CH102BS/CH202BS: CHEMISTRY

B.Tech. I Year I Sem-(CSE, EEE), II Sem-(CE, ME, ECE & EIE)   L T   P C
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UNIT-I (MOT, CFT & BAND THEORY)

Molecular orbital Theory (MOT):

- Atomic and Molecular orbital's.
- Linear Combination of Atomic Orbital's (LCAO).
- Molecular orbital's of diatomic molecules.
- Molecular orbital energy level diagrams of N_2, O_2 and F_2 molecules.
- π molecular orbital's of butadiene and benzene.

Crystal Field Theory (CFT):

- Salient Features of CFT
- Crystal Field Splitting of transition metal ion d- orbitals in Tetrahedral, Octahedral and square planar geometries.

Band structure of solids:

- Band structure of solids
- Effect of doping on conductance.

UNIT-II (WATER AND ITS TREATMENT)

- Introduction – hardness of water
- Causes of hardness
- Types of hardness: temporary and permanent
- Expression and units of hardness
- Estimation of hardness of water by complexometric method.
- Potable water and its specifications.
- Steps involved in treatment of water – Disinfection of water by chlorination and ozonization.
- Boiler feed water and its treatment – Calgon conditioning, Phosphate conditioning and Colloidal conditioning.
- External treatment of water – Ion exchange process.
- Desalination of water – Reverse osmosis.
- Numerical problems.

UNIT-III (ELECTROCHEMISTRY, BATTERIES AND CORROSION)

Electrochemistry:
- Electro chemical cells.
- Electrode potential, standard electrode potential.
- Types of electrodes – calomel, Quinhydrone and glass electrode.
- Nernst equation
- Determination of pH of a solution by using quinhydrone and glass electrode.
- Electrochemical series and its applications.
- Numerical problems.
- Potentiometric titrations.

Batteries:
- Primary (Lithium cell)
- Secondary batteries (Lead – acid storage battery and Lithium ion battery).

Corrosion and its control:
- Causes and effects of corrosion.
- Theories of chemical and electrochemical corrosion.
- Mechanism of electrochemical corrosion.
- Types of corrosion: Galvanic, water-line and pitting corrosion.
- Factors affecting rate of corrosion.
- Corrosion control methods- Cathodic protection– Sacrificial anode and Impressed current cathodic methods.
- Surface coatings – metallic coatings – methods of application.
- Electroless plating of Nickel.

UNIT-IV (STEREOCHEMISTRY, REACTION MECHANISM AND SYNTHESIS OF DRUG MOLECULES)

Stereochemistry:
- Introduction to representation of 3-dimensional structures.
- Structural and stereoisomers.
- Configurations, symmetry and chirality.
- Enantiomers, diastereomers, optical activity and Absolute configuration. Conformation alanalysis of n- butane.

Reaction Mechanism:
- **Substitution reactions:**
  Nucleophilic substitution reactions: Mechanism of S_N1, S_N2 reactions.

- **Electrophilic and nucleophilic addition reactions:**
  Addition of HBr to propene. Markownikoff and anti Markownikoff's additions. Grignard additions on carbonyl compounds.

- **Elimination reactions:**
  Dehydro halogenation of alkylhalides. Saytzeff rule.

- **Oxidation reactions:**
  Oxidation of alcohols using $KMnO_4$ and chromic acid.

- **Reduction reactions:**
  Reduction of carbonyl compounds using $LiAlH_4$ & $NaBH_4$. Hydroboration of olefins.

Synthesis of drug molecules:
- Structure, synthesis and pharmaceutical applications of Paracetamol and Aspirin.

UNIT-V (SPECTROSCOPIC TECHNIQUES AND APPLICATIONS)

- Principles of spectroscopy,
- Selection rules and applications of electronic spectroscopy, vibrational and rotational spectroscopy.
- Basic concepts of Nuclear magnetic resonance Spectroscopy, chemical shift.
- Introduction to Magnetic resonance imaging.

SUGGESTED TEXT BOOKS

1. Physical Chemistry, by P.W. Atkins
2. Engineering Chemistry by P.C.Jain & M.Jain; Dhanpat Rai Publishing Company (P) Ltd., New Delhi.
3. Fundamentals of Molecular Spectroscopy, by C.N. Banwell
4. Organic Chemistry: Structure and Function by K.P.C. Volhardt and N.E.Schore, 5th Edition.
5. University Chemistry, by B.M. Mahan, Pearson IV Edition.
6. Engineering Chemistry (NPTEL Web-book), by B.L. Tembe, Kamaluddin and M.S. Krishnan.

UNIT-I

MOLECULAR ORBITAL THEORY

INTRODUCTION:
1. VBT fails to answer the certain questions:
   Why O_2 is paramagnetic in nature?
   Why He_2 molecule does not exist?
2. The MOT was developed to provide answers to more complex questions.
3. This also helps in predicting molecular properties like Bond order, Bond length, Stability and magnetic property.
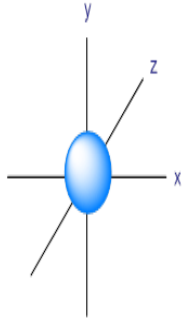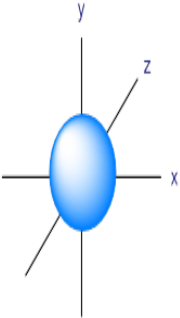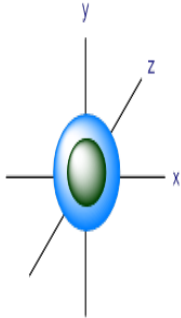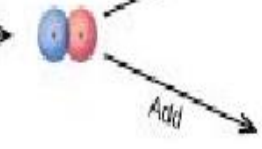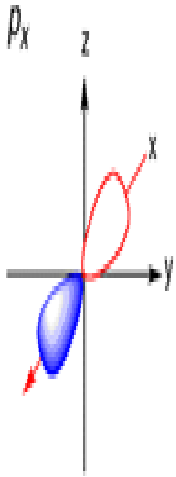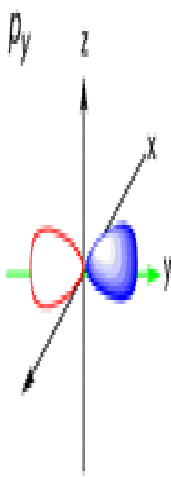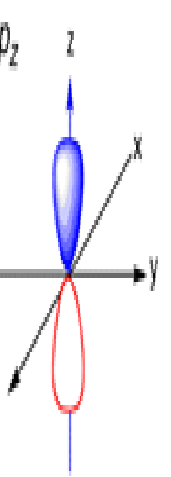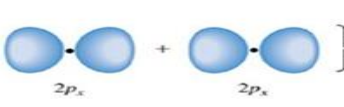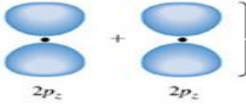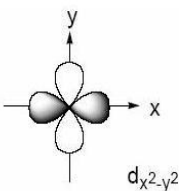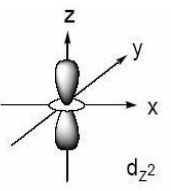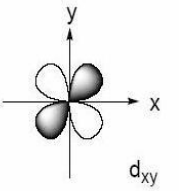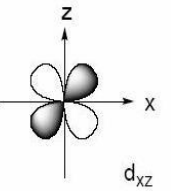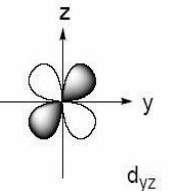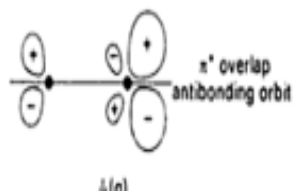
SILENT FEATURES OF MOLECULAR ORBITAL THEORY

1. The electrons in a molecule are present in various molecular orbitals as the electrons of atom are present in various atomic orbitals.

2. Atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

3. While an electron in an atomic orbital it is influenced by one nucleus, in a molecular orbital it is influenced by two (or) more nucleus depending upon the number of atoms in a molecule.

4. Atomic orbital is mono-centric and molecular orbital is poly-centric.

5. The number of molecular orbital formed is equal to the number of combining atomic orbitals.

6. When two atomic orbitals combine, two molecular orbitals are formed that are:
   i. Bonding molecular orbital (BMO).
   ii. Antibonding molecular orbital (ABMO).

7. Bonding molecular orbital (BMO) has lower energy and hence more stability than the corresponding Antibonding molecular orbital.

8. The electron probability distribution around a nucleous in an atom is given by an atomic orbital; the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.

DIFFERENCE BETWEEN ATOMIC ORBITAL AND MOLECULAR ORBITAL

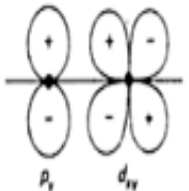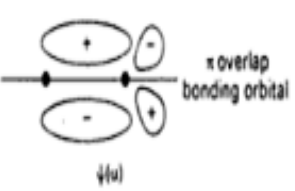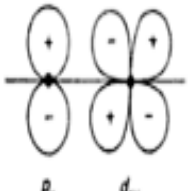| ATOMIC ORBITAL	MOLECULAR ORBITAL
1. Atomic orbital is the region having the highest probability of finding an electron in an atom.	Molecular orbital is the region having the highest probability of finding an electron of a molecule.
2. Atomic orbitals are formed by the electron cloud around the atom.	Molecular orbitals are formed by the fusion of atomic orbital's that have nearly the same energy.
3. The shape of atomic orbitals is determined by the type of the atomic orbital (s, p, d or f).	The shape of the molecular orbital is determined the shapes of atomic orbitals that make the molecule.
4. Schrodinger equation is used.	Linear combination of atomic orbital's (LCAO) is used.
5. Atomic orbital is mono centric as it is found around a single nucleus.	Molecular orbital is polycentric as it is found around different nuclei.

6. Single nucleus affects the electron cloud in atomic orbital's	Two more nuclei affect the electron cloud in molecular orbitals.
1s atomic orbital / 2s atomic orbital (node not shown) / 2s atomic orbital (node shown)	Atomic orbitals — Combine atomic orbitals — Molecular orbitals: Subtract → Antibonding orbital, σ_s^*; Add → Bonding orbital, σ_s
p_x, p_y, p_z	$2p_x + 2p_x \rightarrow \sigma_{2p}^*$ (antibonding), σ_{2p} (bonding); $2p_y + 2p_y \rightarrow \pi_{2p}^*$ (antibonding), π_{2p} (bonding); $2p_z + 2p_z \rightarrow \pi_{2p}^*$ (antibonding), π_{2p} (bonding)
$d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, d_{yz}	Atomic orbitals — Molecular orbitals: p_y, d_{xy} → π overlap bonding orbital $\psi(u)$; p_y, d_{xy} → π^* overlap antibonding orbital $\psi(g)$

LINEAR COMBINATION OF ATOMIC ORBITALS

- Atomic orbitals can be expressed by wave function (ψ) which represents the amplitude of the electron waves.

- These are obtained from the solution of Schrodinger wave equation, but this cannot be solved for the system with more than one electron.

