

Atomic and Molecular structure.

① What does the atom actually look like?

John Dalton - 1803 - Proposed atoms where solid spheres (indivisible)

J.J. Thomson - 1897 - discovered electrons

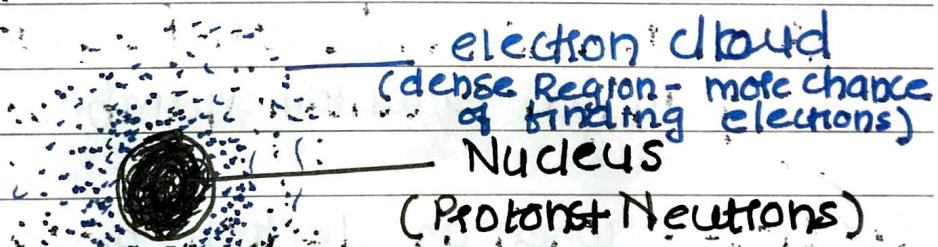
1904 - Plum-pudding model of atom.

Ernest Rutherford 1911 - Nuclear model of atom.

Niel's Bohr - 1913 - Planetary model of atom.

Schrodinger - 1926 - electron cloud model

Schrodinger discovered that electrons move around the nucleus in specific energy levels as a cloud not in orbits. The electron cloud is the region of negative charges, which surrounds the nucleus. Orbitals are regions, which help us to predict the area in which electrons are found, due to their high probability of containing electrons. Also, the closer the position to the nucleus, the higher chance of finding electrons. This breakthrough established the quantum mechanical model.



The quantum mechanical model is the most advanced and accurate model of the atom used today by chemists and physicists.

what does Quantum Number signify?

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. Each electron in an atom has a unique set of Quantum numbers. Quantum Numbers are important because they can be used to determine the electron configuration of an atom and the probable location of the atom's electrons and also understand the characteristics of atoms.

In atom there are four quantum numbers:

① Principal Quantum Number: The principal electron shell is designated as ' n '. Because ' n ' describes the most probable distance of the electrons from the nucleus.

$$n = 1, 2, 3, 4 \dots$$

K, L, M, N \dots (letter denoting orbitals)

$n=1$ - 1s - First shell

$n=2$ - 2s, 2p - Second shell

It is therefore possible to define which circular orbital is under consideration by specifying the principal quantum number.

2. Note - When an electron moves from one orbit to another a single sharp line should be observed in the spectrum. But the hydrogen spectrum revealed fine structure. This splitting of lines was observed explained by Sommerfeld due to some elliptical orbit that precessed in space around the

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nucleus. When $n=1$ there is circular orbit
 $n=2$ there is a circular and elliptical orbit
 $n=3$. There is a circular, elliptical and various elliptical orbit; so define these different orbit a second quantum number called the azimuthal Quantum Number - which tells the shape of the orbitals s, p, d, f.

spherical s - sharp
dumbbell p - principal (lines seen in atomic spectra)
double dumbbell - diffuse
complex f - fundamental

3. Electron Spin Quantum Number: It designates the direction of the electron spin and may have a spin of $+1/2 \uparrow$ and $-1/2 \downarrow$.

$$m_s = \pm 1/2$$

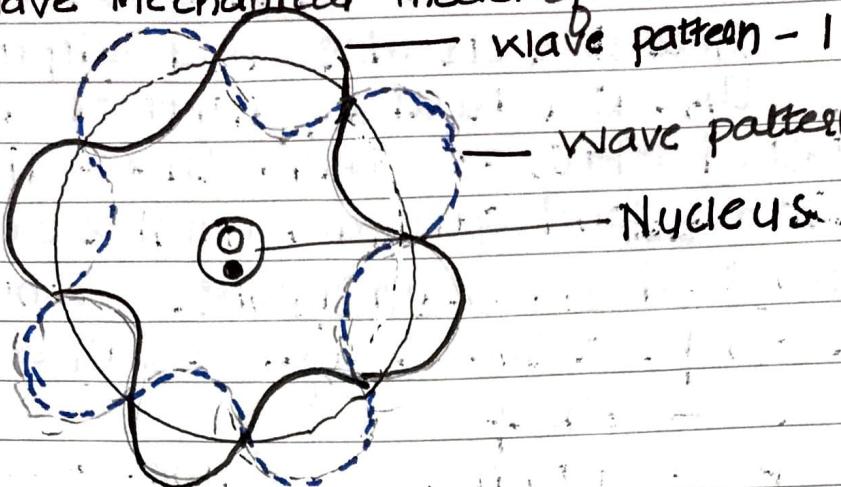
(some spectral line split still further into two lines (a doublet)).

