DIAMAGNETISM AND PARAMAGNETISM

Diamagnetic substances

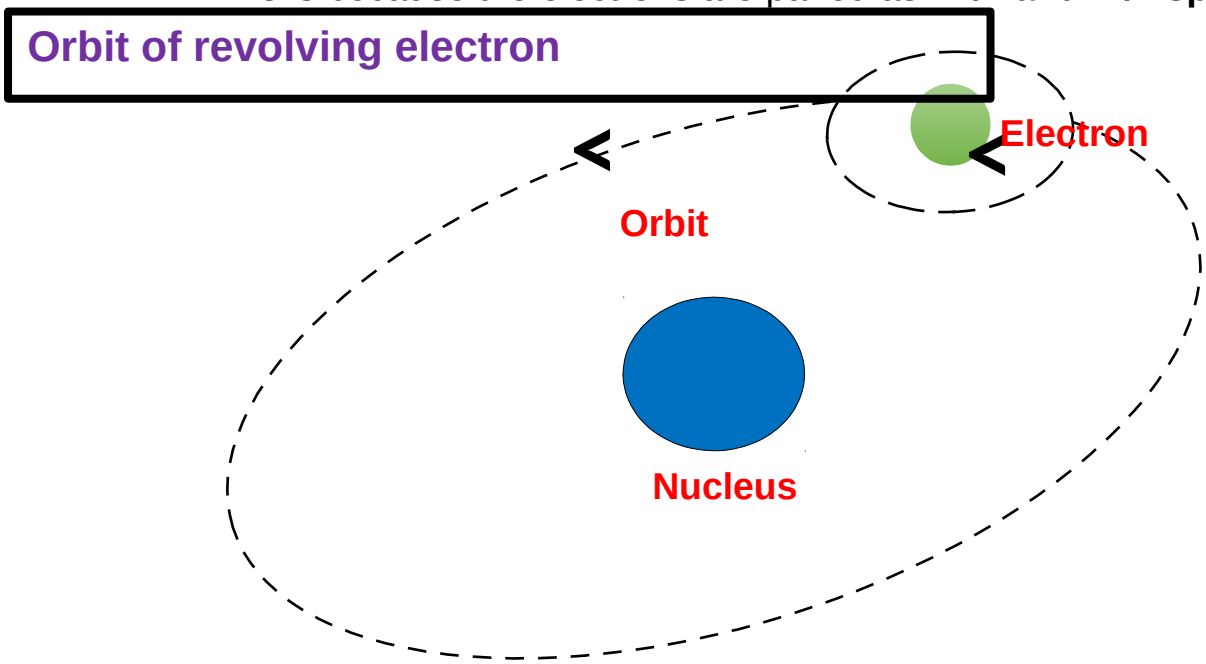
- Atoms with paired electrons are called **diamagnetic.**
- Diamagnetic substances **repel from the magnet.**
- The resultant spin moment is **zero.**

