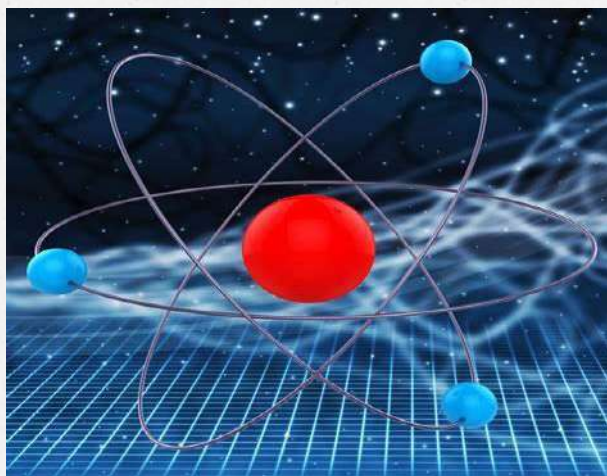


ATOMIC AND MOLECULAR STRUCTURE

UNIT-I



PTU-SYLLABUS

- o Unit I Atomic and molecular structure Schrodinger equation. Particle in a box solution and their applications for conjugated molecules and nanoparticles. Molecular orbitals and energy level diagrams of diatomic molecules. Equations for atomic and molecular orbitals. Pi-molecular orbitals of butadiene and benzene and aromaticity. coordination numbers and geometries, Crystal field theory and the energy level diagrams for transition metal ions (octahedral and tetrahedral environment) and their magnetic properties. Band structure of solids and the role of doping on band structures.

Molecular Orbital Theory

- According to the Molecular Orbital Theory, individual atoms combine to form molecular orbitals. Thus the electrons of an atom are present in various atomic orbitals and are associated with several nuclei.
- Molecular Orbital Theory is the theory which is used to explain the bonding in molecules that cannot be explained by Valence Bond Theory.
- Valence bond theory only describes the bonding of single or double or triple bonds. It does not provide an explanation for resonance bonding.

Postulates of Molecular Orbital Theory:

1st Postulate: The number of molecular orbitals produced is always equal to the number of atomic orbitals brought by the atoms that have combined.

2nd Postulate: Bonding molecular orbitals are lower in energy than the parent orbitals, and the antibonding orbitals are higher in energy.

Postulates of Molecular Orbital Theory:

3rd Postulate : Electrons of the molecule are assigned to orbitals from lowest to successively higher energy.

4th Postulate: Atomic orbitals combine to form molecular orbitals most effectively when the atomic orbitals are of similar energy.

Conditions for the combination of atomic orbitals

1) The combining atomic orbitals should have comparable energy

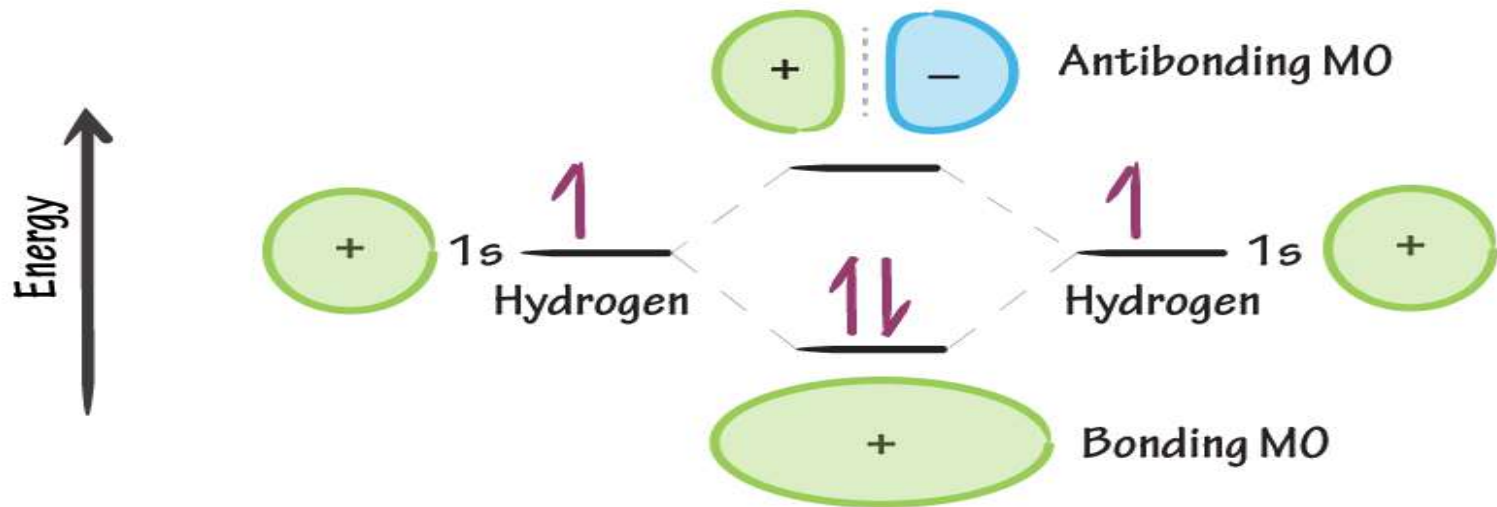
For Ex: For homonuclear diatomic molecules, 1s atomic orbital of one atom can combine with 1s atomic orbital of another atom. 2s can combine with 2s, 2p with 2p and so on. 1s cannot combine with 2s, 2s cannot combine with 2p.

2) The combining atomic orbitals must have proper orientation so that they are able to overlap to a considerable extent.