- So, molecular orbital cannot be obtained from Schrodinger wave equation, to overcome this problem an approximate method known as linear combination of atomic orbitals(LCAO) has been adopted.

- Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1S orbital.

- The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B.

    $\Psi_{MO} = \psi_A \pm \psi_B$
    $\sigma = \psi_A + \psi_B$ (**bonding molecular orbitals**)
    $\sigma^* = \psi_A - \psi_B$(**antibonding molecular orbitals**)

- The molecular orbitals(σ) formed by the addition of atomic orbitals is called the **bonding molecular orbitals** while the molecular orbitals(σ^*) formed by the subtraction of atomic orbitals is called **antibonding molecular orbitals**.
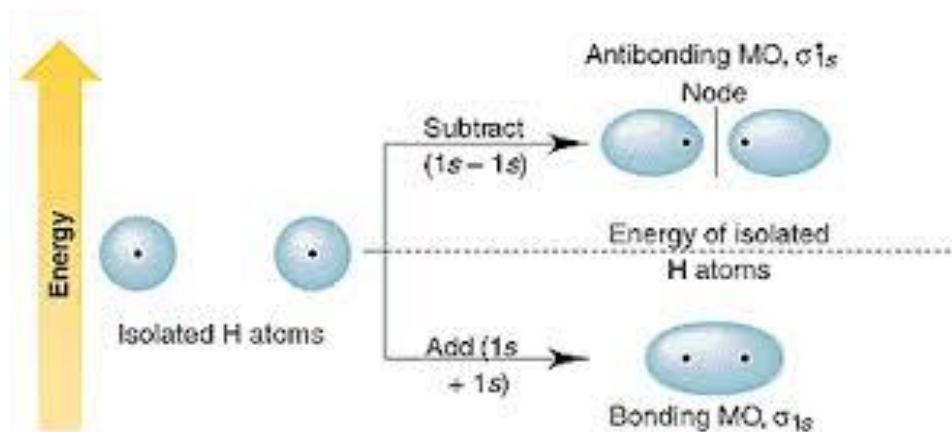
- Electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in the case of and antibonding Molecular Orbital, most of the electron density is located away from the space between the nuclei, hence the repulsion between the nuclei is high.

- Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of atomic orbitals that have combined to form it.

- Electrons placed in the antibonding molecular orbital their destabilizes the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons in the nuclei, which causes a net increase in energy.

- The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

CONDITIONS FOR LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

1. **Same energy of combining orbitals:** The combining atomic orbitals must have same or nearly same energy.
   Eg: This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1S and 2p cannot combine together as they have appreciable energy difference.

2. **Same symmetry about the molecular axis:** The combining atoms should have same symmetry around the molecular axis for proper combination.
   Eg: All the sub-orbitals of 2p have same energy but still, the $2p_z$ orbital of an atom can only combine with a $2p_z$ orbital of another atom but cannot combine with $2p_x$ and $2p_y$ orbital as they have a different Axis of symmetry (the z-axis is considered as the molecular axis of symmetry).

3. **Proper overlap between the atomic orbitals:** The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.

RULES FOR FILLING MOLECULAR ORBITAL ENERGY DIAGRAMS

Aufbau Rule: (lower energy orbitals fill before higher energy orbitals):

This principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels. In this way, the electrons of an atom or ion form the most stable electron configuration possible.

Hund's Rule: (one electron goes into each until all of them are half full before pairing up):

In Hund's rule every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

Pauli Exclusion Principle: **(No two electrons can be identified by the same set of quantum numbers):** This principle states that no two electrons can be identified by the same set of quantum numbers. This is actually why we have the spin quantum number, ms, to ensure that two electrons within the same orbital have unique sets of quantum numbers.

ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITAL FOR SIMPLE DIATOMIC MOLECULES

H_2, He_2, Li_2, Be_2, B_2, C_2, N_2

O_2, F_2, Ne_2
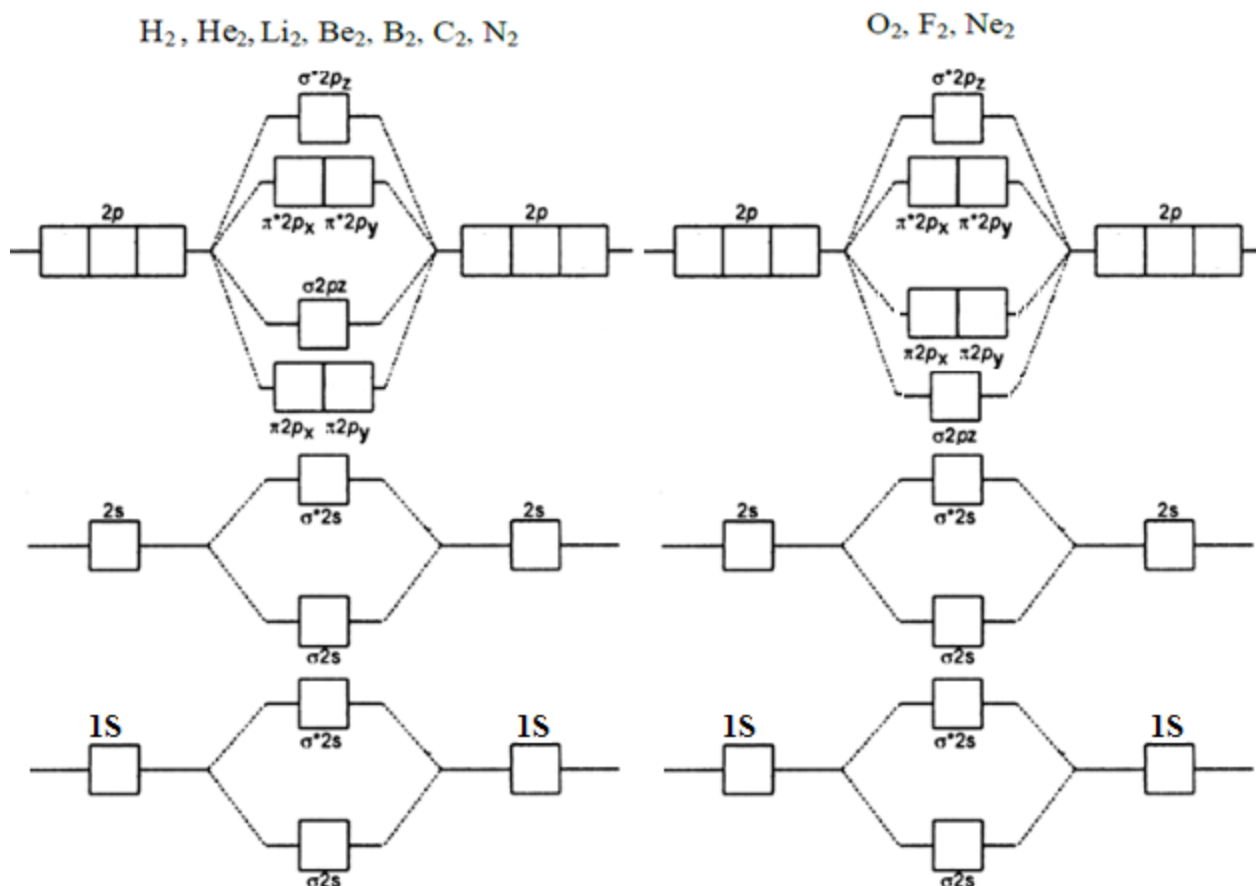
- **The order of energy levels of the Homonuclear Molecular Orbitals(14 – electrons and below) in the order of increasing energy as follows:**

$$\sigma \,(1S) < \; \sigma^* \,(1S) < \; \sigma \,(2S) < \; \sigma^* \,(2S) < \pi(2p_x = 2p_y) < \sigma \,(2p_z) \; < \pi(2p_x^* = 2p_y^*) < \sigma \,(2p_z^*)$$

- **The order of energy levels of the Homonuclear Molecular Orbitals(14 – electrons above) in the order of increasing energy as follows:**

$$\sigma \,(1S) < \; \sigma^* \,(1S) < \; \sigma \,(2S) < \; \sigma^* \,(2S) < \sigma \,(2p_z) < \pi(2p_x = 2p_y) < \pi(2p_x^* = 2p_y^*) < \sigma \,(2p_z^*)$$

MOLECULAR ORBITAL DIAGRAMS FOR DIATOMIC MOLECULES

HYDROGEN		
H_2	H_2^+	H_2^-
Bond Order: $\frac{1}{2}$ [Nb-Na]=$\frac{1}{2}$[2-0]=1	**Bond Order:** $\frac{1}{2}$ [Nb-Na]=$\frac{1}{2}$[1-0]=$\frac{1}{2}$	**Bond Order:** $\frac{1}{2}$ [Nb-Na]=$\frac{1}{2}$[2-1]=$\frac{1}{2}$
Stability: Stable - exist	**Stability:** Stable - exist	**Stability:** Stable - exist
Magnetic Property: Diamagnetic	**Magnetic-Property:** Paramagnetic	**Magnetic-Property:** Paramagnetic

HELIUM	
, He_2, 1s	He_2^+
Bond Order:$\frac{1}{2}$ [Nb-Na]=$\frac{1}{2}$[2-2]=0	**Bond Order:** [Nb-Na]=$\frac{1}{2}$[2-1]=$\frac{1}{2}$
Stability: Not exist	**Stability:** Stable - exist
Magnetic-Property: Diamagnetic	**Magnetic-Property:** Paramagnetic

LITHIUM	BERYLLIUM
Li$_2$	**Be$_2$**
Electronic configuration: $1S^2, 2S^1 \times 2 = 6 \ e^-$	**Electronic configuration:** $1S^2, 2S^2 \times 2 = 8 \ e^-$
Bond Order: ½ [Nb-Na]=½[4-2]=1	**Bond Order:** ½ [Nb-Na]=½[4-4]=0
Stability: Stable-exist(in the gas phase)	**Stability:** Not-exist
Magnetic-Property: Diamagnetic	**Magnetic-Property:** Diamagnetic
BORON	CARBON
B$_2$	**C$_2$**
Electronic configuration: $1S^2, 2S^2, 3P^1 \times 2 = 10 \ e^-$	**Electronic configuration:** $1S^2, 2S^2, 3P^2 \times 2 = 12 \ e^-$
Bond Order: ½ [Nb-Na]=½[6-4]=1	**Bond Order:** ½ [Nb-Na]=½[6-2]=2
Stability: Stable-exist	**Stability:** Stable-exist (: C=C :)
Magnetic-Property: Paramagnetic	**Magnetic-Property:** Diamagnetic

MOLECULAR ORBITAL ENERGY DIAGRAMS OF NITROGEN

Using Lewis structures, we predict a triple bond. MO theory also predicts 3 bonds, which match the experimental very short strong bond. Notice that in MO theory, the "lone pairs" (the 2 mostly non-bonding σ MOs) are shared over both atoms, and have different energies.