4. Magnetic Quantum Number - zeeman showed that if atoms were placed in a strong magnetic field additional lines appeared on the spectrum. This is because elliptical orbits can only take up certain orientations with respect to the external field rather than precessing freely. Each of these orientation is associated with fourth Quantum number m_l . Thus a single line in the normal spectrum will appear $(2l+1)$ lines if a magnetic field is applied.

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Louis de Broglie - 1924.
(Wave Nature and Particle nature of electron.)

Wave Mechanical model of the Atom.



Dual Nature of matter

- Energy viewed as waves and matter as particles.
- Electrons exhibit a dual nature in which they not only have mass but possess wave like properties as well.

Wave Mechanical model

- Dense centrally located positive nucleus
- Electron no longer pictured in fixed orbits but as regions of differing energy levels where they are most likely to be found called orbitals

A region with an atom where the chances of an electron being present there, is 90% of the time is called atomic orbitals. In the Heisenberg Uncertainty principle, it is stated that the position, as well as the energy of the electron, cannot be known. If we have more information about the electron's energy, the information about the electron's position is less and vice versa.

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 Molecular orbital theory.
 When nuclei of two atom come close to each other their atomic orbitals interacts to form molecular orbitals.

- Each molecular orbitals is describe by the wave function Ψ .
- Ψ^2 represents the probability density or electron charge density.
- Each molecular orbitals wave function is associated with a set quantum numbers.
- Electron fill the molecular orbitals in the same way as they fill the atomic orbitals.
- Electron in molecular orbitals belongs to all the nuclei present in the molecule.
- Each electron in molecular orbitals has a spin $+1/2$ and $-1/2$.
- The molecular orbitals are designated as σ , π , δ

Wave function describing the Molecular orbitals

- Linear combination of atomic orbitals (LCAO)
- Atomic orbital roughly must have same energy.
- Maximum overlap
- In order to produce bonding and antibonding orbitals, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line or both must change symmetry in identical manner.

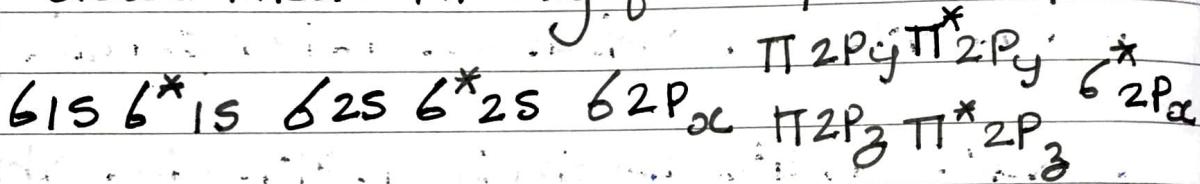
Molecular orbitals - In the same way that each atomic orbitals has a particular energy and may be defined by four quantum numbers. Molecular orbitals has a definite energy and is also defined by four quantum numbers.

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Rules for adding electrons to Molecular orbitals

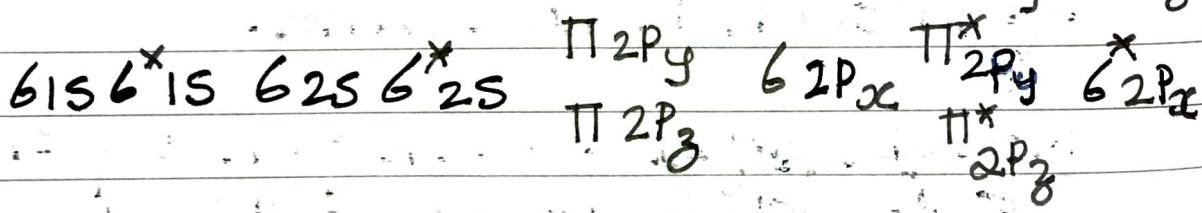
1. Aufbau Principle - The molecular orbital with lowest energy are filled first
2. Pauli exclusion principle - Each molecular orbital may hold upto two electrons; provided that they have opposite spin.
3. Hund's Rule - When several orbitals have the same energy, electrons will be arranged so as to give the maximum number of unpaired spins.

Energy level for Molecular orbitals : The order of energy of molecular orbitals has been determined mainly from Spectroscopic data



→ increasing energy.

However, spectroscopic studies have revealed that the above sequence of energy level of MOs is not correct for all molecules. In case of homonuclear diatomic molecule of second row upto Nitrogen ($Li_2, Be_2, B_2, C_2, N_2$) $62P_\alpha$ is higher than $\Pi 2P_y, \Pi^* 2P_3$.



(Mixing of $62S$ and $62P_{3\alpha}$ upto N_2)
 6^*2S and $6^*2P_{3\alpha}$

Electronic configuration of Molecule and molecular Behaviour.

