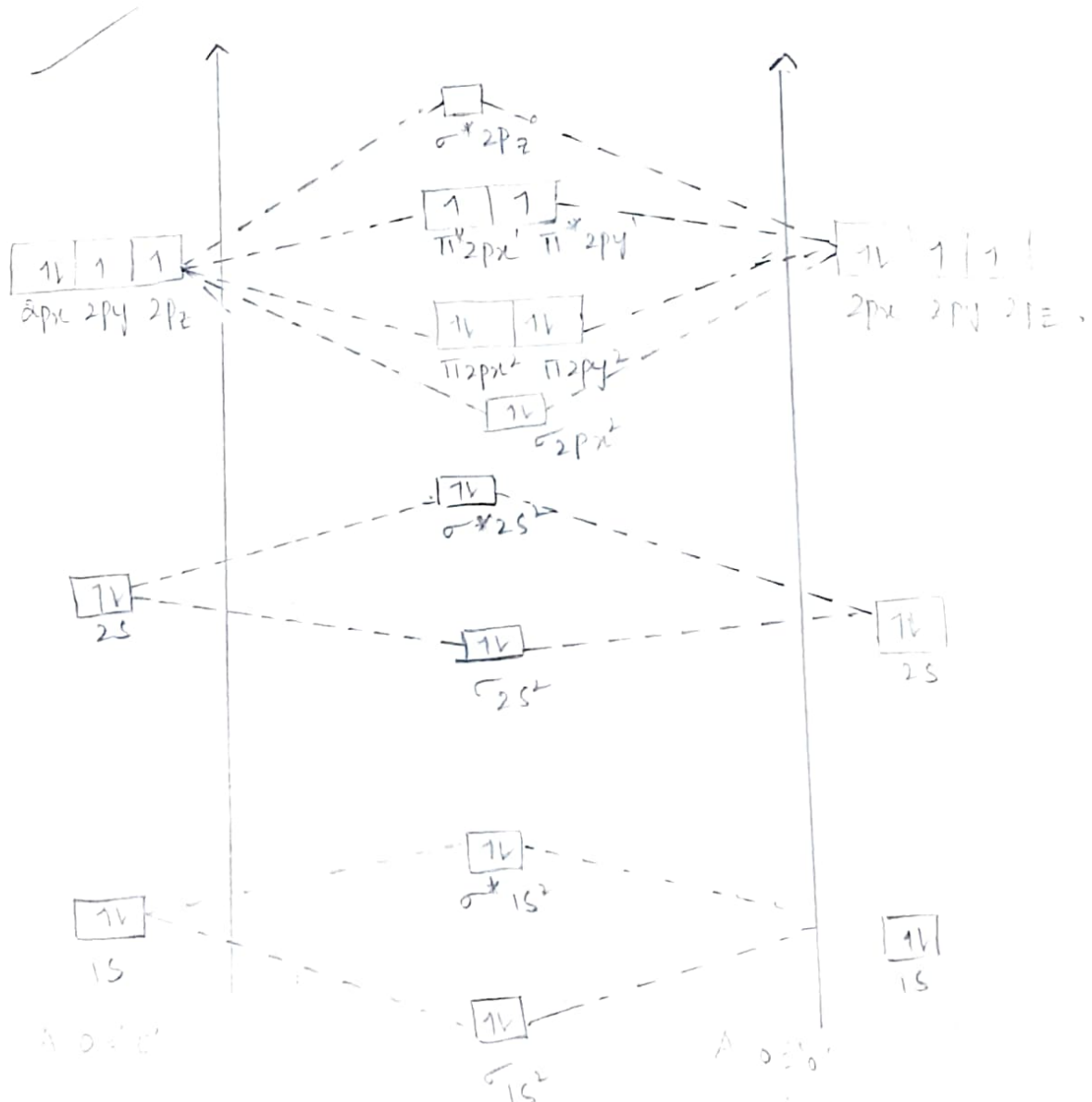
$$B.O = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [10 - 6]$$

$$= 2$$

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It is para magnetic.