NITROGEN
N_2
Electronic configuration: [He^1, $2S^2$, $3P^3 \times 2 = 10$ e$^-$
Bond Order: ½ [Nb-Na]=½[8-2]=3
Stability: Stable-exist $(: N \equiv N :)$
Magnetic-Property: Dimagnetic
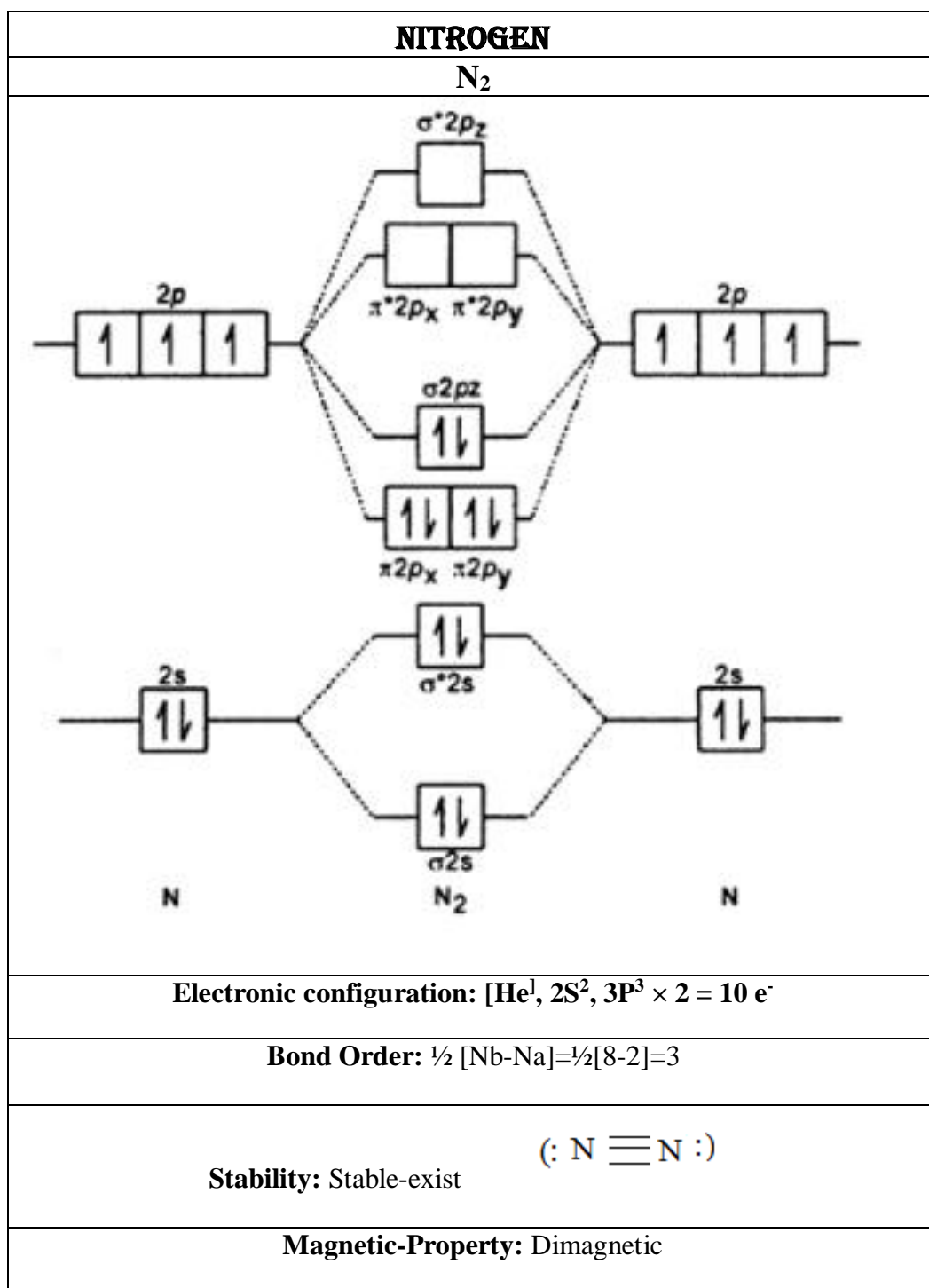
MOLECULAR ORBITAL ENERGY DIAGRAMS OF OXYGEN

Using Lewis structures, we predict 2 bonds and no unpaired electrons. MO theory also predicts 2 bonds, but correctly predicts 2 unpaired electrons. This is a longer and weaker bond than in N_2 as we would expect. If we reduce O_2 by adding electrons, they go into the π^* orbitals, and make the bond weaker; this matches experimentsm showing that peroxide has a longer, weaker bond than O_2.

Electronic configuration: [He], $2S^2$, $3P^4 \times 2 = 12$ e$^-$
Bond Order: ½ [Nb-Na]=½[8-4]=2
Stability: Stable-exist
Magnetic-Property: Paramagnetic

MOLECULAR ORBITAL ENERGY DIAGRAMS OF FLUORINE
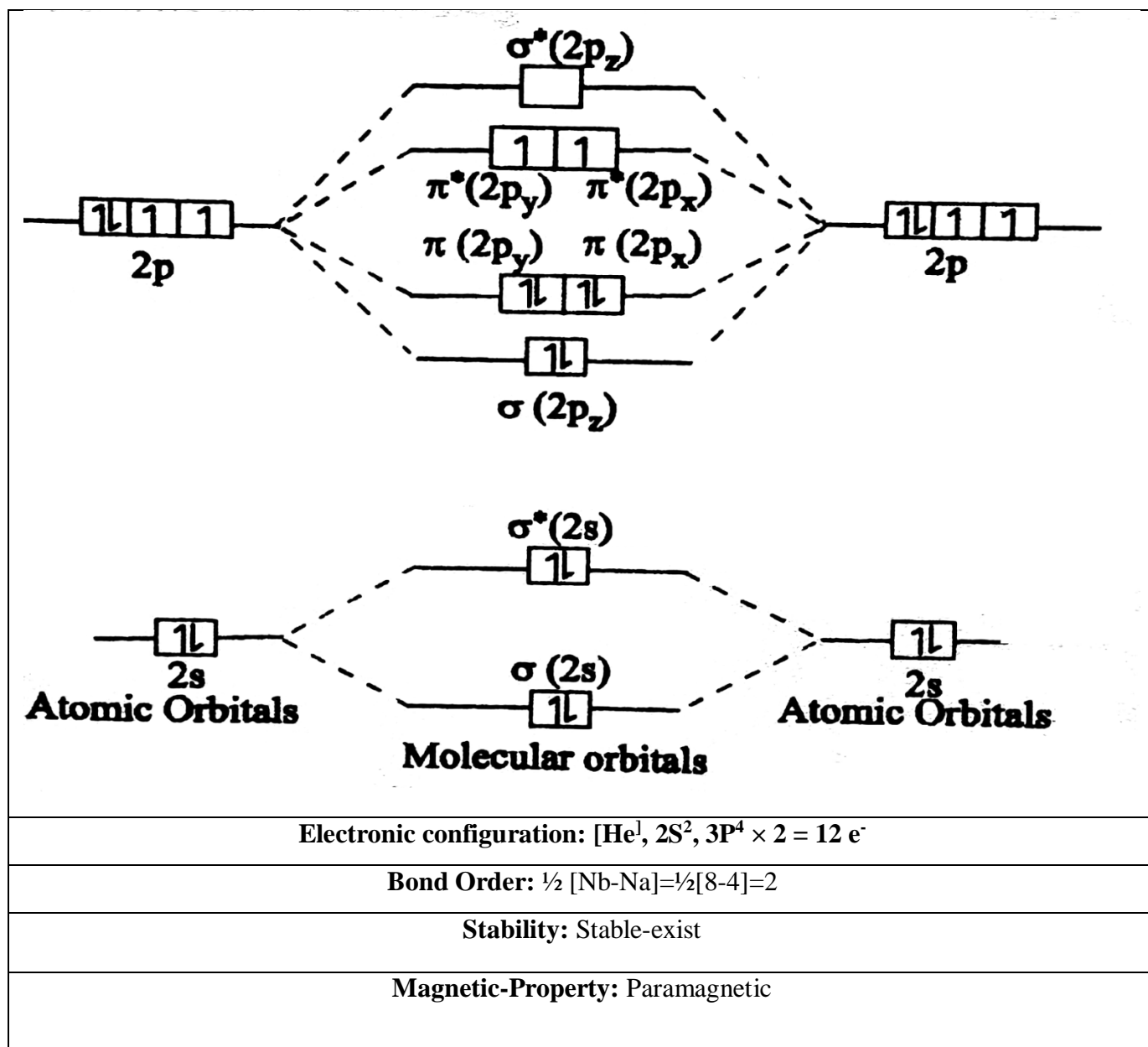
Using Lewis structures, we predict 1 bond. MO theory also predicts 1 bond. This matches experiments showing a long, weak bond.

FLUORINE
F_2

Electronic configuration: [He], $2S^2$, $3P^5 \times 2 = 14$ e$^-$
Bond Order: ½ [Nb-Na]=½[8-6]=1
Stability: Stable-exist
Magnetic-Property: Diamagnetic

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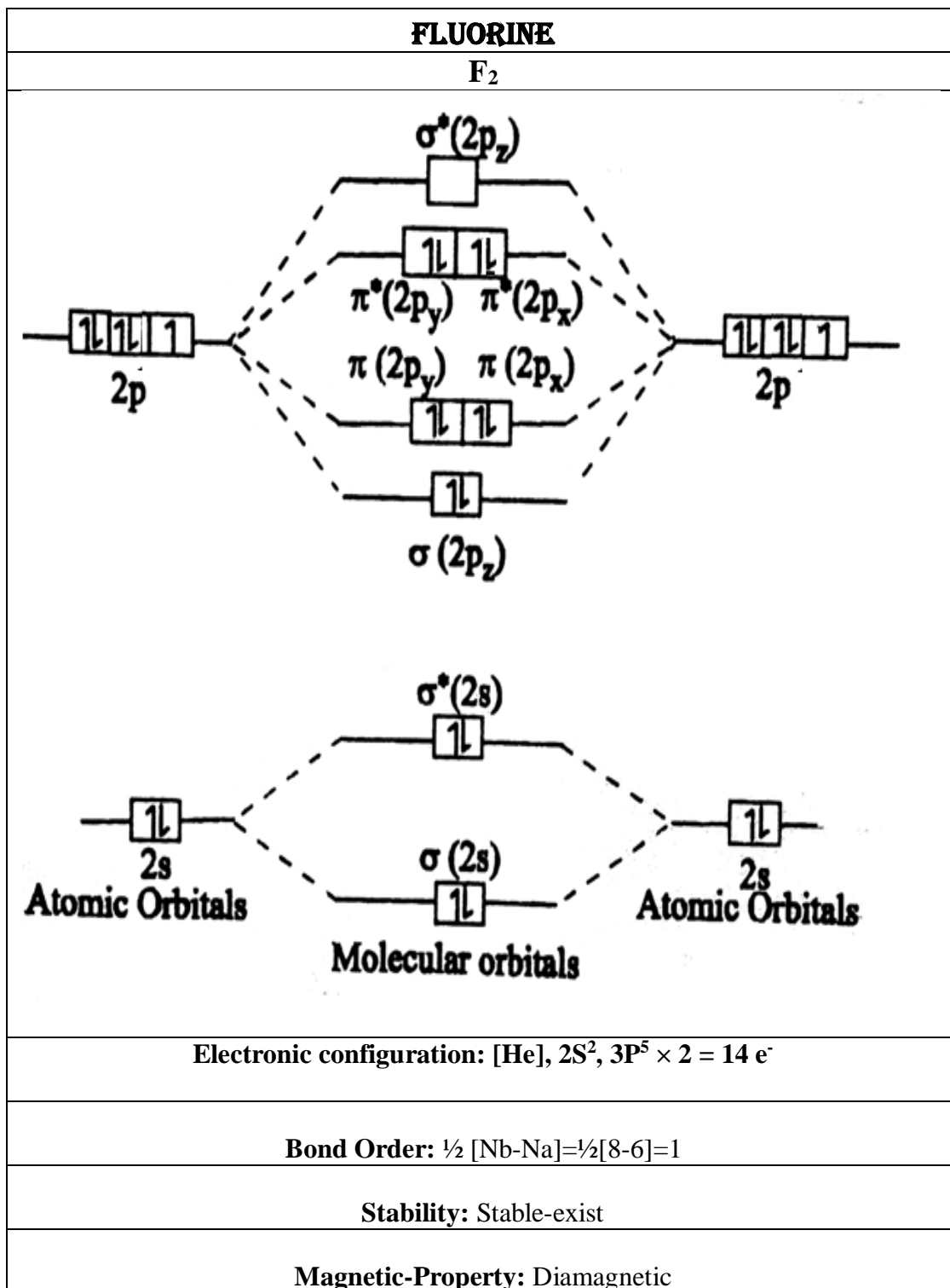
π MOLECULAR ORBITAL'S OF BENZENE