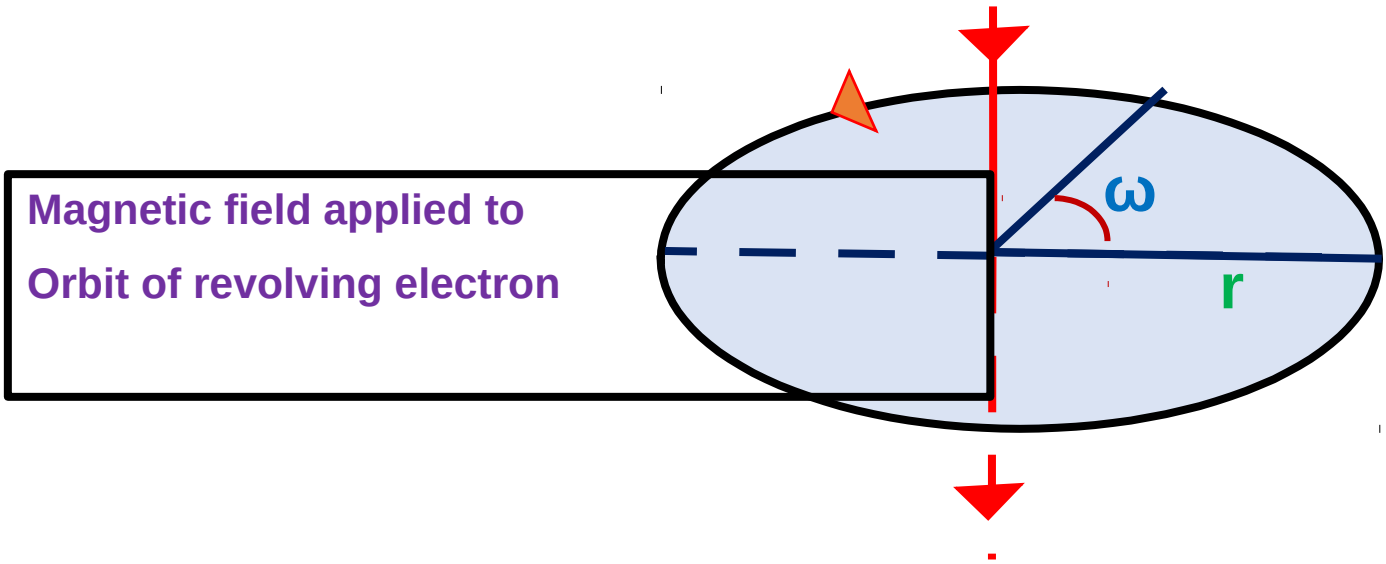
Paramagnetic substances

- Atoms with unpaired electrons are called **paramagnetic.**
- Paramagnetic substances **attract to the magnet.**
- They **have resultant spin moment.**

LANGEVIN'S THEORY OF DIAMAGNETISM:

- Theory of diamagnetism was first worked out by **Paul Langevin** in **1905.**
- Langevin applied the **electronic theory** to explain the magnetic behaviour of the substances.
- According to this theory, the atom of a diamagnetic substance is such that the **resultant magnetic moment of the atom as a whole is zero.**
- This is because the electrons are paired as **+1/2 and -1/2 spin.**





- When an **external field is applied** to such an atom, there occurs a **uniform processional motion (slow movement)** of electron orbits relative to each other.
- Thus, that atom as a **whole possesses a negative magnetic moment but not zero.**
- The magnetic moment per gram atom will be

$$\sum \Delta\mu_A = \frac{-N e^2 H Z}{6m} . \sum r^2$$

Where **Δμ** is **change in magnetic moment**

e is electronic charge

H is magnetic field strength

Z is atomic number

r is radius of electron circular orbit

m is mass of the electron moving in a circular orbit

$\Delta\mu_A$ is change in magnetic moment of atom 'A'

N is the Avogadro's number

- **LANGEVIN'S THEORY OF PARAMAGNETISM:**
- **Explained paramagnetic behaviour of substances on the basis of kinetic theory.**
- He assumed that the molecules of paramagnetic substance contain **permanent magnets due to rotating electrons.**
- When placed in an external field they **tend to orient themselves with their magnetic axis in the direction of the field.**
- However, this tendency will be opposed by the collisions **due to thermal motion** between the molecules.
- As a result, there will be an **equilibrium distribution of the axes with respect to the direction of the field.**
- He further extended the theory to determine the **number of unpaired electrons present in the compound** with the use of following formula,