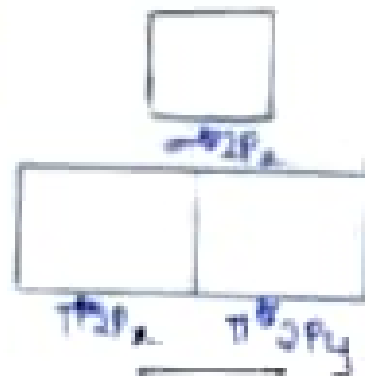


Atomic Oxygen molecule possess two e⁻ hence behaves as paramagnetic.

$$\underline{\underline{Zn}} - N_2 = 7 = 1s^2 2s^2 2p^3$$



N-PO



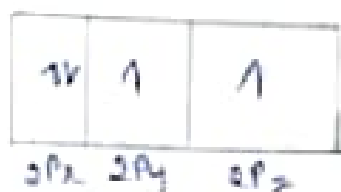
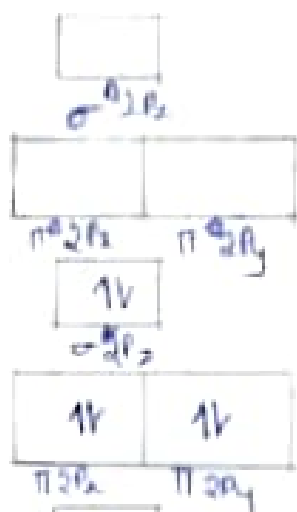
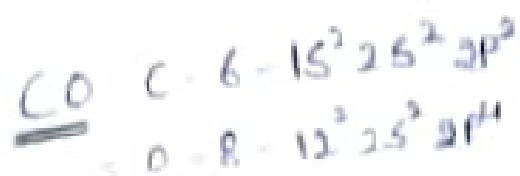
N-PO



N-PO

$$1s^2 < 2s^2 < 2p^6 < 3s^2 < 3p^4$$

$$\frac{1}{2}(10-4) = \frac{6}{2} = 3 \text{ (diamagnetic)}$$

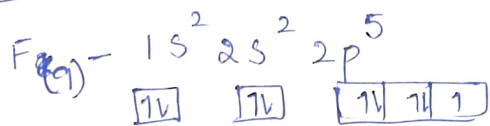


$$1s^2 < \sigma 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 = \pi 2p_y^2 < \sigma 2p_z^2$$