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- Benzene consists of two equivalent Lewis structures, each with three double bonds that alternate with three single bonds, it is planar.

- In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon single bond (1.53 Å) and the carbon—carbon double bond (1.34 Å), All C—C bond lengths are equal.

$$CH_3-CH_3 \quad CH_2=CH_2$$
$$1.53\ Å \qquad 1.34\ Å$$

1.39 Å

The C–C bonds in benzene are equal and intermediate in length.

The electrons in the π bonds are **delocalized** around the ring.

120°

Benzene—A planar molecule

sp^2 hybridized
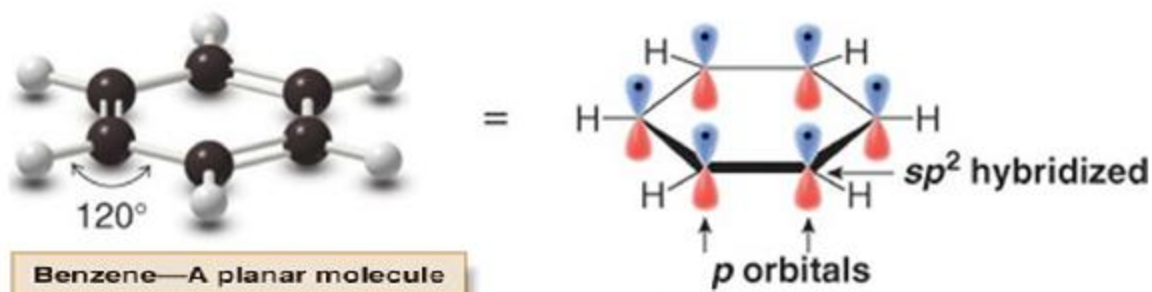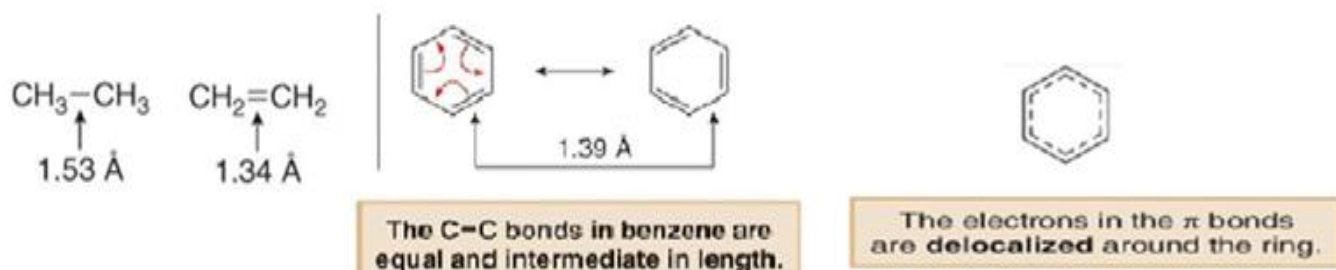
p orbitals

- Molecular orbital theory describes bonds as the mathematical combination of atomic orbitals that form a new set of orbitals called molecular orbitals (MOs).
- A molecular orbital occupies a region of space in a molecule where electrons are likely to be found.
- The combination of two *p* orbitals can be:
  CONSTRUCTIVE (with like phases interacting).
  DESTRUCTIVE (with opposite phases interacting).

- Consider benzene. Since each of the six carbon atoms in benzene has a *p* orbital, six atomic *p* orbitals combine to form six molecular orbitals (MOs).

phases interact.

increased electron density between the nuclei

π bonding molecular orbital

Opposite phases interact.

no electron density between the nuclei

π* antibonding molecular orbital

The antibonding MO is vacant.

π*

Energy

p orbital

p orbital

π

Two electrons occupy the bonding MO.
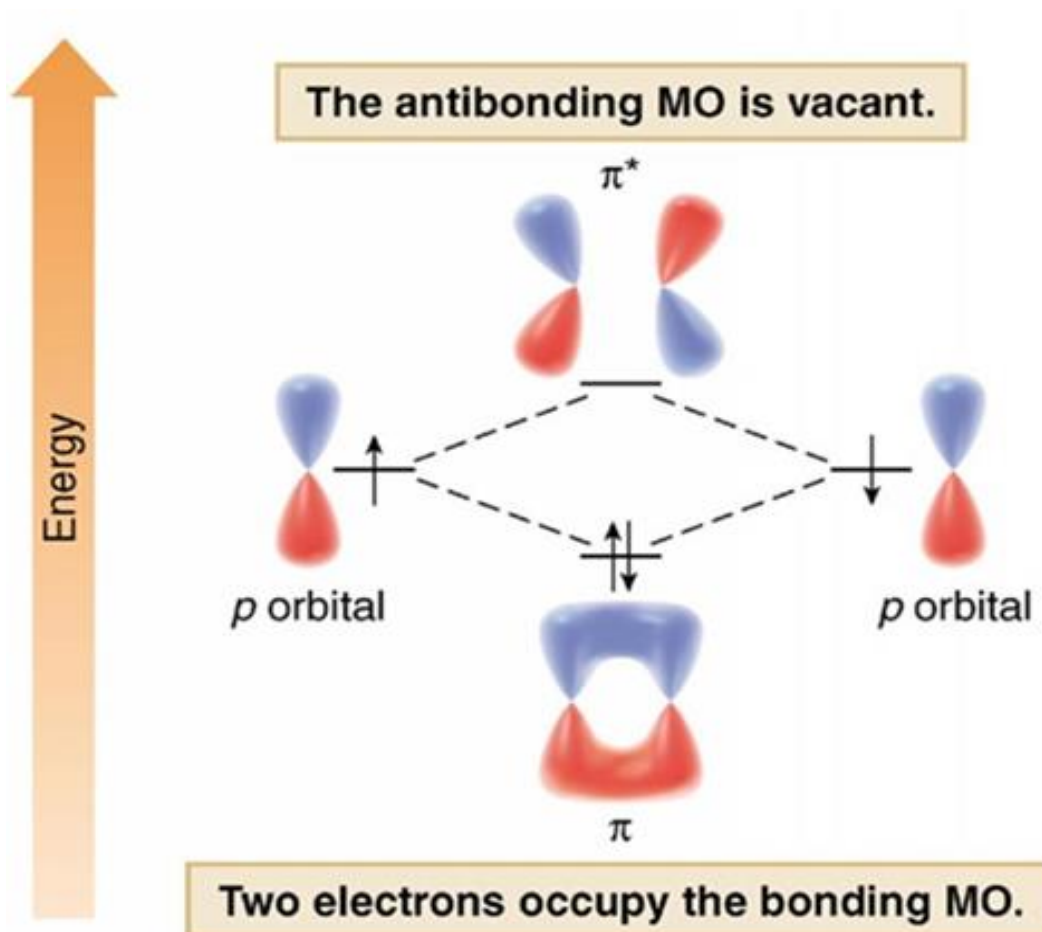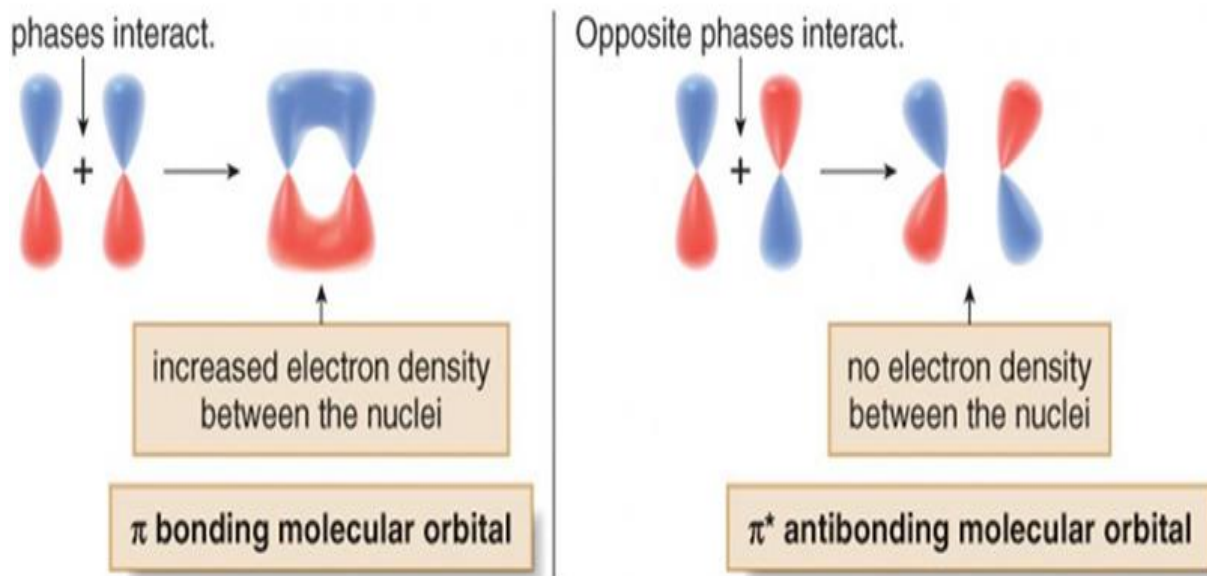
MOST IMPORTANT FEATURES OF THE SIX BENZENE MOLECULAR ORBITALS:

- The larger the number of bonding interactions, the lower in energy the molecular orbitals.