where χ_M is the **molar susceptibility**

$$\chi_M = \frac{N.\ \mu^2}{3KT}.\ [(n(n+2)]$$

N is **Avogadro's number**

K is **Boltzmann's constant**

T is Temperature

μ is **permanent magnetic moment**

n is **number of unpaired electrons**

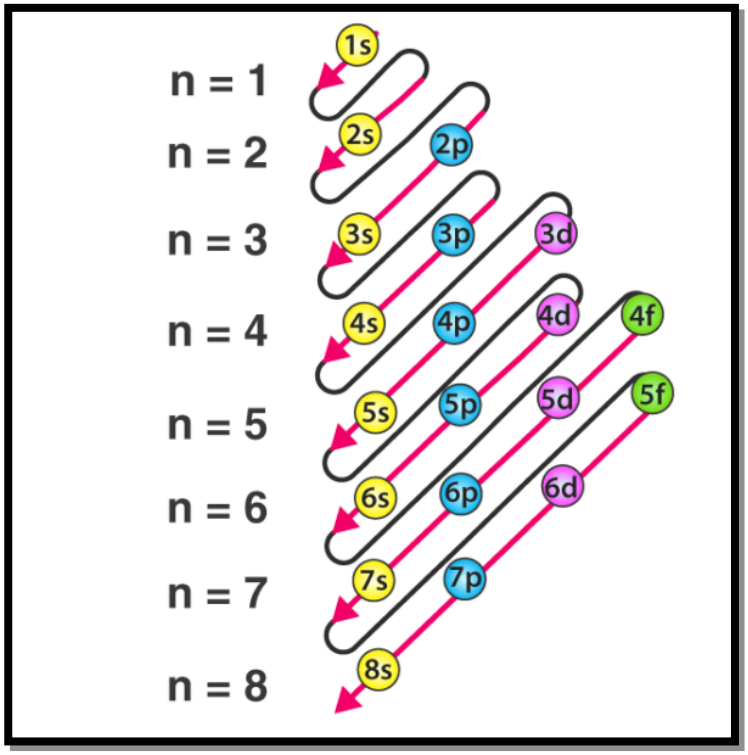
Table: Molar Susceptibilities

Paramagnetic	χ_M X 10^{-6}	Diamagnetic	χ_M X 10^{-6}
Aluminium	+ 0.65	Bismuth	- 1.39
Potassium	+ 0.52	Copper	- 0.09
Air	+ 24.16	Water	- 0.72
Oxygen	+3449.0	Hydrogen	- 4.00
Ferrous Sulphate	+10,200.0	Ammonia	- 17.92
Nickel Chloride	+6145.0	Carbon dioxide	- 21.00
Cobalt Sulphate	+10,000.0	Carbon tetra chloride	- 66.36
Nickel Oxide	+54.00	Hydrogen Sulphide	- 25.50

INTERPRETATION OF PARAMAGNETIC PROPERTY OF OXYGEN AND NITRIC OXIDE MOLECULE

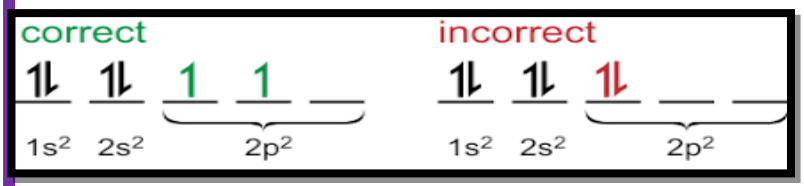
Aufbau's principle:

In the ground state of an atom or ion, **electrons** fill atomic orbitals of the lowest available energy levels before occupying higher levels.



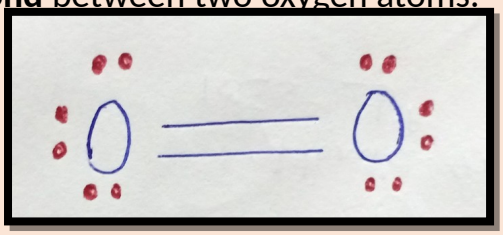
Hund's rule: **Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.**

For eg, Consider Carbon atom with atomic number = 06



1. Oxygen molecule (Homonuclear)

- Represented by **double bond** between two oxygen atoms.