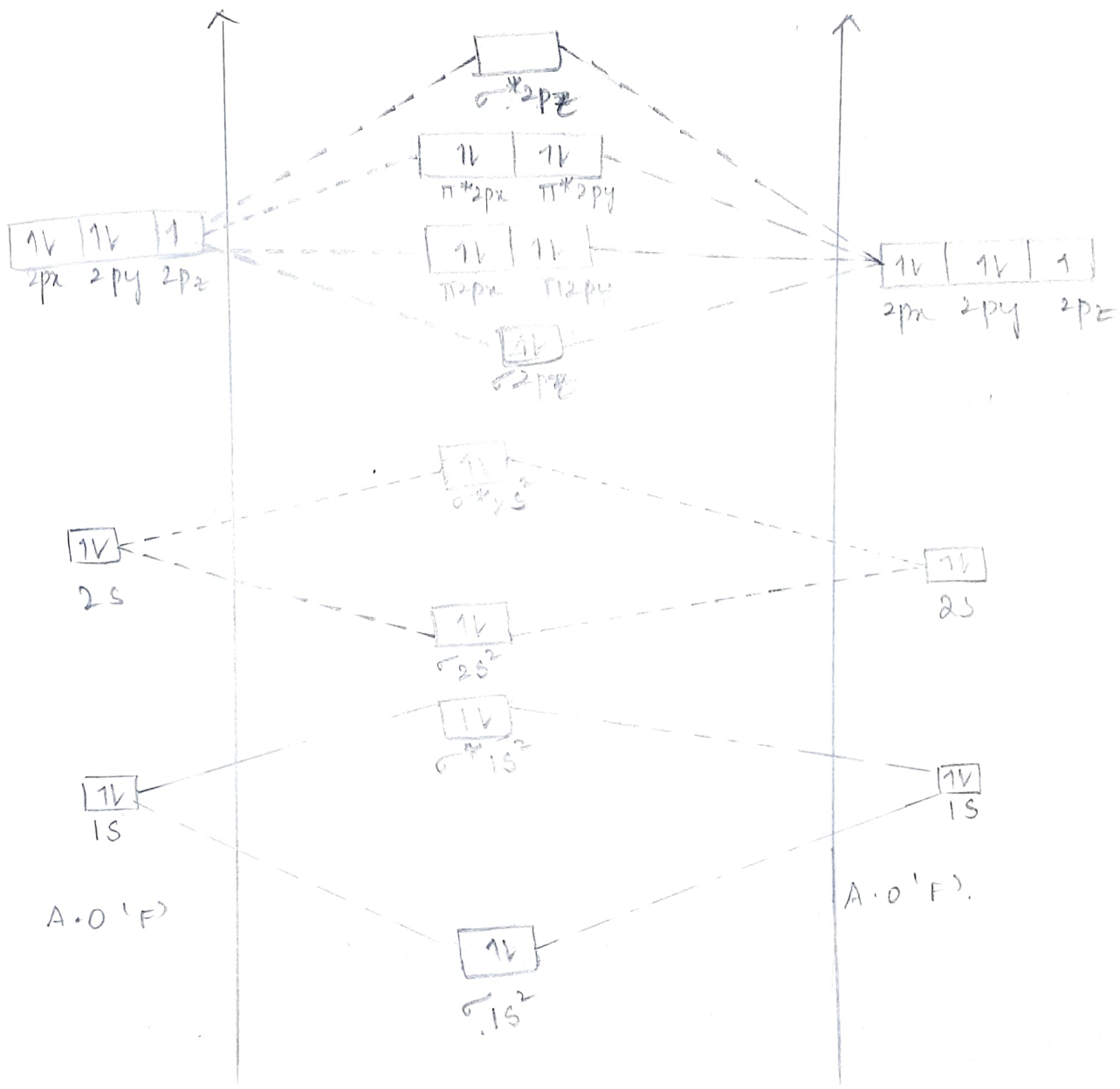
$$\frac{1}{2}(10-4) = 3 \text{ diamagnetic}$$

As there are no unpaired electrons in CO hence it is stable & diamagnetic in nature.