① If there are unpaired electrons - paramagnetic.
paired electrons - diamagnetic

② N_a - Number of Antibonding electrons
 N_b - Number of Bonding electrons.

$N_a = N_b$ or $N_a > N_b$ - No bond is formed.

$N_b > N_a$ - Molecule is stable and bond is formed

3. The relative stability of molecule can be measured by introducing new concept Bond order

$$\text{Bond order} = \frac{1}{2} (N_b - N_a)$$

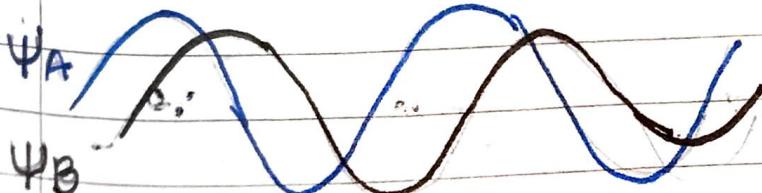
Bond order = zero or Negative (unstable)
= Positive (stable)

4. Bond order \propto Bond length.

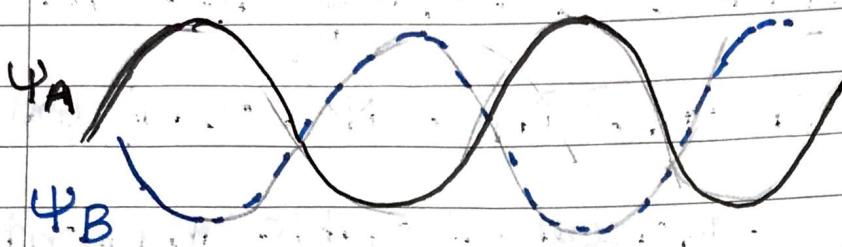
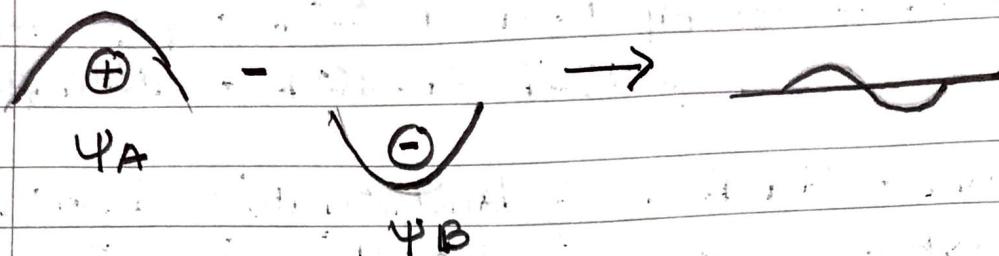
Formation of Bonding Molecular orbital Ψ_b



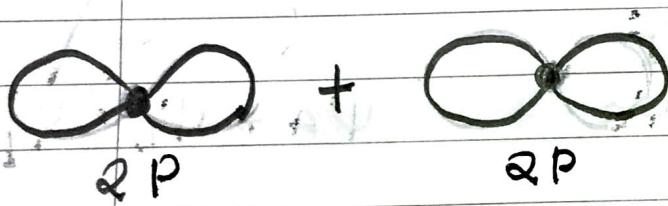
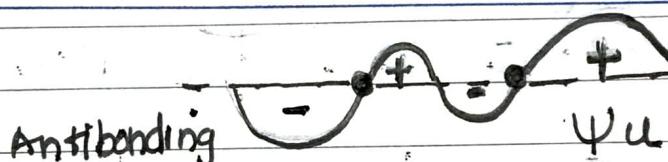
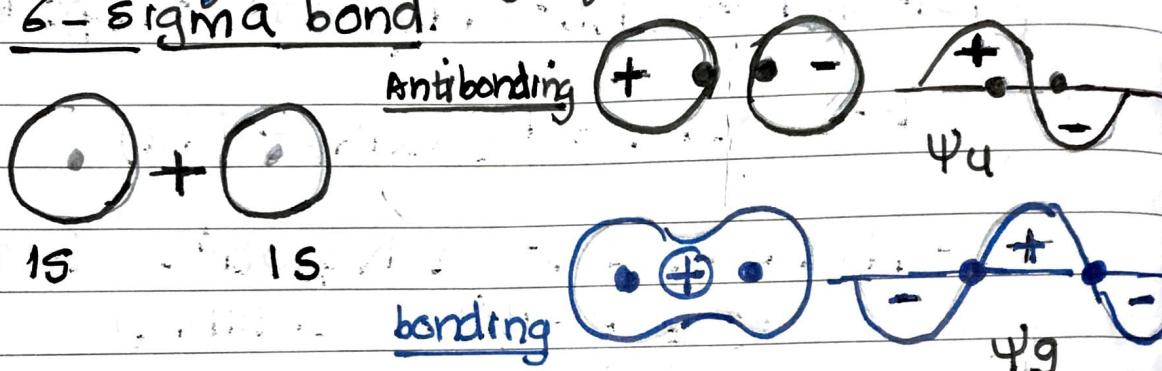
$$\Psi_A + \Psi_B = \Psi_b$$