- But **molar susceptibility** of oxygen found to be **3449 x 10^{-6}** and it is **paramagnetic** in nature.
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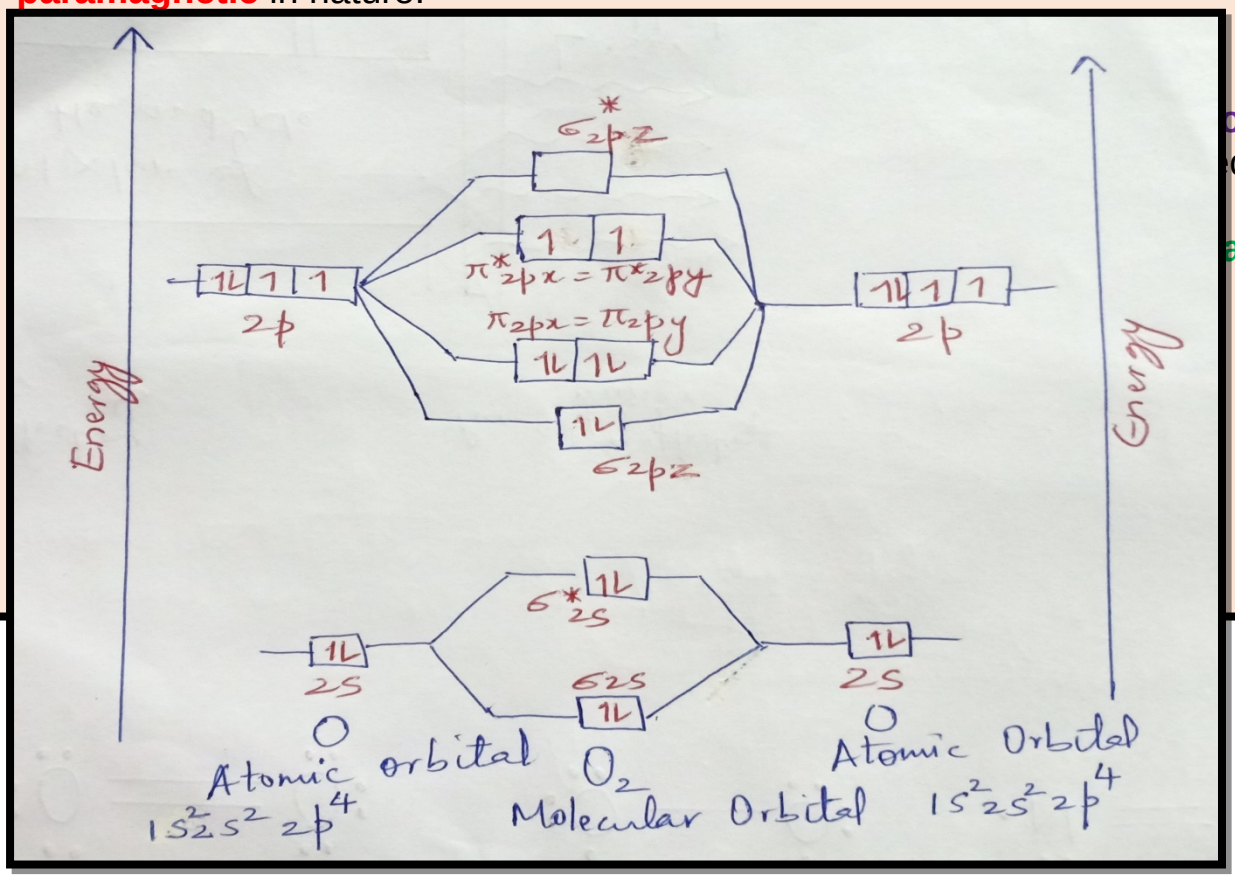
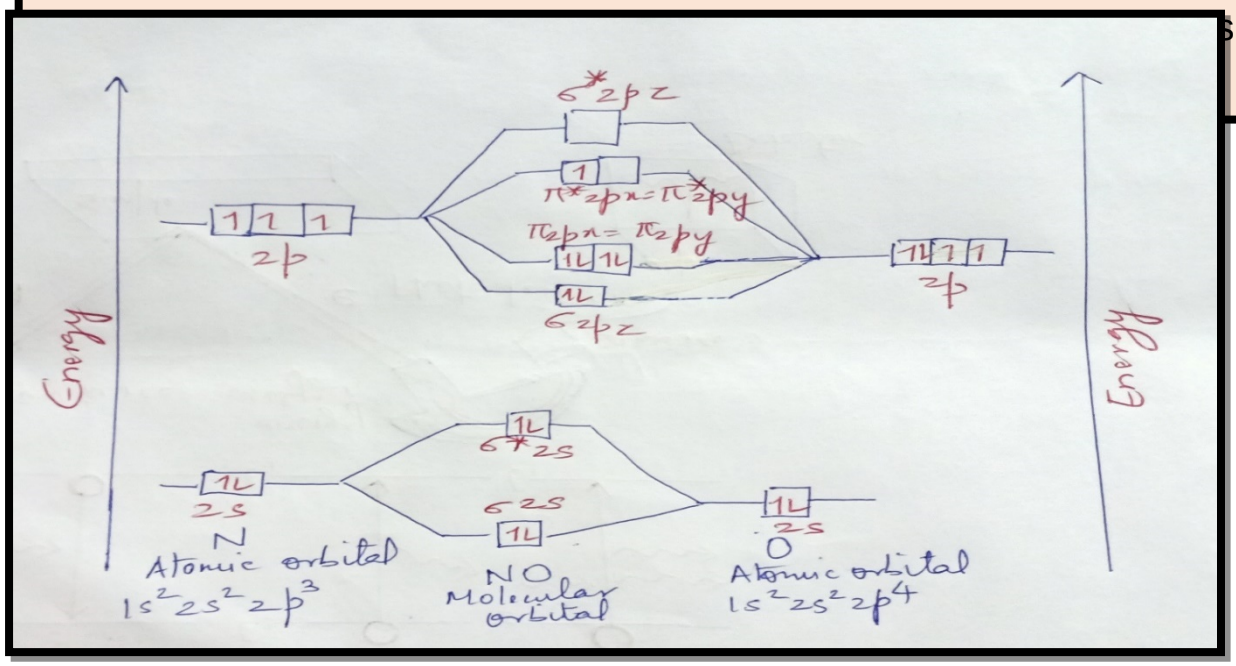


2. Nitric oxide molecule (Heteronuclear)

- **Paramagnetic in nature indicates that it must have unpaired electrons.**
- This can be explained by **Molecular Orbital Theory.**
- **Atomic orbital of Nitrogen and Oxygen atoms overlap to form σ and π orbitals.**
- **15 valence electrons are added in the molecular orbital of Nitric oxide according to Aufbau principle.**
- **Last electron goes into π^*_{2px} antibonding orbital according to Hund's rule.**



- Nitric oxide shows **paramagnetic property in gaseous state.**
- In **solid state, it shows diamagnetic property.**
- It means that in solid state **two odd electrons of two nitric oxide molecules go for inter-molecular spin coupling** and give the formation of dimer structure.