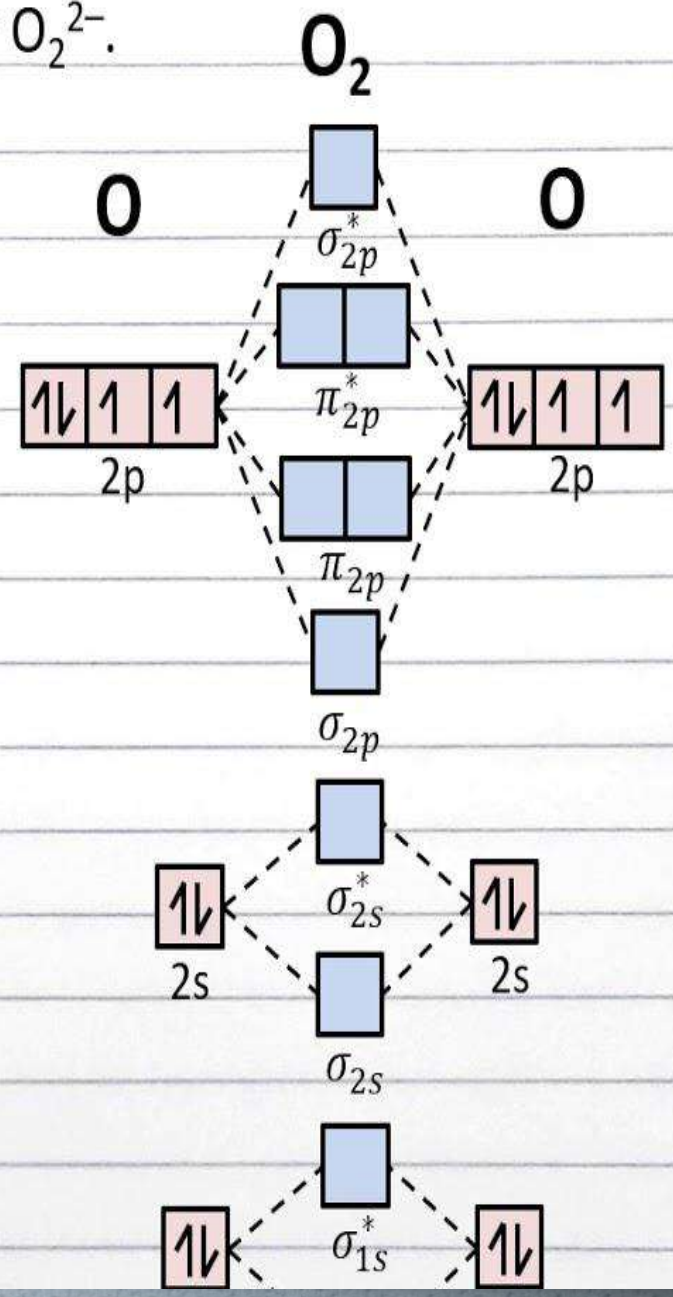
3) The extent of overlapping should be large. Greater the overlap, greater will be the electron density between the nuclei.

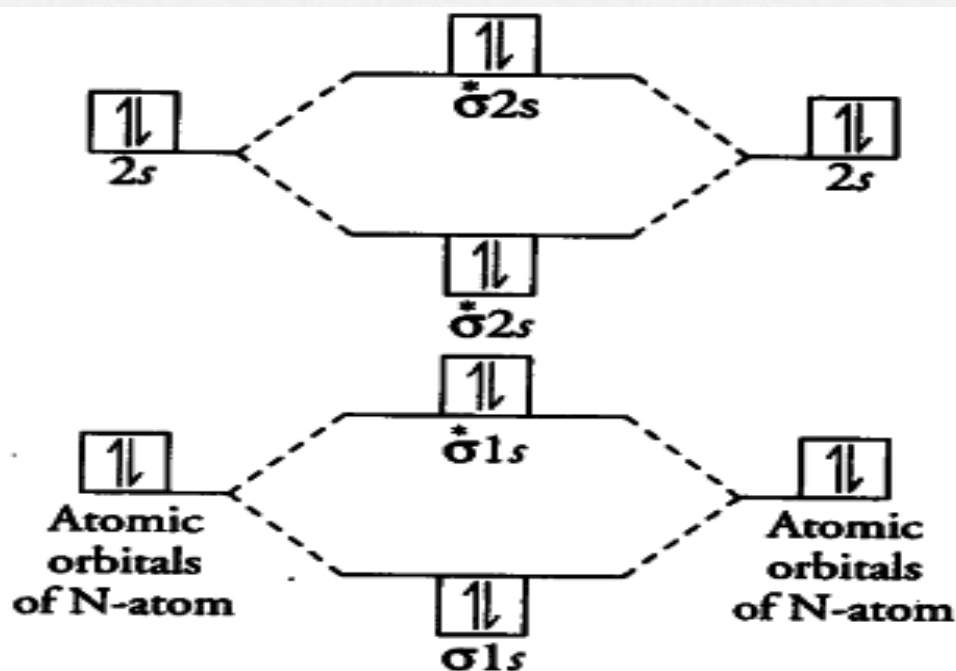
Orbital Interaction Diagram

Molecular hydrogen: H₂



Create a molecular orbital diagram for O_2^{2-} .





Molecular orbitals of N_2 molecule

$$\text{Bond order} = \frac{1}{2} [N_b - N_a] = \frac{1}{2} (10 - 4) = 3$$

Bond order value of 3 means that N_2 contains a triple bond.

Formation of O_2 molecule using molecular orbital theory.

- o Oxygen molecule O_2 : The electronic configuration of oxygen ($z=8$) in the ground state is $1s^2, 2s^2, 2p^4$.
- o Each oxygen atom has 8 electrons, hence in O_2 molecule there are 16 electrons.
- o Therefore, the electronic configuration of O_2 is as follows :
- o $O_2: KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2px})^2=(\pi_{2py})^2(\pi_{2px})^1=(\pi_{2py}^*)^1$

Crystal Field Theory, Postulates and its Limitations

Postulates of Crystal Field Theory

Crystal Field Theory (CFT) is a type of physical theory that describes the interaction of a metal center with its surrounding ligands. CFT can be used to explain the electronic properties of transition metal complexes, such as their color, magnetic properties, and spectroscopic properties. CFT is based on the assumption that the interaction between the metal ion and its ligands is electrostatic in nature, and that the ligands can be treated as point charges.