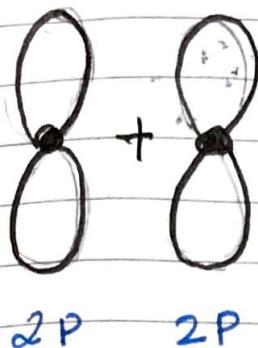
Formation of Antibonding orbital Ψ_a



concept of symmetry of molecular orbitals 6 - sigma bond



π-bonds (Pi)



Antibonding
 ψ_g



Bonding ψ_u

The molecular orbital wave functions are designated by ψ_g g - gerade
 ψ_u u - ungerade.

Rotate the orbitals (C.M.O) about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same the orbitals is gerade and if the sign changes then orbitals is ungerade.

Molecular orbital Diagram for Homonuclear molecule (i) Be_2 (ii) O_2

(i) Beryllium - Be - Atomic Number - 4.

Atom - 1 Be

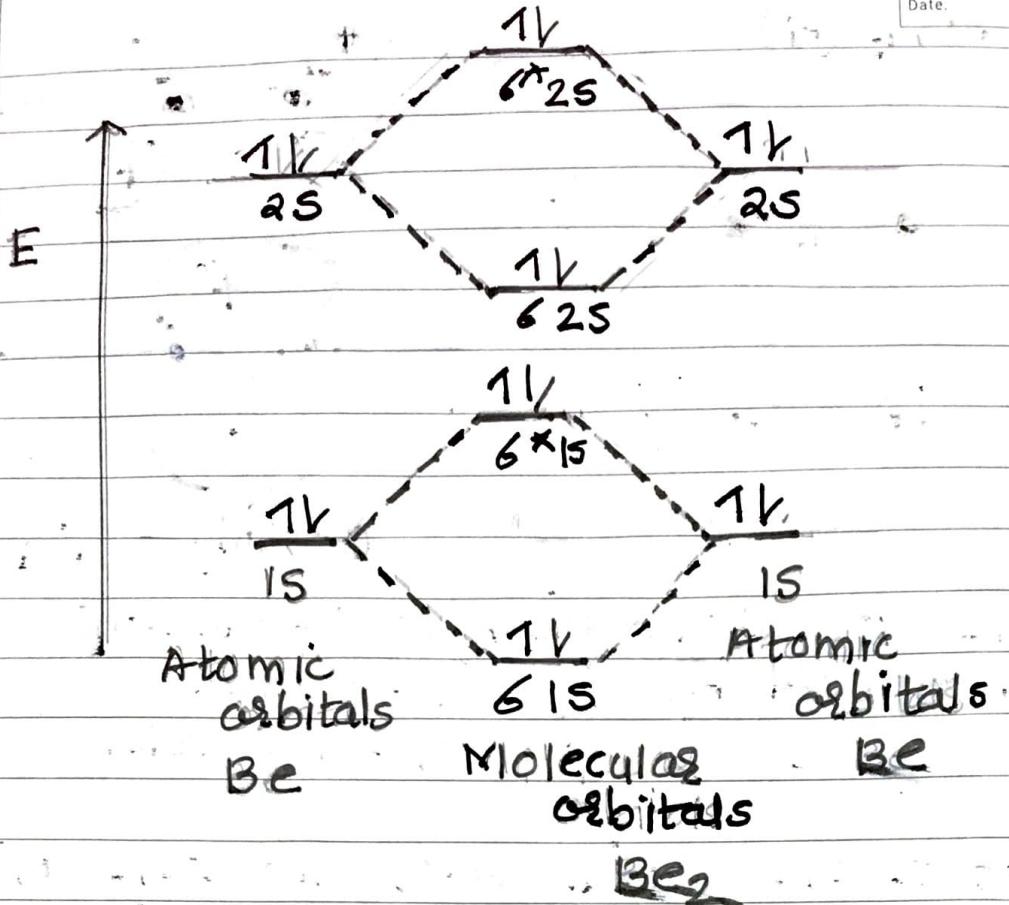
Atom - 2 - Be

Atomic configuration.