- The larger the number of nodes, the higher in energy the molecular orbitals.

- Three molecular orbitals are lower in energy than the starting p orbitals, making them **Bonding Molecular Orbitals**.

- Whereas three molecular orbitals are higher in energy than the starting p orbitals, making them **Anti Bonding Molecular Orbitals**.

- Two pairs of molecular orbitals with the same energy are called **Degenerate Orbitals**.

- The highest energy orbital that contains electrons is called the **Highest Occupied Molecular Orbital (HOMO)**.

- The lowest energy orbital that does not contain electrons is called the **Lowest Unoccupied Molecular Orbitals(LUMO).**

Benzene

6 π electrons within six 2p orbitals

(# nodal planes)   (# nodes)

Ψ_6 — (3)   — Ψ_6 (5)

Ψ_4 — (2) — Ψ_5 — Ψ_5 (4)

— Ψ_4 (3)

non-bonding energy level

Ψ_2 (1) Ψ_3 Ψ_3 (2)

Ψ_2 (1)

Ψ_1 (0) Ψ_1 (0)

benzene, (ψ_2 & ψ_3) and (ψ_4 & ψ_5) are ___degenerate___.
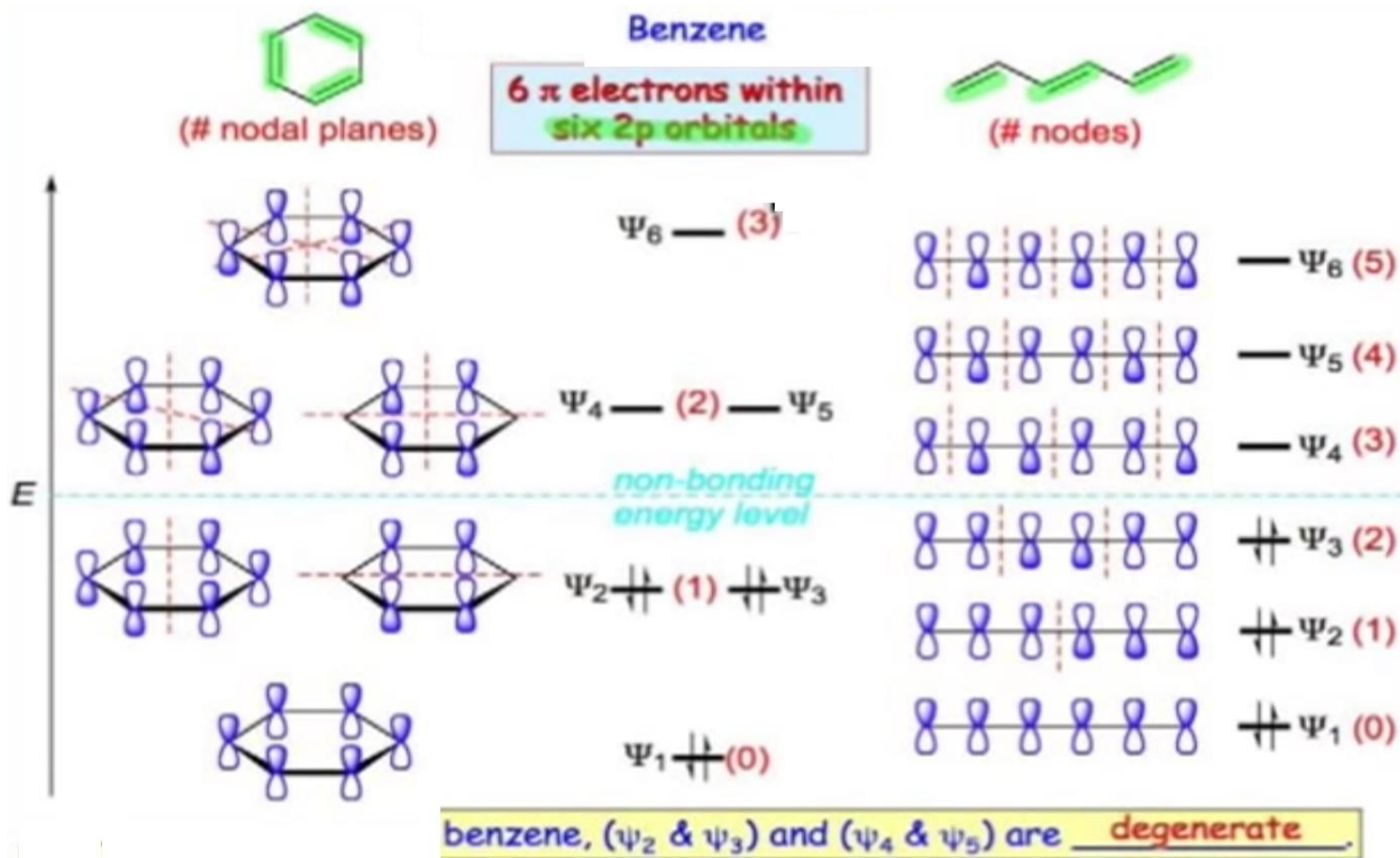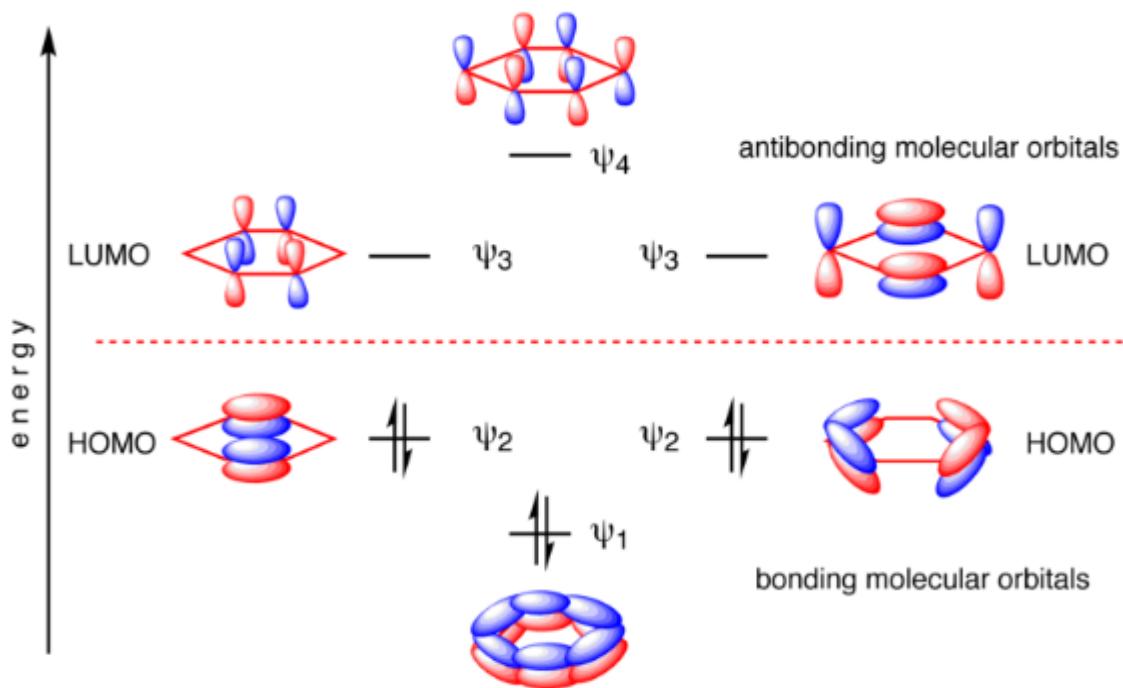
the π molecular orbitals for benzene. The dashed line represents the energy of an isolated
p orbital – all orbitals below this line are bonding, all above it are antibonding.
Benzene has six electrons in its π system so all the bonding MOs are fully occupied

π MOLECULAR ORBITAL'S OF 1,3-BUTADIENE

- As the name suggests, 1,3-butadiene is composed of 4 carbons with two adjacent pi bonds.
- In these two pi bonds are conjugated, all four p orbitals are all aligned with each other, and build up into a larger pi system.
- It's for this reason that we can describe the electron density in butadiene with resonance forms.
- Since butadiene consists of 4 individual p orbitals, the pi-system of butadiene will contain 4 pi **molecular orbitals**.

Butadiene

major
resonance form

minor
resonance form

4 conjugated p-orbitals
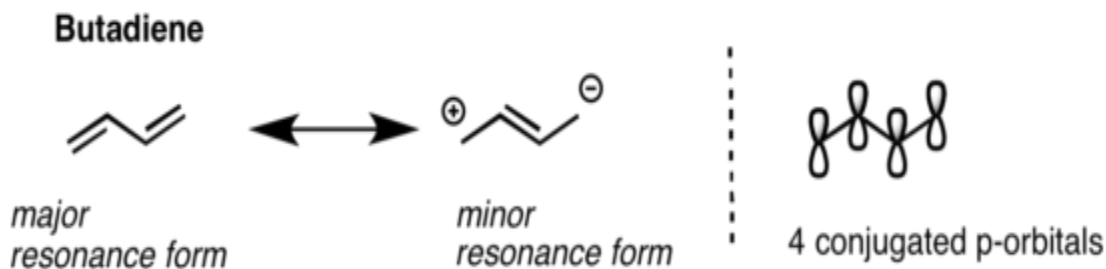
Lowest-Energy Molecular Orbital (π_1):

- The lowest energy molecular orbital will have p orbitals with phases in complete alignment with each other and form **four Consecutive P-Orbitals** all aligned the same way.

- We could have also drawn the pi-system with all the shaded lobes pointing up.

- The constructive overlap between the lobes results in a pi orbital that extends over the entire length of the pi system (above right).

- There are **zero nodes** between the p orbitals themselves.

- A physical interpretation of this orbital is that an electron in this orbital is delocalized over the length of the pi system.

Lowest-energy pi orbital in the butadienyl system has zero nodes

π_1 C   C   C   C   C C C C

0 nodes between p-orbitals
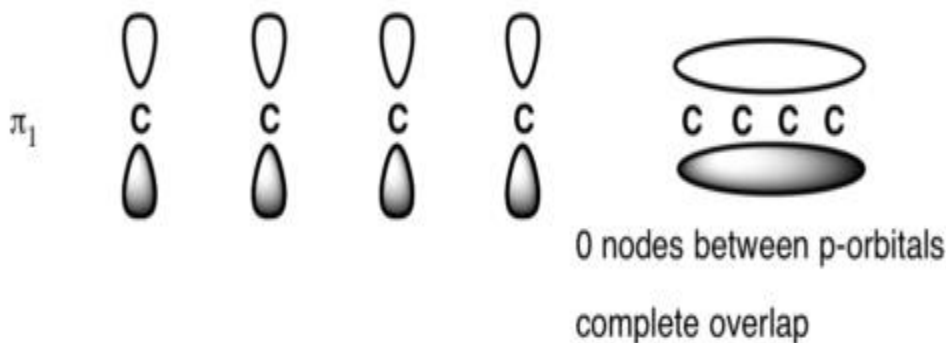
complete overlap

T**he Highest-Energy Molecular Orbital (π_4):**

- The highest energy molecular orbital will have p orbitals with phases incomplete alignment with each other and form **four Destructive P-Orbitals**.