F₂ Molecular orbital:-



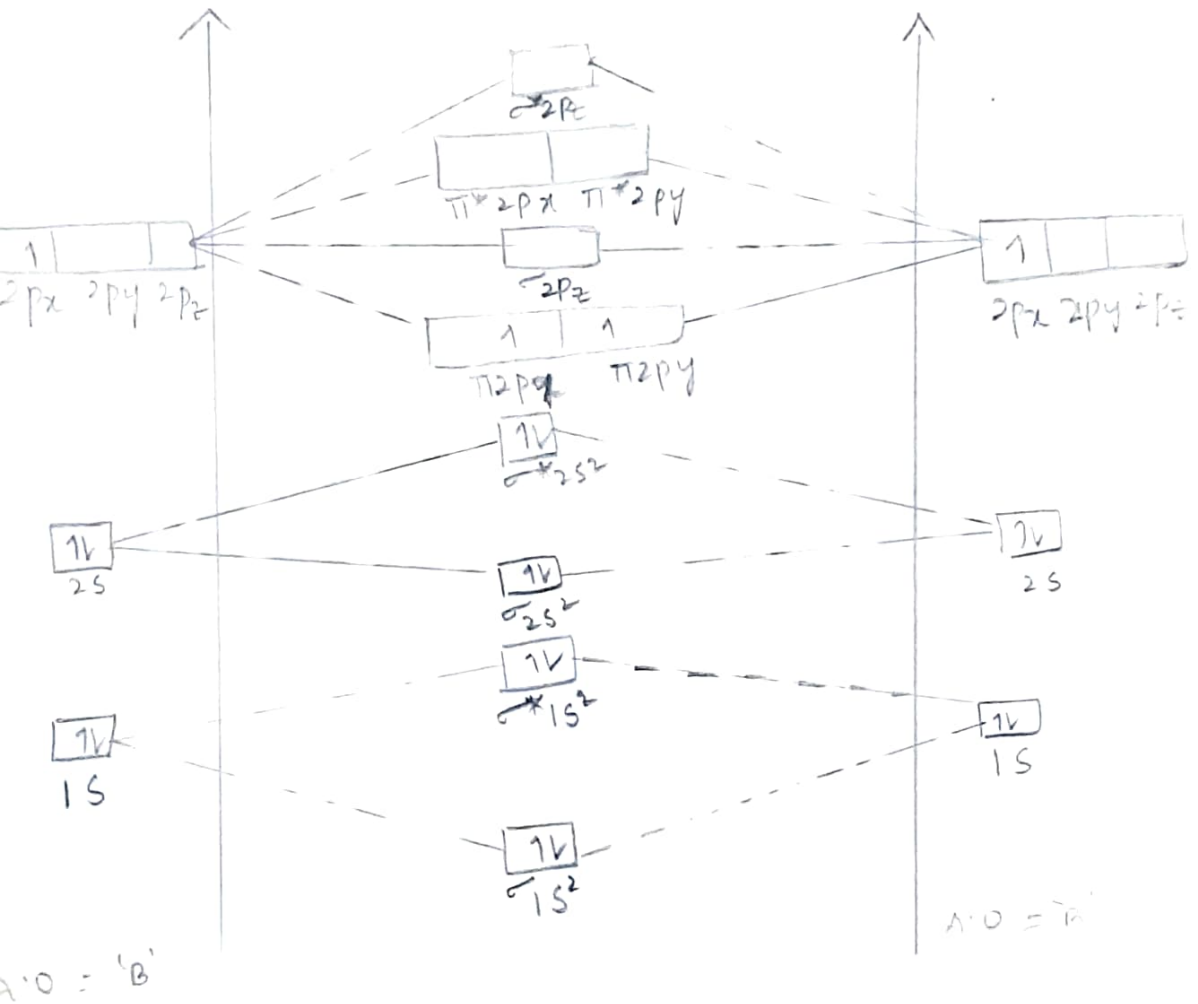
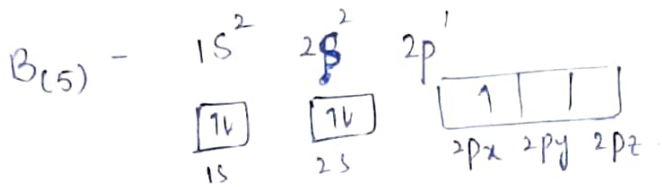
B₂



$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_{2p} = \pi_{2p} < \pi_{2p}^* < \pi_{2p}^* < \sigma_{2p}^*$$