$1s^2, 2s^2$

$1s^2, 2s^2$

(since the are same atoms, the atomic orbitals should be shown at same level.)

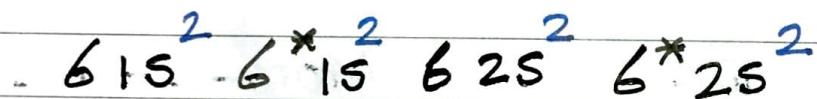


$$\text{Bond order} = \frac{1}{2} (\text{N}_b - \text{N}_a)$$

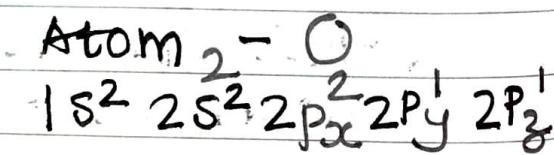
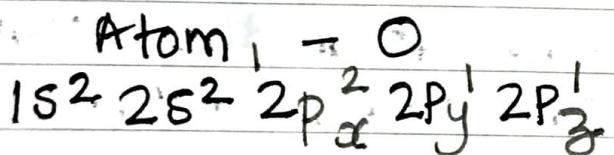
$$= \frac{1}{2} (4 - 4) = \text{Zero}$$

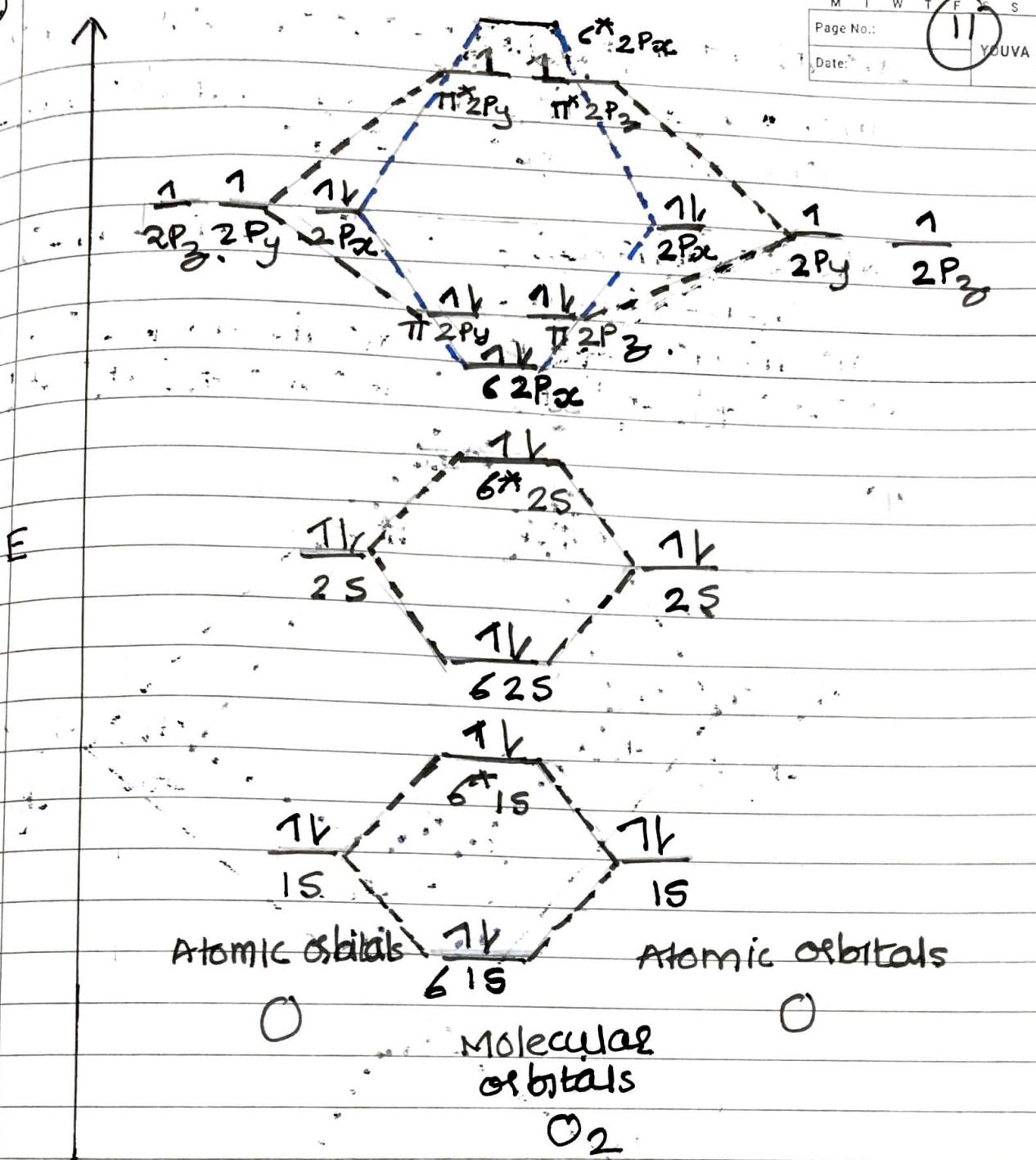
Magnetic Property - diamagnetic

Electron configuration - Molecule - Be₂