The basic premise of CFT is that the crystal field energy is the total energy of the metal center due to its interactions with the surrounding ligands. The metal center can be treated as an electron donor, and the ligands as electron acceptors. The strength of the crystal field depends on the number of ligands, their charge, and their distance from the metal center.

The CFT postulates are a set of assumptions used to describe the electrostatic interactions between a metal center and its surrounding ligands. These postulates are:

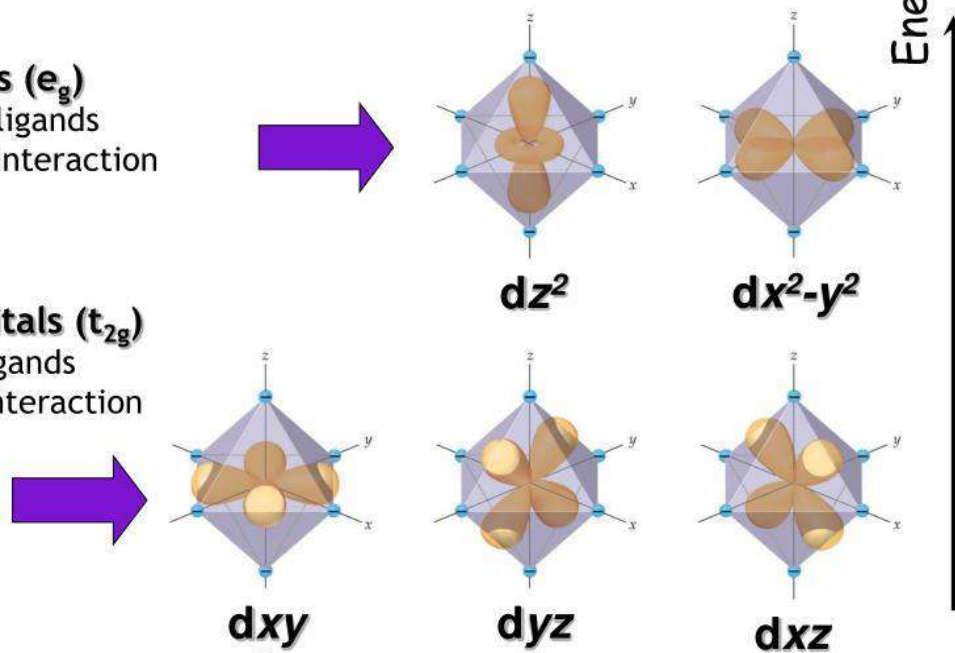
Crystal Field Splitting (Octahedron)

dz^2 & dx^2-y^2 orbitals (e_g)

- Point directly at the ligands
- Stronger (repulsive) interaction with the ligands

dxy , dyz & dxz orbitals (t_{2g})

- Point between the ligands
- Weaker (repulsive) interaction with the ligands

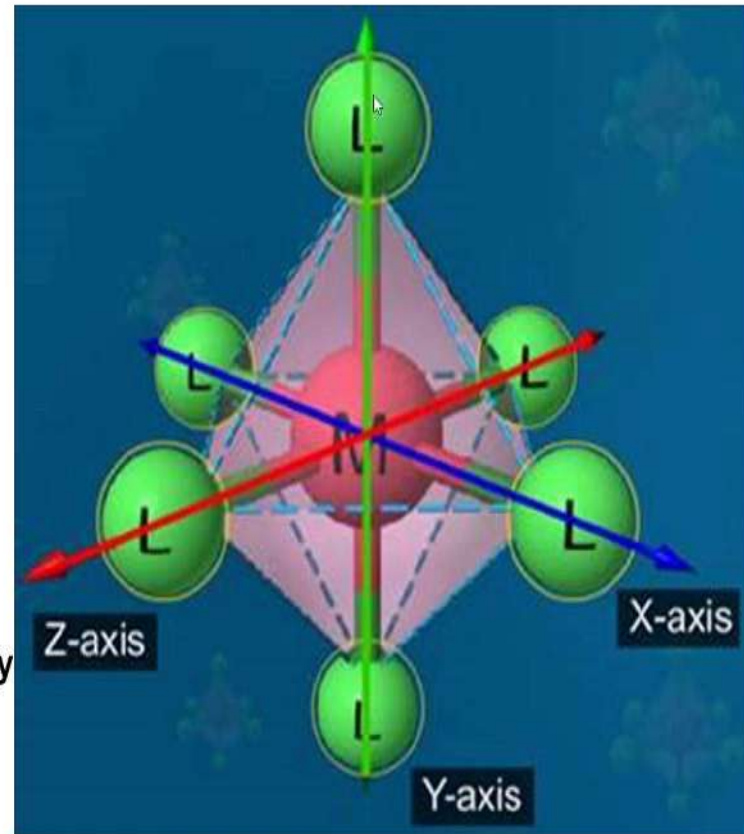


Electrons in d-orbitals are repelled from the electrons in the ligands. The repulsion is stronger for electrons in d-orbitals pointing directly at the ligands.

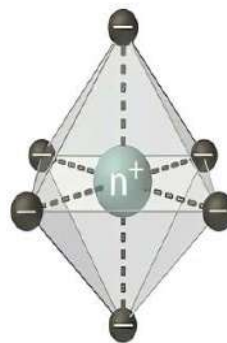
Crystal field splitting in octahedral complexes

In octahedral complexes, the metal ion is at the centre of the octahedron, and the six ligands lie at the six corners of the octahedron along the three axes X, Y & Z.