- Destructive overlap between the lobes results in a pi orbital that extends over the entire length of the pi system (above right).

- There are **nodes** between the p orbitals themselves.

- A physical interpretation of this orbital is that an electron in this orbital is delocalized over the length of the pi system Just draw n (4 in our case) p orbitals and alternate the phases of each.

- The highest energy orbital that contains electrons is called the **Highest Occupied Molecular Orbital (HOMO)**.

- The lowest energy orbital that does not contain electrons is called the **Lowest Unoccupied Molecular Orbitals(LUMO).**

Molecular Orbital Diagram for Butadiene   4 π electrons

Nodes

π_4 C   C   C   C   3   ———

π_3 C   C   C   C   2   ——— Lowest unoccupie molecular orbital (LUMO)

π_2 C   C   C   C   1   Highest occupied molecular orbital (HOMO)

π_1 C   C   C   C   0

energy

16
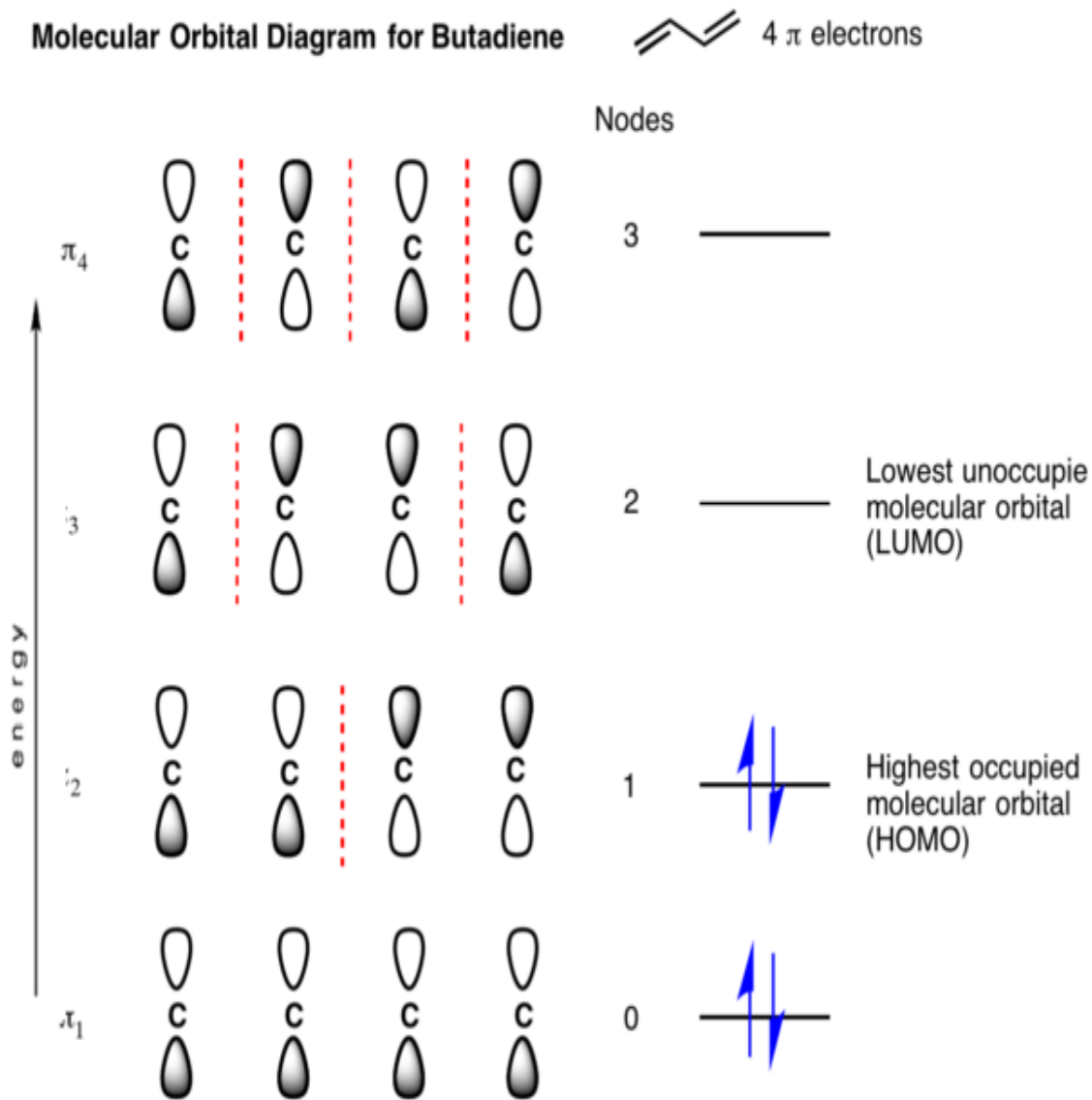
CRYSTAL FIELD THEORY

INTRODUCTION:

a. **Crystal Field Theory** describes the breaking of degeneracy of electron orbital states of *d-orbitals*, due to a static electric field produced by a surrounding charge distribution (anion neighbors).

b. CFT successfully accounts for magnetic properties, colors, Hydration enthalpies of transitional metal complexe**s.**

c. CFT was developed by physicists **BETHE** and **VAN VLECK** in the 1930's.

SILENT FEATURES OF CRYSTAL FIELD THEORY

i. The transition metal ion is surrounded by the ligands with lone pairs of electrons (The complex is a combination of central ion surrounded by the ligands like Anions (or) Neutral ions.

ii. In ligands all type of anions regarded as point charges and Neutral ions as ion dipoles.

iii. The interactions between the Metal ion and the ligand (anion (or) negative ends of ion dipoles) are purely electrostatic.

iv. The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly *d-orbitals.*

v. In the case of free metal ion, all the five *d-orbitals* have the same energy. Such orbitals having the same energies are called *degenerate orbitals.*

vi. These *degenerate d*-orbitals split into two sets with an energy difference.
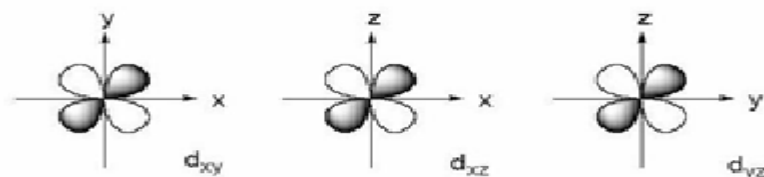
d_{xy}, d_{xz} and d_{yz} orbitals will be lower in energy(less repulsion) - referred to as t$_2$g
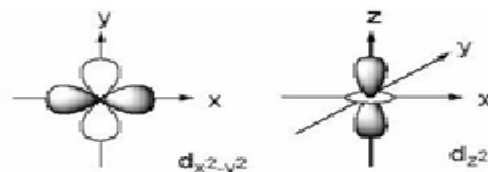
d_z^2 and $d_{x^2-y^2}$, which will have higher energy(more repulsion) - referred to as eg.

CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d-ORBITALS

1. According to crystal field theory, the interaction between a transition metal and <u>ligands</u> arises from the attraction between the positively charged metal cation and negative charge on the non-bonding electrons of the ligand.

2. The theory is developed by considering energy changes of the five degenerate d-orbitals upon being surrounded by an array of point charges consisting of the ligands.

3. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the d-orbitals and farther away from others, causing a loss of degeneracy.

4. The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges.

5. Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy.
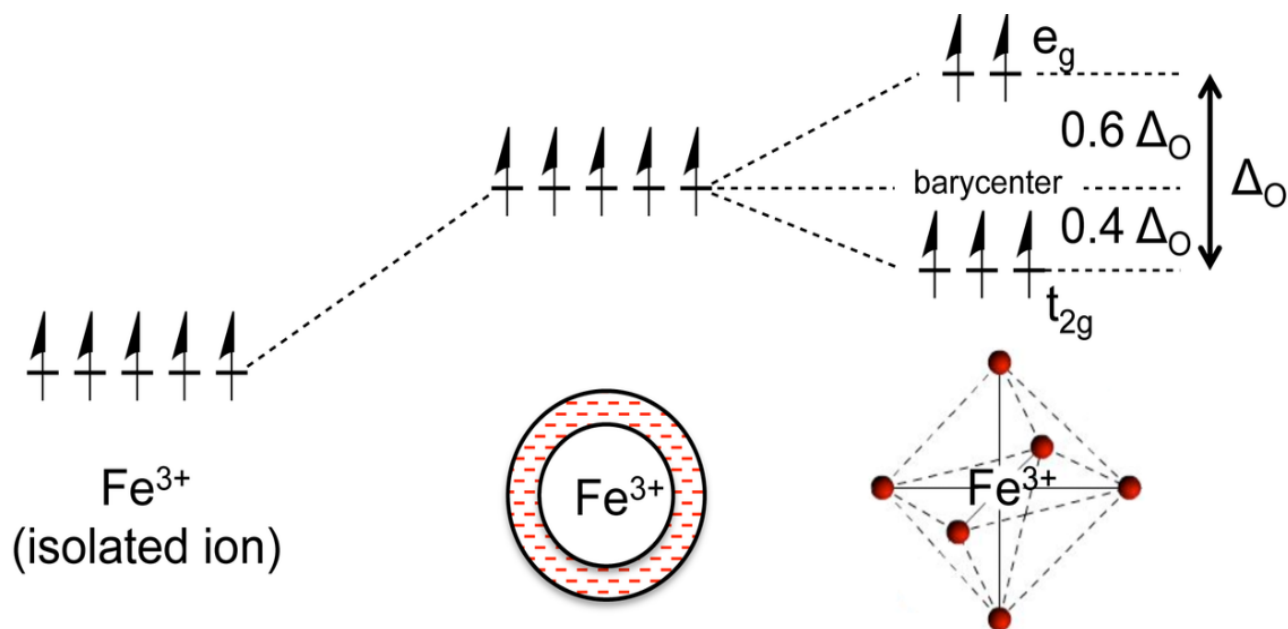
CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d – ORBITALS IN OCTAHEDRAL GEOMETRY

1. In octahedral complex; here six ligands form an octahedron around the metal ion.

2. In octahedral symmetry the d-orbitals split into two sets with an energy difference:
    i. d_{xy}, d_{xz} and d_{yz} orbitals will be lower in energy(less repulsion).
    ii. d_{z^2} and $d_{x^2-y^2}$, which will have higher energy(more repulsion).

3. The three lower-energy orbitals are collectively referred to as t_{2g}, and the two higher-energy orbitals as e_g.

4. In an octahedral complex, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at some of the ligand while the d_{xy}, d_{xz} and d_{yz} orbitals are not.

5. This enhances the repulsion between electrons in a metal d_{z^2} and $d_{x^2-y^2}$ orbital and the donated electron pair from the ligand, raising the energy of these metal orbitals relative to the other three.

6. The difference in energy between these two sets of d-orbitals is called the crystal field splitting $\triangle$or 10 Dq, its magnitude depends on the metal and the nature of the ligands.