2. oxygen - O Atomic Number - 8

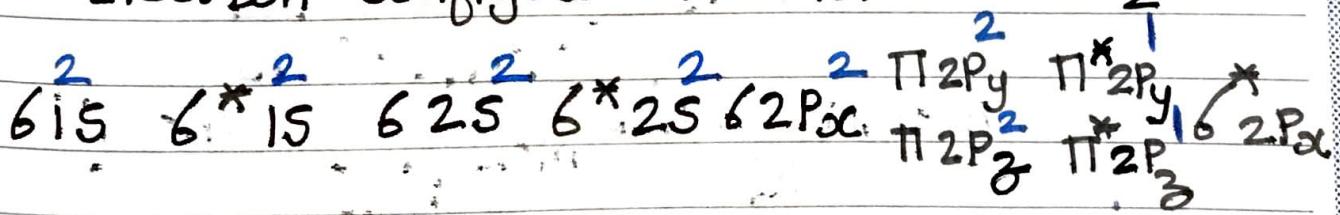




$$\begin{aligned}
 \text{Bond order} &= \frac{1}{2} (N_b - N_a) \\
 &= \frac{1}{2} (10 - 6) = 2
 \end{aligned}$$

Magnetic Property - Paramagnetic

Electron configuration - Molecule O₂



(Atomic orbitals should be shown at different levels)

Molecular orbital diagram for Heteronuclear molecule

① CO ② NO

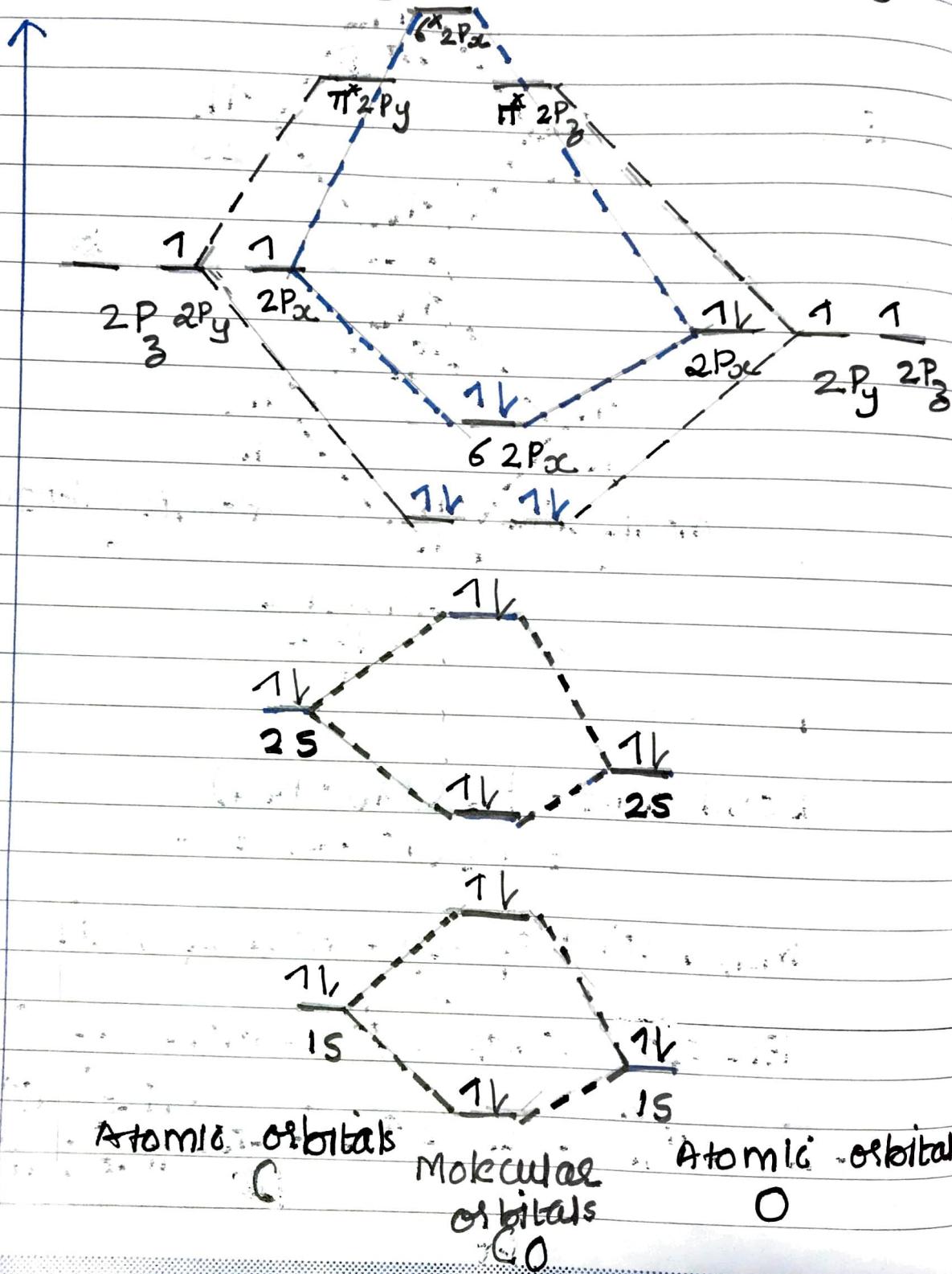
Carbon monoxide - CO (since $14e^-$, hence like N_2)