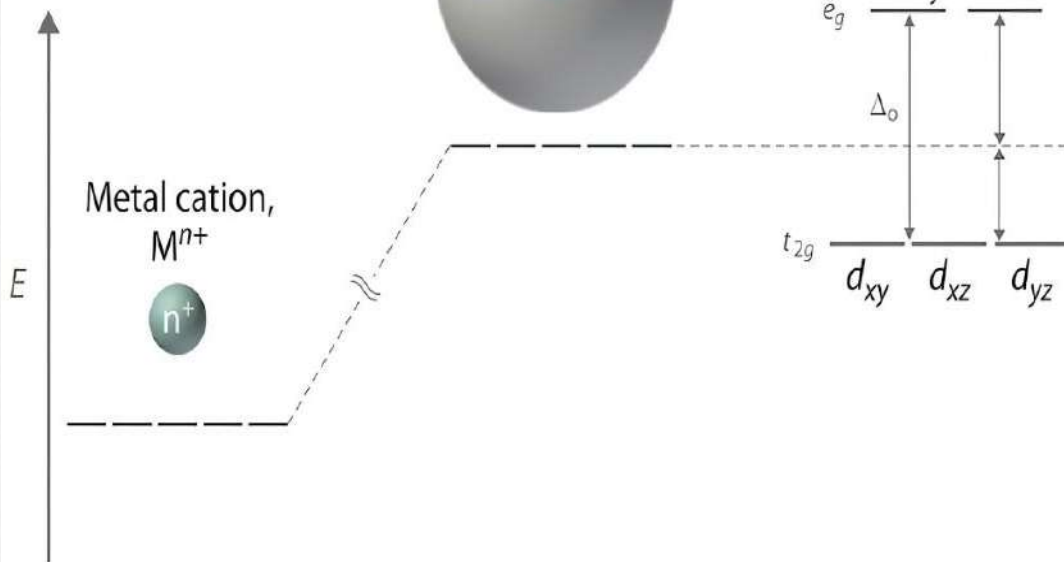
- ❖ The $d_{x^2-y^2}$ and d_{z^2} orbitals are together known as the e_g set of orbitals.
- ❖ The d_{xy} , d_{xz} and d_{yz} orbitals are collectively known as the t_{2g} set of orbitals.



Negative charges distributed uniformly over surface of a sphere



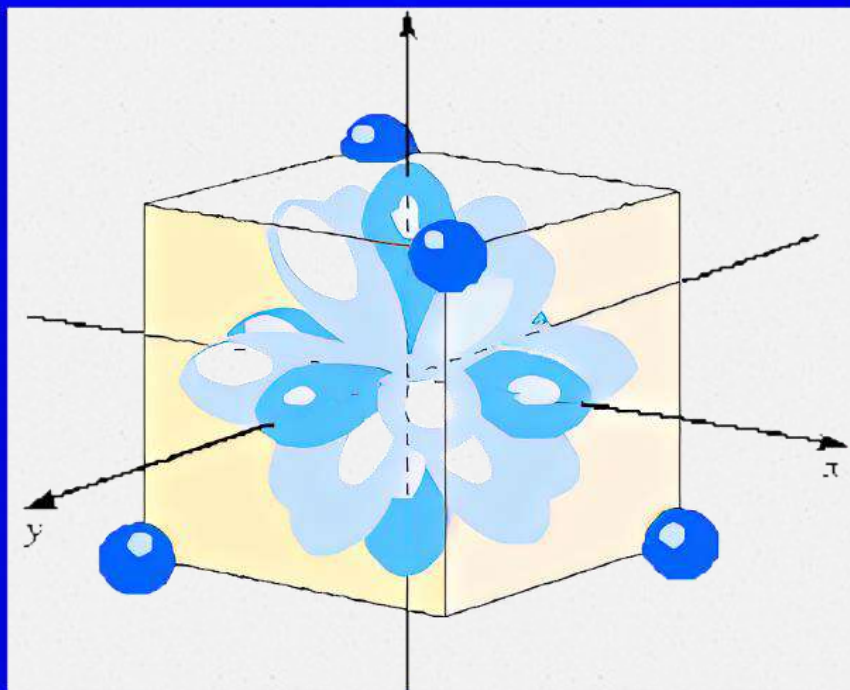
Negative charges located at vertices of an octahedron