$$B.O = \frac{1}{2}(n_b - n_a) = \frac{1}{2}(10 - 8) = \frac{2}{2} = 1$$

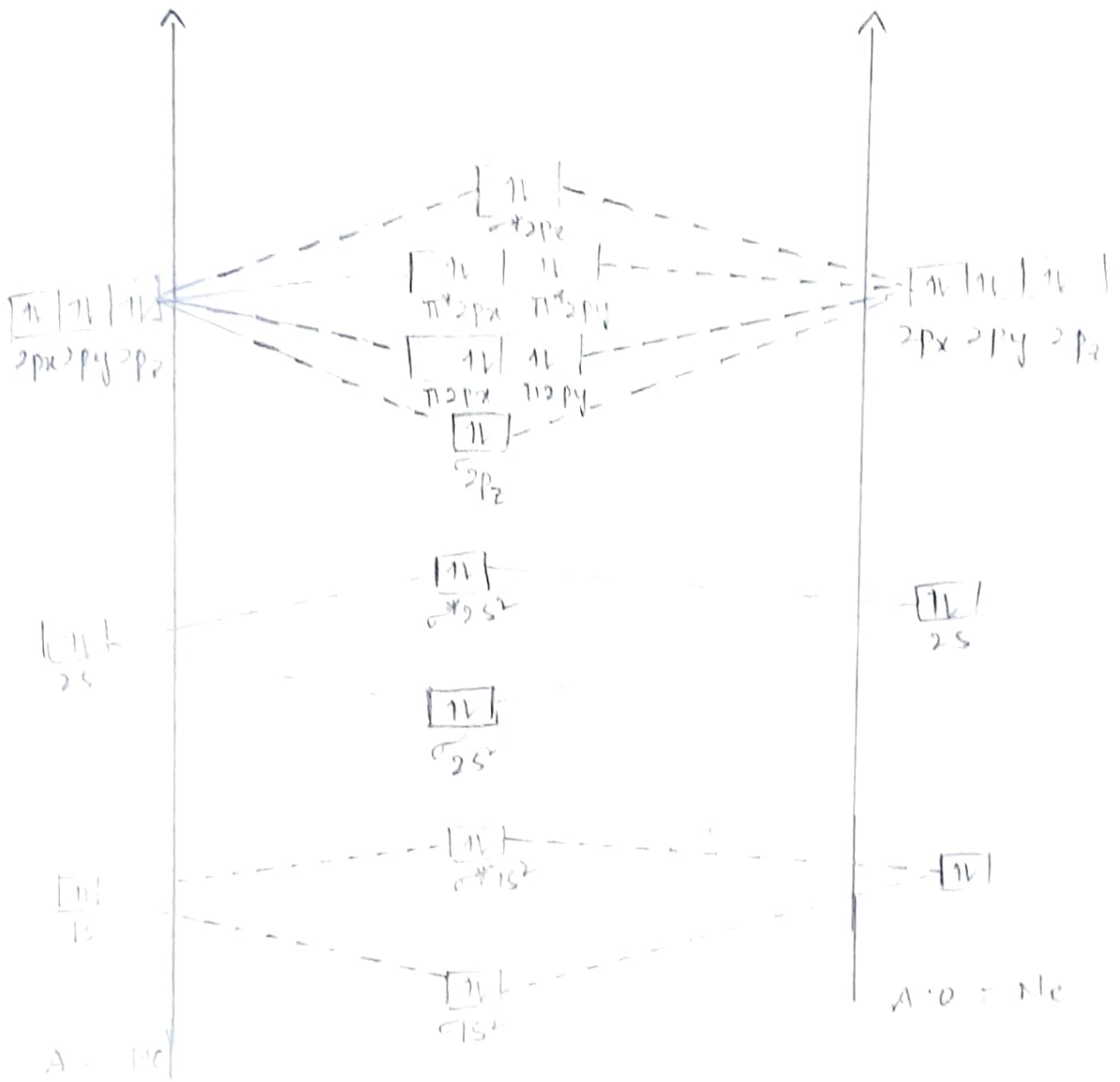
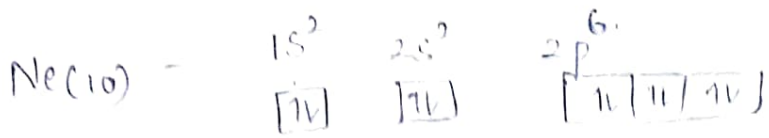
M.O of B_2^- :-



$$\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi 2p_x = \pi 2p_y$$

$$B.O = \frac{1}{2} (n_b - n_a) = \frac{1}{2} (6 - 4) = \frac{1}{2} (2) = 1$$

M.O of Ne.



$$\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2p}^2 < \pi_{2p}^4 = \pi_{2p}^2 < \pi_{2p}^{*4} = \pi_{2p}^{*2} < \sigma_{2p}^2$$

$$B.O = \frac{1}{2} (n_b - n_a) = \frac{1}{2} (10 - 10) = 0.$$

* All noble gases have zero order.