Atomic No - C - 6

$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Atomic Number O - 8

$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

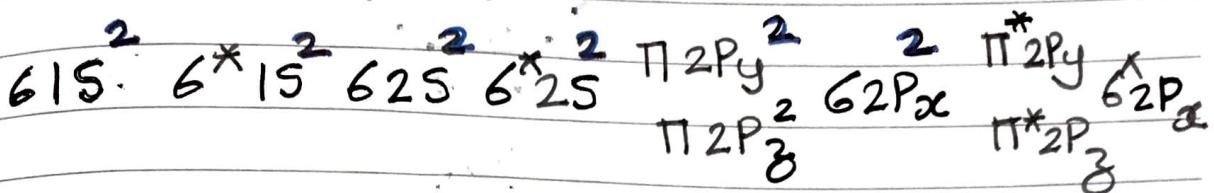


$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

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

Magnetic Property - diamagnetic

Electron configuration - molecule C₂O



Bond order for CO⁺ (one e⁻ from bonding orbital removed)

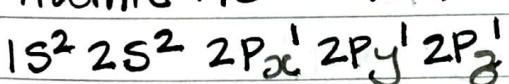
$$= \frac{1}{2}(9 - 4) = 2.5$$

Bond order for CO⁻ (one extra electron goes in $\pi^* 2P_y$).