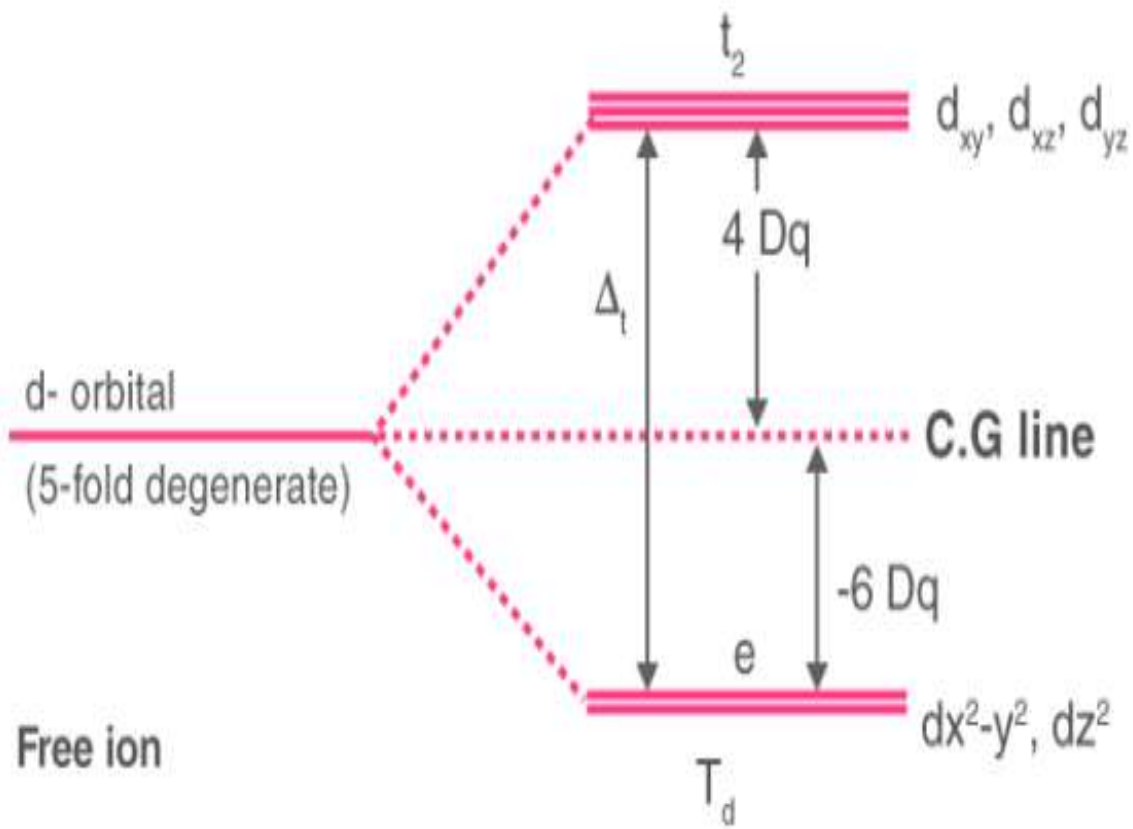




Tetrahedral Crystal Field

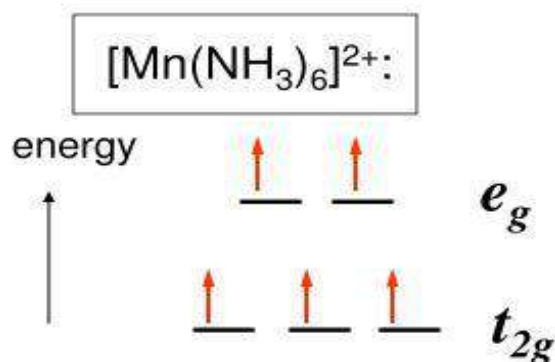
- In a tetrahedral structure, the ligands are located at opposite corners of a cube enclosing the axes.





Crystal Field Stabilization Energy (CFSE) of d^5 and d^{10} ions:

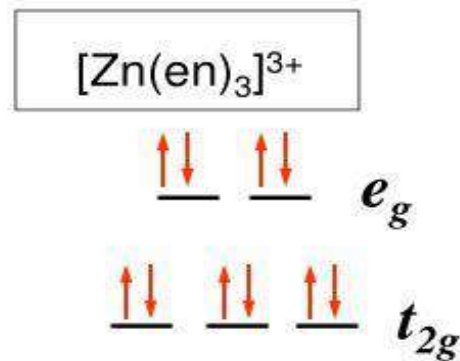
The CFSE for high-spin d^5 and for d^{10} complexes is calculated to be zero:



$$\Delta = 22,900 \text{ cm}^{-1}$$

$$\text{CFSE} = 10,000(0.4 \times 3 - 0.6 \times 2)$$

$$= 0 \text{ cm}^{-1}$$



$$\Delta = \text{not known}$$

$$\text{CFSE} = \Delta(0.4 \times 6 - 0.6 \times 4)$$

$$= 0 \text{ cm}^{-1}$$

Crystal Field Stabilization Energy (CFSE):

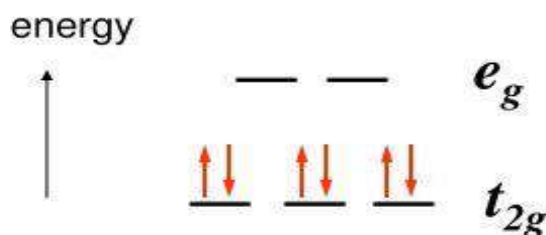
When splitting of the d sub-shell occurs, the occupation of the lower energy t_{2g} level by electrons causes a stabilization of the complex, whereas occupation of the e_g level causes a rise in energy. Calculations show that the t_{2g} level drops by 0.4Δ , whereas the e_g level is raised by 0.6Δ . This means that the overall change in energy, the CFSE, will be given by:

$$\text{CFSE} = \Delta(0.4n(t_{2g}) - 0.6n(e_g))$$

where $n(t_{2g})$ and $n(e_g)$ are the numbers of electrons in the t_{2g} and e_g levels respectively.

Calculation of Crystal Field Stabilization Energy (CFSE):

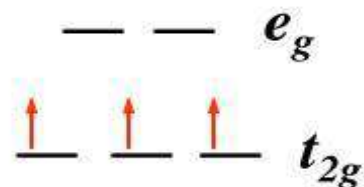
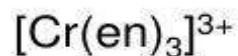
The CFSE for some complexes is calculated to be:



$$\Delta = 22,900 \text{ cm}^{-1}$$

$$\text{CFSE} = 22,900(0.4 \times 6 - 0.6 \times 0)$$

$$= 54,960 \text{ cm}^{-1}$$

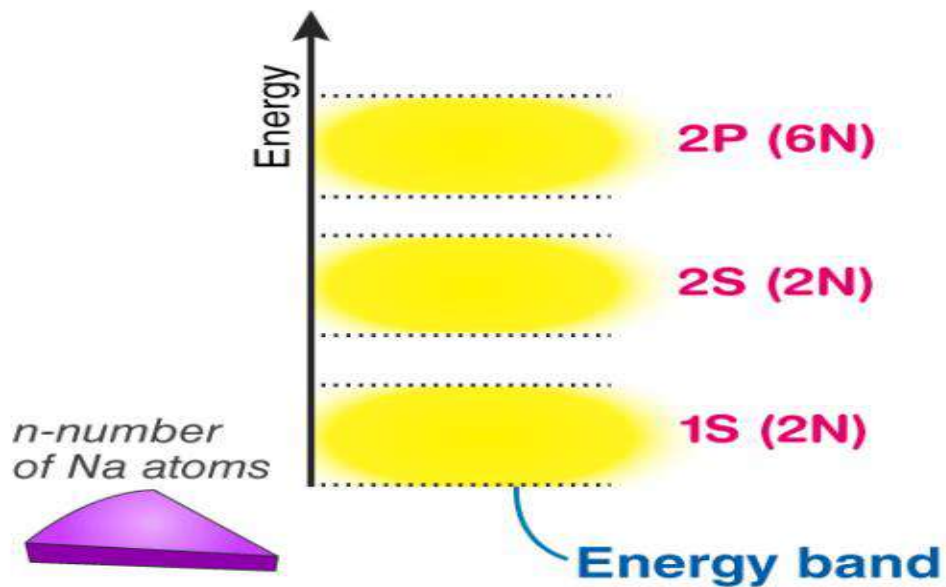


$$\Delta = 21,900 \text{ cm}^{-1}$$

$$\text{CFSE} = 21,900(0.4 \times 3 - 0.6 \times 0)$$

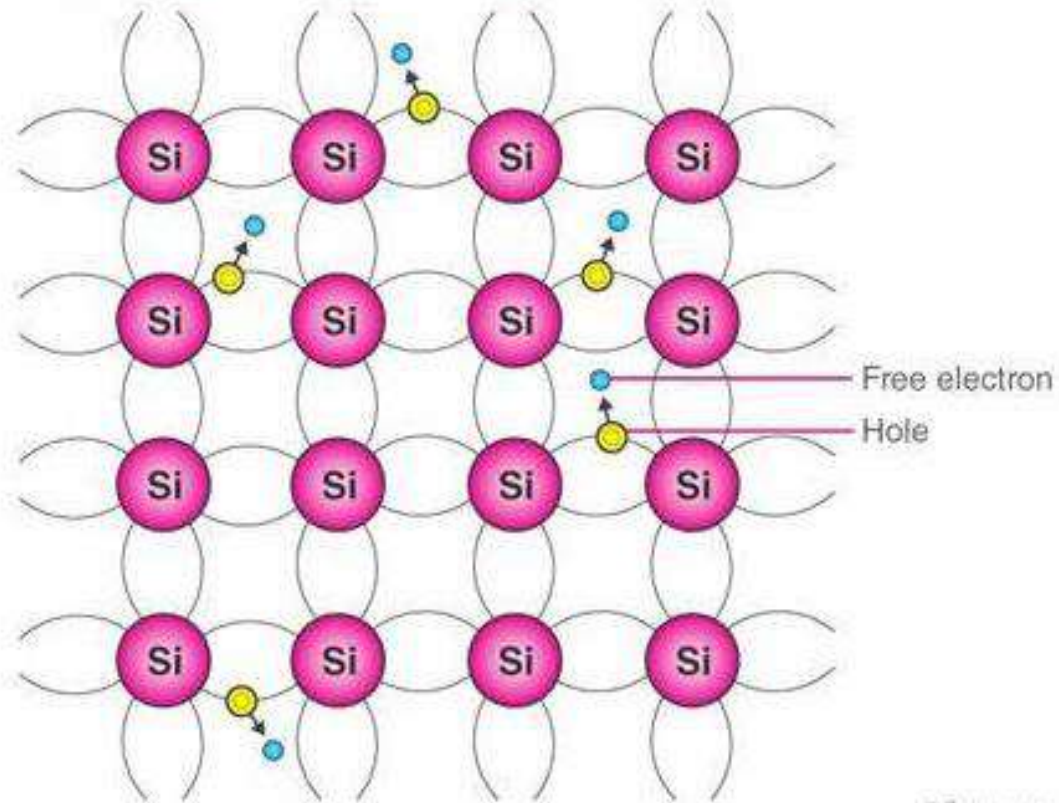
$$= 26,280 \text{ cm}^{-1}$$

BAND THEORY OF SOLIDS

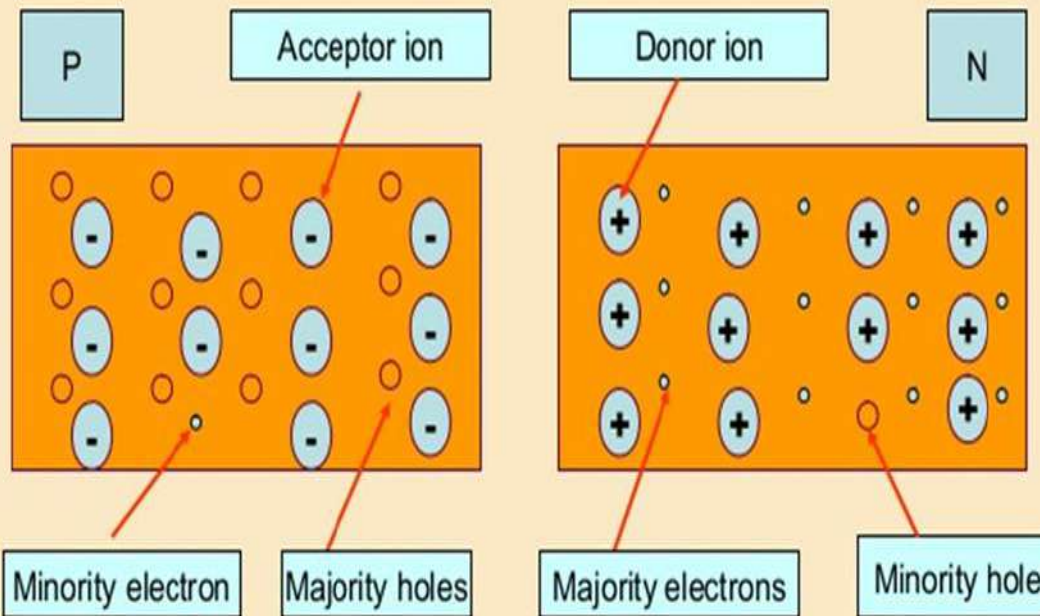


Energy levels inside a molecule made up of n -number of Na atoms

INTRINSIC SEMICONDUCTORS

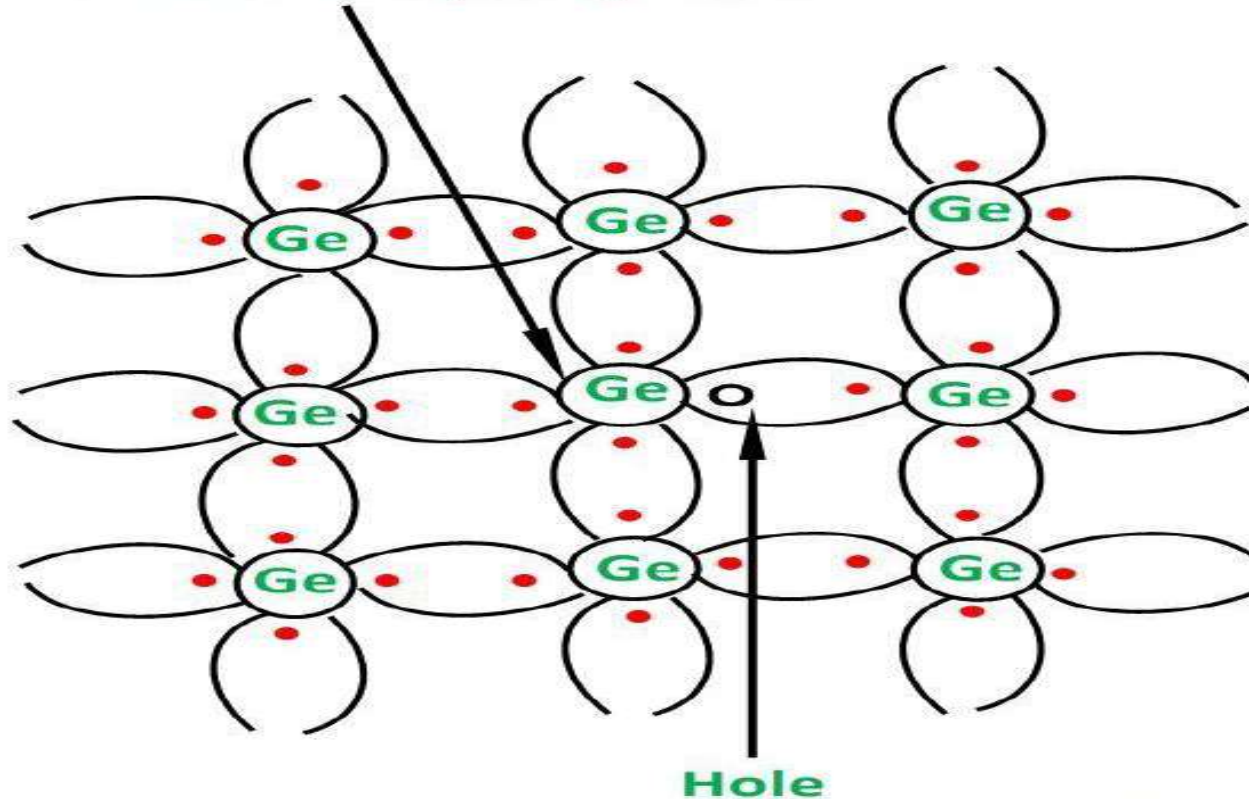


Types of Semiconductor

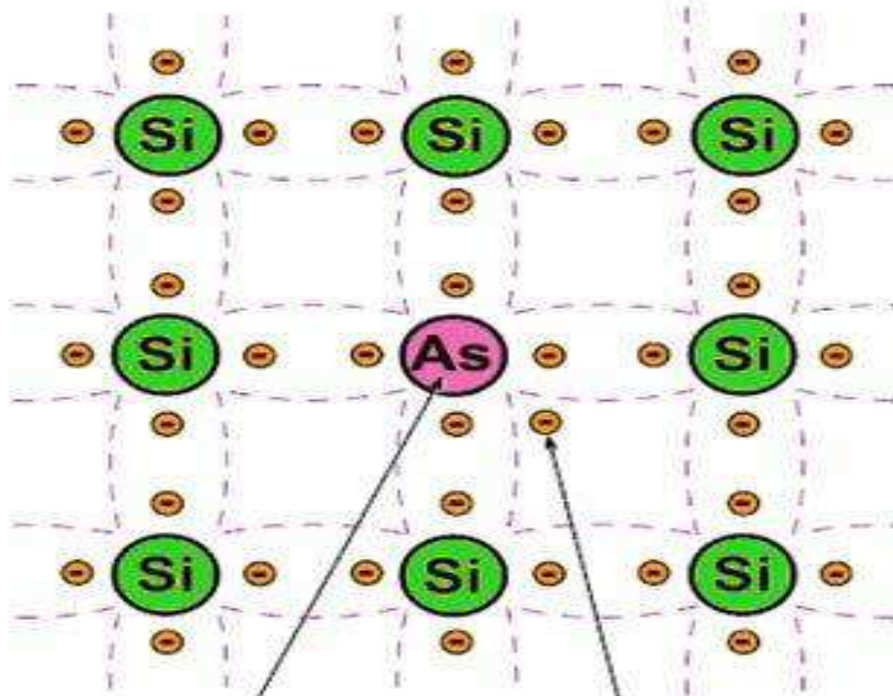


P-TYPE SEMICONDUCTOR

Trivalent Impurity Atom



"N"-Type Semiconductor



Arsenic Atom

Free Unbound
Electron

SCHRODINGER WAVE EQUATION

Erwin Schrodinger proposed that if the electron is wave-like, it should obey the same equation of motion as all other known types of wave motion obey. On the basis of this simple idea, he substituted the value of de-Broglie relation (i.e. $\lambda = \frac{h}{mv}$) into the classical equation for wave motion. Thus, the equation obtained should describe the wave motion of the electron and is called *Schrodinger wave equation*. The equation can be written in many forms. The simplest form of equation is given below :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

where E = Total energy of the electron i.e., K.E. + P.E.