$$= \frac{1}{2}(10 - 5) = 2.5$$

a. Nitric oxide - NO

Atomic NO - N - 7



Atomic Number O - 8

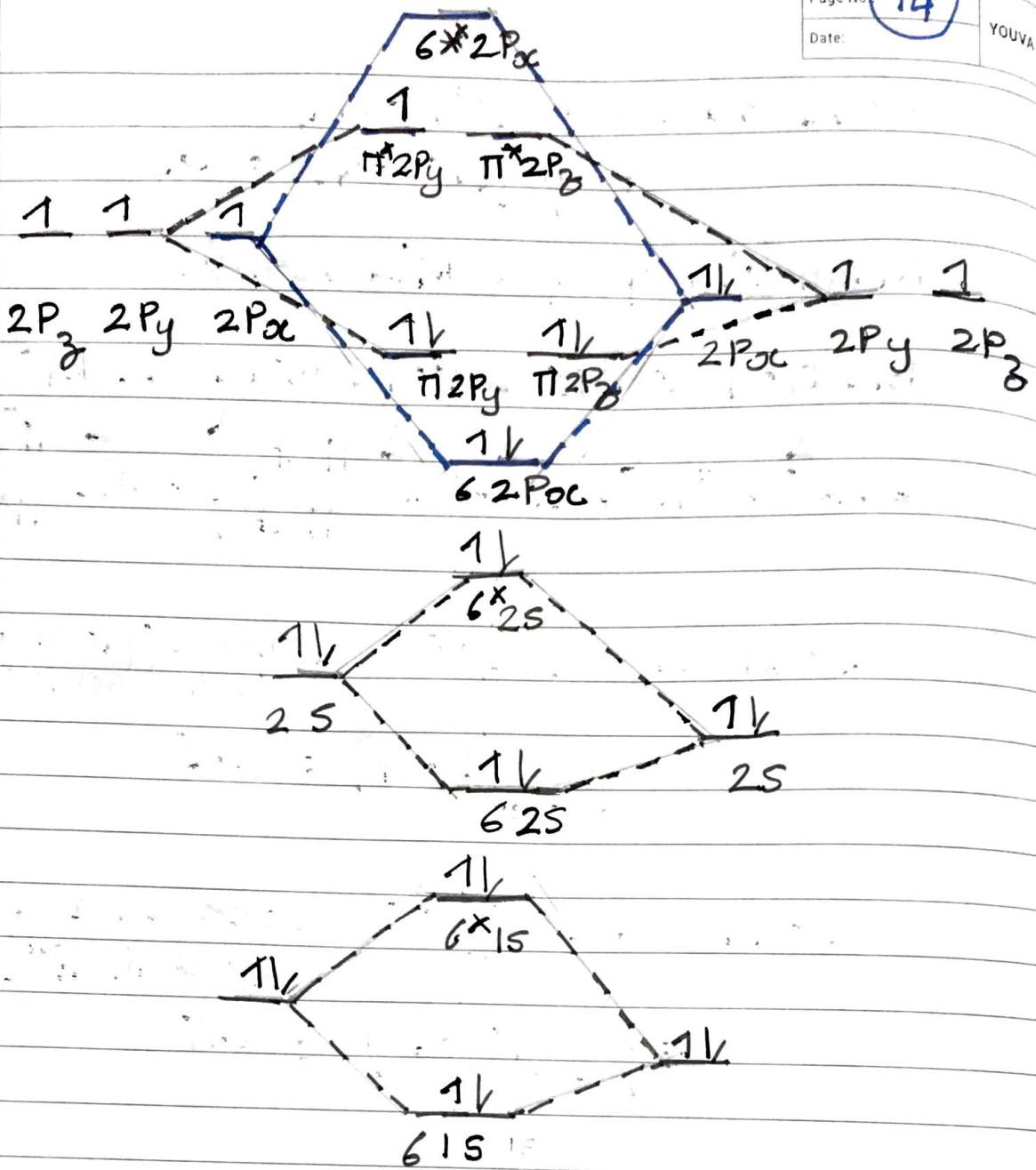


Total Number of electrons in NO - 15e⁻

The order of energy level of various molecular orbital are the same as for homonuclear diatomic molecule after Nitrogen.

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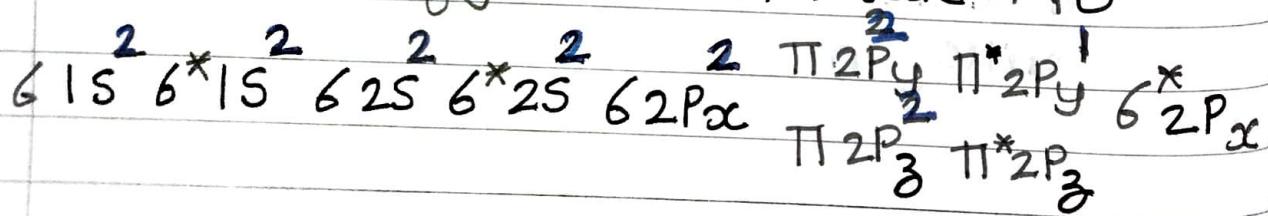


$$\text{Bond order} = \frac{1}{2} (N_B - N_A)$$

$$= \frac{1}{2} (10 - 5) = 2.5$$

Magnetic Property - Paramagnetic

Electron configuration - Molecule NO



Distinguish Between Bonding and Antibonding Orbitals

Bonding Orbitals

1. formed by addition of atomic orbitals

$$\Psi_{(MO)_b} = \Psi_A + \Psi_B$$

Antibonding Orbitals

- formed by subtraction of atomic orbitals.

$$\Psi_{(MO)_a} = \Psi_A - \Psi_B$$

2. when signs of the lobes of atomic orbitals is same
3. high electron density between the nuclei of two atoms.
4. They are stable
5. Have lower energy than either of atomic orbitals
6. Designated by σ, π, δ

- when sign of the lobes of atomic orbitals is different
- low electron density between the nuclei of two atoms

They are unstable
Have higher energy than either of atomic orbitals

Designated by $\sigma^*, \pi^*, \delta^*$

Distinguish between σ MO and π MO

σ -Molecular orbital

1. The lobes of the A.O are in line with the internuclear axis
2. Formed by head on collision of atomic orbitals
3. Electron density along the internuclear axis is maximum.
4. Bonding M.O are gerade and antibonding ungerade.
5. Stronger bonds

π Molecular orbital

- The lobes of A.O are perpendicular to the internuclear axis.

Formed by lateral overlap of atomic orbitals
Electron density along internuclear axis is zero.
Bonding M.O are ungerade
Antibonding gerade.
Weak bonds comparatively.