V = Potential energy of the electron i.e., work done against the attractive force when the electron moves away from the nucleus.

m = Mass of the electron

h = Planck's constant

The simplest form of the equation can be derived by de-Broglie idea of dual nature of matter applied to an electron within all atoms.

Total energy, (E) of an electron = Kinetic energy + Potential energy

$$= \frac{1}{2}mv^2 + V = \frac{1}{2} \frac{(mv)^2}{m} + V \quad \dots(1.1)$$

From de-Broglie equation,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad mv = \frac{h}{\lambda}$$

where m is the mass of an electron, v is its velocity, and h is the Planck's constant.

Substituting this value of mv in equation (1.1), we get

$$E = \frac{h^2}{2\lambda^2 m} + V$$

or
$$-\frac{1}{\lambda^2} = \frac{2m}{h^2}(E - V) \quad \dots(1.2)$$

The basic principle of quantum theory is that matter can be regarded as wave and the equation for such a wave motion of a vibrating string can be represented as :

$$\psi = A \sin \frac{2\pi x}{\lambda} \quad \dots(1.3)$$

where ψ is a wave function,

x is the displacement,

λ is the wave length, and

A is the amplitude of the wave.

λ is the wave length, and A is the amplitude of the wave.

Differentiating the function, ψ , with respect to x , we get

$$\frac{d\psi}{dx} = A \left(\cos \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right)$$

4

$$= A \cdot \frac{2\pi}{\lambda} \cdot \cos \frac{2\pi x}{\lambda}$$

Differentiating again, we get

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= \frac{2\pi A}{\lambda} \left(-\sin \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right) \\ &= -\frac{4\pi^2}{\lambda^2} \left(A \sin \frac{2\pi x}{\lambda} \right) \end{aligned}$$

From equation (1.3), we get

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad \dots(1.4)$$

From equation (1.2),

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \quad \dots(1.4)$$

Putting the value of $\frac{1}{\lambda^2}$ from equation (1.2) in the above equation, we have

$$\frac{d^2\psi}{dx^2} = -4\pi^2\psi \left[\frac{2m}{h^2}(E-V) \right] = \frac{8\pi^2m}{h^2}(E-V)\psi$$

Substituting the value of λ from equation (1.2) in equation (1.3), we obtain

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E-V)\psi = 0$$

When the electron moves in three directions x , y and z , the above equation becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{h^2}(E-V)\psi = 0 \quad \dots(1.5)$$

This is the Schrödinger wave equation. It relates the wave function ψ of the electron with its energy E . It is a second order differential equation and can be solved only for certain definite values of energy (E) possessed the electron under reference.

PROPERTIES OF Psi (Wave function)

The various values of ψ which have been derived from the wave equation corresponding to definite values of energy (eigen values) are called eigen functions.

Only those wave functions which satisfy certain conditions are acceptable. These conditions are imposed on the wave equation as boundary conditions and can be summarised as follows :

- (i) ψ must be single-valued and finite, i.e., for each value of the variables x, y, z , there is only one definite, value of the function ψ .
- (ii) ψ must be continuous, i.e. there must not exist any sudden changes in ψ as the variables are changed.
- (iii) ψ must become zero at infinity.

WAVE MECHANICAL MODEL OF HYDROGEN ATOM

Hydrogen atom and hydrogen atom like species e.g. He^+ , Li^{2+} , Be^{3+} etc. resemble with one another in having one electron around their nuclei, but they differ in their nuclear charges. The hydrogen atom consist of an electron (e^-) and proton of charge $+e$. Hydrogen like species have one electron with e^- charge and their nucleus has ze^+ charge, where z is the atomic number of such atoms.

The Schrodinger wave equation for the motion of a single particle is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots(1.23)$$

where m = mass of the particle, E = total energy of the particle,

V = the potential energy of the particle, and

x, y, z = co-ordinates of the particle.

For hydrogen like atom reduced mass (μ) = $\frac{m_e \times m_n}{m_e + m_n}$ replaces the mass where m_e and m_n are the masses of the electron and the nucleus respectively. It may be noted that $\mu < m_e$.

A hydrogen like atom can have two kinds of motions:

- (i) Revolution of electron around the nucleus, and
- (ii) The translational motion of the system i.e., centre of mass (nucleus).

Assuming that the nucleus centre of mass is not moving, we consider only the revolution of the electron around the nucleus. Hence, E represents the electronic energy.

The equation (1.23) for a hydrogen-like atom takes the following form:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 \mu}{h^2} (E - V) \psi = 0 \quad \dots(1.24)$$

x , y and z are the co-ordinates of the centre of mass of the system.

This equation is identical to that of a single particle of mass μ (equal to that of the electron) moving in a field of potential V .

For the hydrogen like electron is moving under the central field of the nucleus.

By Coulomb's law, force of attraction between these particles is given as:

$$F = \frac{Ze^2}{r^2} \quad \dots(1.25)$$

where $+Ze$ is the charge on the nucleus and $-e$ that on the electron and r is the distance between the two.

Force acting between the particles according to Coulomb's law.

$$F = \frac{-e \cdot Ze}{r^2} = \frac{-Ze^2}{r^2}, \quad V = \int_{\infty}^r F \cdot dr = \int_{\infty}^r \frac{-Ze^2}{r^2} = \frac{-Ze^2}{r} \quad \dots(1.26)$$

The potential energy is the work necessary to take electron to infinity from its equilibrium.