7. The gain in energy by preferential filling up of orbitals by electrons is known as Crystal field stabilization energy (CFSE).
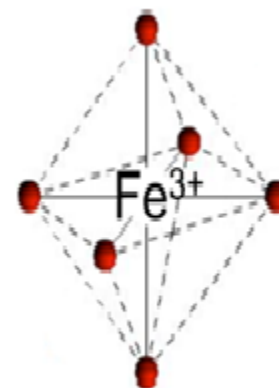
8. Greater the amount of CFSE of the complex, greater is the stability.

9. **Example:** $[Fe(CN)_6]^{3-}$ strong field ligand and low spin complex.

CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d-ORBITALS IN TETRAHEDRAL GEOMETRY

1. The splitting of the d-orbitals in a tetrahedral crystal field can be understood by connecting the vertices of a tetrahedron to form a cube, as shown in the picture:
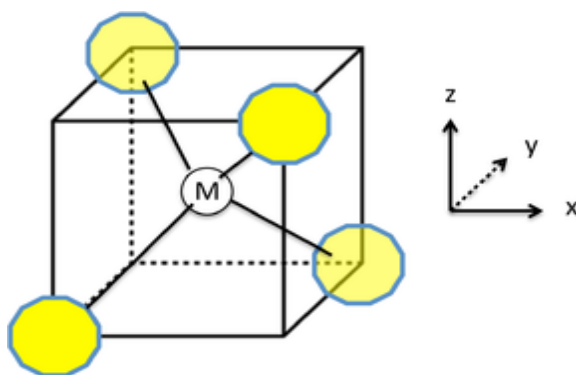
2. The tetrahedral M-L bonds lie along the body diagonals of the cube. The d_{z^2} and $d_{x^2-y^2}$ orbitals point along the axes, i.e., towards the faces of the cube, and have the least contact with the ligand lone pairs.

3. Therefore these two orbitals form a low energy, doubly degenerate (eg) set. The d_{xy}, d_{yz}, and d_{xz} orbitals point at the edges of the cube and form a triply degenerate (t_{2g} set). While the

t_{2g} orbitals have more overlap with the ligand orbitals than the eg set, they are still weakly interacting compared to the eg orbitals of an octahedral complex.

4. The resulting crystal field energy diagram is shown at the right. The splitting energy, Δ_t, is about 4/9 the splitting of an octahedral complex formed with the same ligands.

5. For 3d elements, Δ_t is thus small compared to the pairing energy and their tetrahedral complexes are always high spin.

6. **Note** that we have dropped the "g" subscript (doubly degenerate -eg) set because the tetrahedron does not have a center of symmetry.
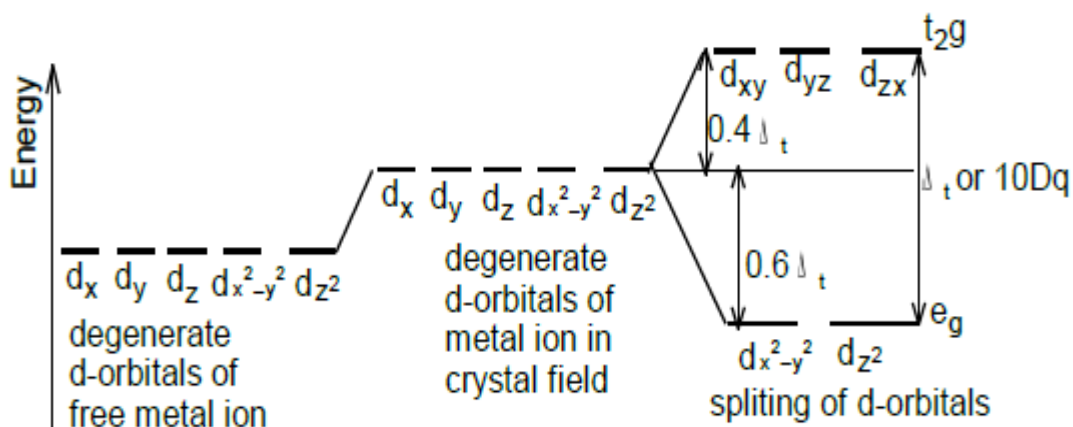
7. Crystal field splitting of tetrahedral complex is lesser than that in octahedral complex is, due to less number of ligands(4-ligands), so the field is small and the direction of the orbitals does not coincide with that of ligands.

8. **Example:** $[CoCl_4]^{2-}$ weak field ligand, high spin complex.

CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d-ORBITALS IN SQUARE PLANAR GEOMETRY

1. The square planar geometry can then be considered as a deformation of the octahedral geometry, which will occur along the z-axis.

2. The z-axis contains the two axial atoms (top and bottom of the octahedron), so that four atoms stay in position and the symmetry. This will lift the degeneracy of most orbitals.
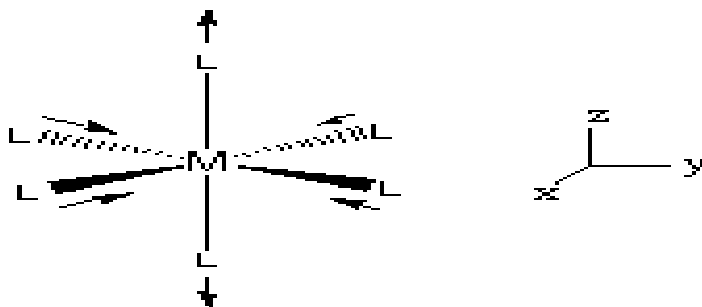
3. Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane. As the z-ligands move away, the ligands in the square plane move a little closer to the metal.

4. The orbital splitting diagram for square planar coordination can thus be derived from the octahedral diagram. As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy. The d_{z2} orbital falls the most, as its electrons are concentrated in lobes along the z-axis. The d_{xz} and d_{yz} orbitals also drop in energy, but not as much. Conversely, the d_{x2-y2} and the d_{xy} orbitals increase in energy.
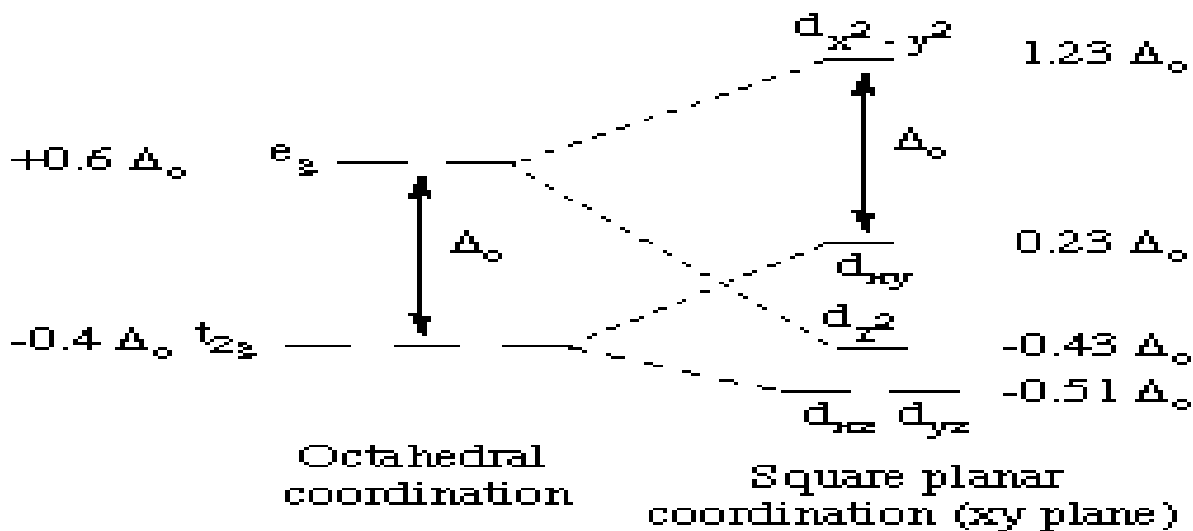
5. The splitting diagram for square planar complexes is more complex than for octahedral and tetrahedral complexes, and is shown below with the relative energies of each orbital.

6. The *dx2- y2* orbital will still be high in energy, but the orbital will be stabilised, because there are no more ligands in this direction. Due to the breaking of the octahedral symmetry, the three orbitals at the bottom of the octahedral diagram will no longer be degenerate. One of them - the one along the *xy* plane - will acquire a higher energy and the other two will be further stabilised.

7. Example: $[Ni(CN)_4]^{2-}$ strong field ligand and low spin complex.

BAND STRUCTURE OF SOLIDS

The electronic band structure is an energy schema to describe the conductivity of conductors, insulators, and semiconductors.

The schema consists of two energy bands (valence and conduction band) and the band gap. The valence electrons - which serve as charge carriers - are located in the valence band, in the ground state the conduction band is occupied with no electrons. Between the two energy bands there is the band gap; its width affects the conductivity of materials.

The energy bands

If we consider a single atom, there are according to the Bohr model of atoms sharply distinct energy levels, which may be occupied by electrons. If there are multiple atoms side by side they are interdependent, the discrete energy levels are fanned out. In a silicon crystal, there are approximately 10^{23} atoms per cubic centimeter, so that the individual energy levels are no longer distinguishable from each other and thus form broad energy ranges.
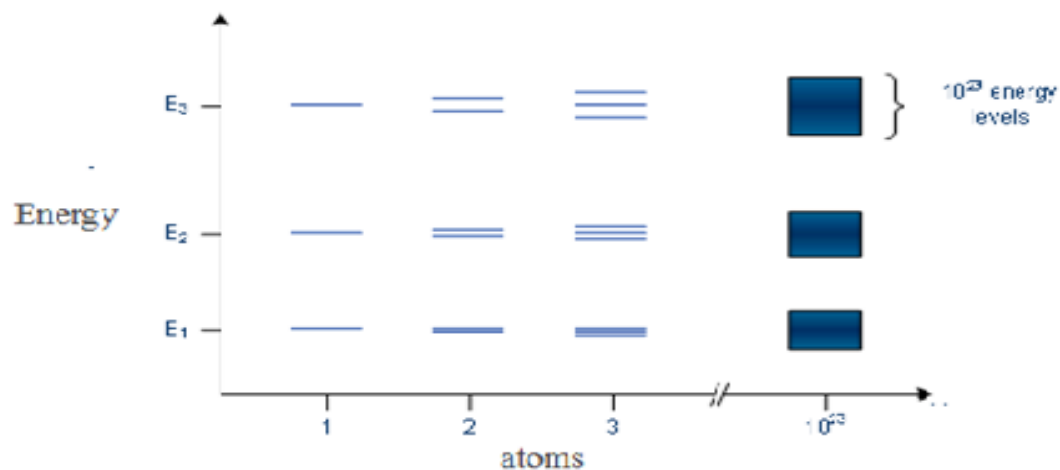
The width of the energy bands depends on how strongly the electrons are bound to the atom. The valence electrons in the highest energy level interact strongly with those of neighboring atoms and can be solved relatively easily from an atom; with a very large number of atoms, a single electron can no longer be assigned to one single atom. As a result, the energy bands of the individual atoms merge to a continuous band, the valence band. Bands - very closely spaced orbitals with not much difference in Energy. In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.
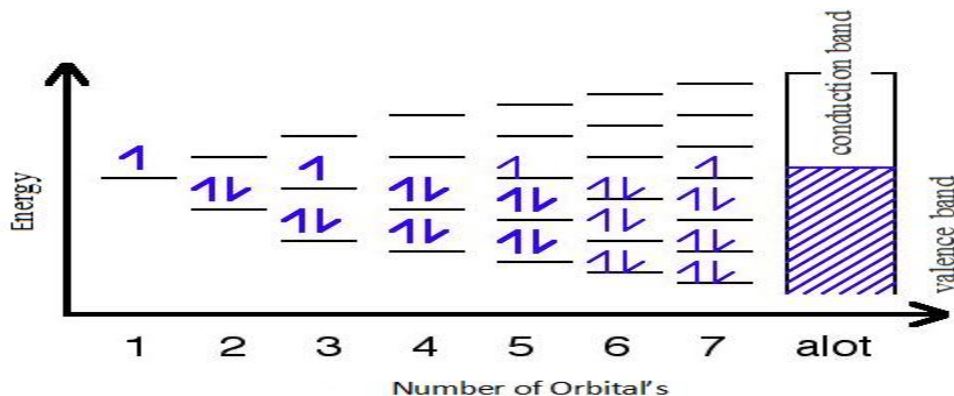
Example:

Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.
Bands will follow a trend as you go across a period:
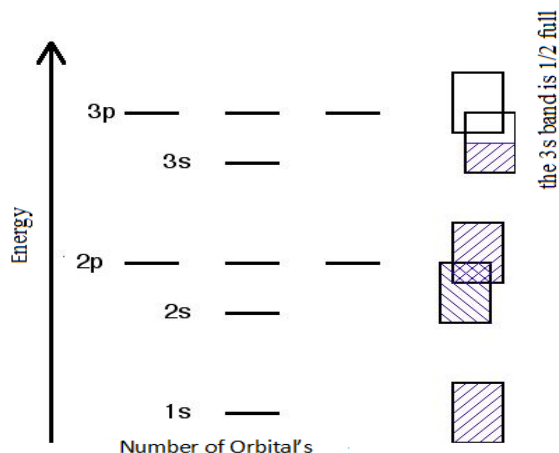
- In Na, the 3s band is 1/2 full.
- In Mg, the 3s band is full.
- In Al, the 3s band is full and the 3p ban is 1/2 full... and so on.

BAND STRUCTURE OF CONDUCTORS, SEMICONDUCTORS & INSULATORS

The band model of conductors:
In conductors, the valence band is either not fully occupied with electrons, or the filled valence band overlaps with the empty conduction band. In general, both states occure at the same time, the electrons can therefore move inside the partially filled valence band or inside the two overlapping bands. In conductors there is no band gap between the valence band and conduction band.
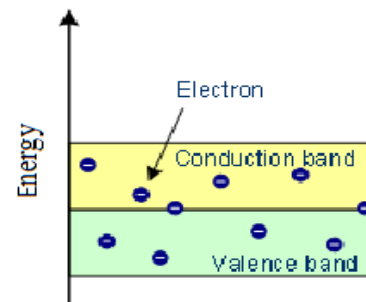
The band model of semiconductors:

In semiconductors, band gap is so small that even at room temperature electrons from the valence band can be lifted into the conduction band. The electrons can move freely and act as charge carriers. In addition, each electron also leaves a hole in the valence band behind, which can be filled by other electrons in the valence band. Thus one gets wandering holes in the valence band, which
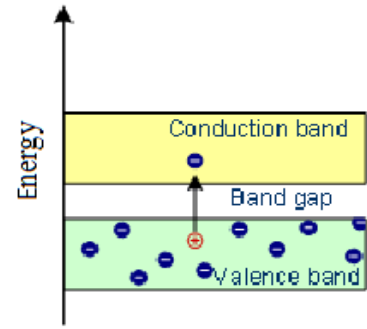
can be viewed as positive charge carriers.

There are always pairs of electrons and holes, so that there are as many negative as positive charges, the semiconductor crystal as a whole is neutral. A pure undoped semiconductor is known as intrinsic semiconductor. Per cubic centimeter there are about 10^{10} free electrons and holes (at room temperature).

The band model of insulators:

In insulators the valence band is fully occupied with electrons due to

the covalent bonds. The electrons cannot move because they're "locked up" between the atoms. To achieve conductivity, electrons from the valence band have to move into the conduction band. This prevents the band gap, which lies in-between the valence band and conduction band.
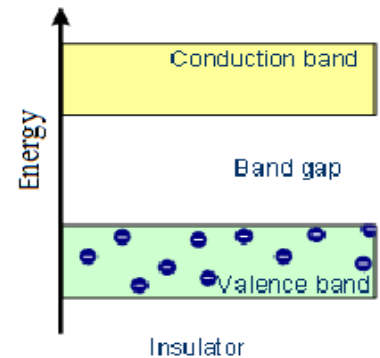
Only with considerable energy expenditure (if at all possible) the band gap can be overcome; thus leading to a negligible conductivity.

DOPING IN SEMICONDUCTORS

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

There are two different kinds of semiconductors:
intrinsic and **extrinsic**.

i. Intrinsic Semiconductors: An intrinsic semiconductor is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. The number of holes will equal the number of electrons that have jumped.
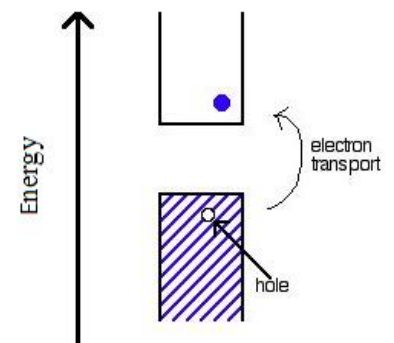
ii. Extrinsic Semiconductors: In extrinsic semiconductors, the band gap is controlled by purposefully adding small impurities to the material. This process is called **doping**. Doping, or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsic semiconductors, the number of holes will not equal the number of electrons jumped. There are two different kinds of extrinsic semiconductors, p-type (positive charge doped) and n-type (negative charge doped).

The
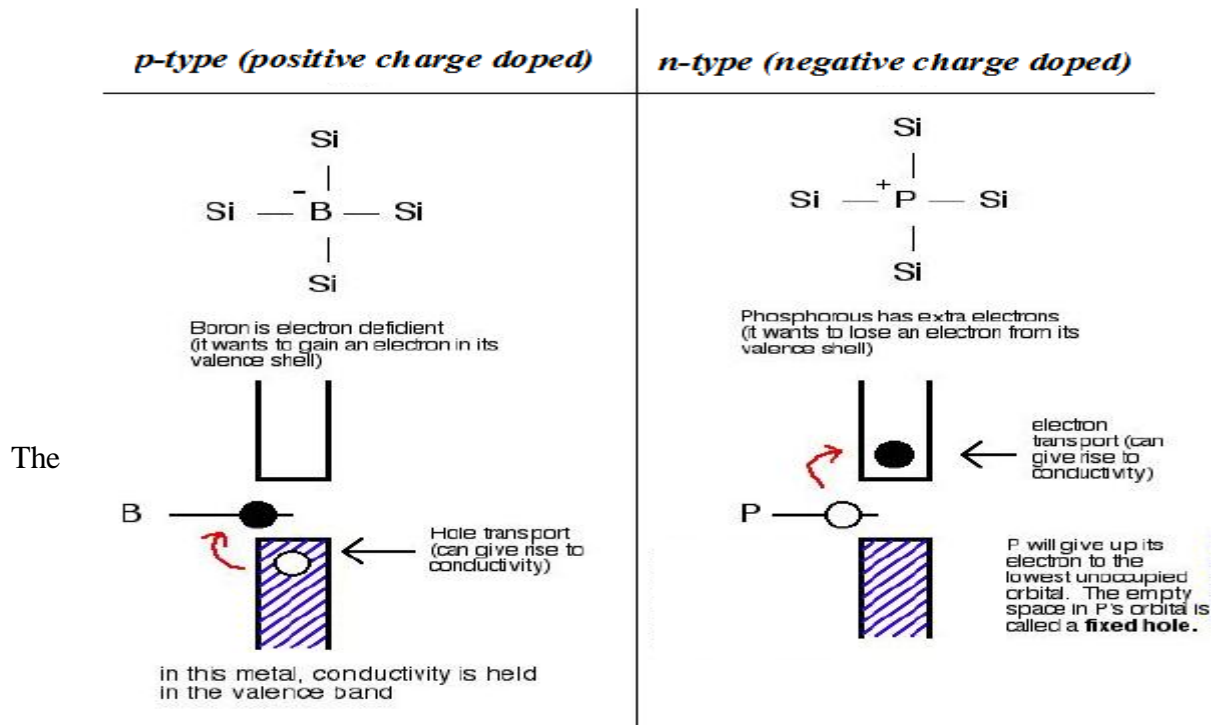
PROBABILITY OF FINDING AN ELECTRON IN THE CONDUCTION BAND

Probability of finding an electron in the conduction band is shown by the equation:

$$P = \frac{1}{e^{\Delta E/RT} + 1}$$

ΔE stands energy gap
t stands for the temperature
R is a bonding constant

Based on energy gap, between the valence band and the conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

Ex: In Carbon (diamond) ΔE- energy gap is 524 kJ/mol and number of electrons per cm^3 is 10^{-27}, it is insulator.

In Si, ΔE- energy gap is 117 kJ/mol and number of electrons per cm^3 is 10^9, it is semiconductor.

In Ge, ΔE- energy gap is 66 kJ/mol and number of electrons per cm^3 is 10^{13}, it is semiconductor.

UNIT-I

Learning objectives:

After completion of this unit the student should be able to:

- Atomic and Molecular orbital's.

- Linear Combination of Atomic Orbital's (LCAO).

- Molecular orbital's of diatomic molecules.

- Molecular orbital energy level diagrams of N_2 molecule.

- Molecular orbital energy level diagrams of O_2 molecule.

- Molecular orbital energy level diagrams of F_2 molecule.

- π molecular orbital's of butadiene.

- π molecular orbital's of benzene.

- Salient Features of Crystal Field Theory.

- Crystal Field Splitting of transition metal ion d- orbitals in Tetrahedral geometry.

- Crystal Field Splitting of transition metal ion d- orbitals in Octahedral geometry.

- Crystal Field Splitting of transition metal ion d- orbitals in square planar geometry.

Short Answer Questions:

1. Distinguish between atomic and molecular orbitals.

2. Describe the atomic orbital diagrams of S, P(X, Y & Z) d-Orbital -t_2g and eg.

3. What is the bond order of N_2 and O_2 molecules?

4. Explain linear combination of atomic orbitals (LCAO) method.

5. What is the energy order of 14 and less than 14 electrons?

6. Explain π molecular energy level diagrams of butadiene.

7. What are the Salient Features of CFT.

8. Draw two sets of *degenerate orbitals* of d-orbitals.

9. Why Crystal field splitting of tetrahedral complex is lesser than that in octahedral complex?

10. Draw crystal Field splitting diagram of transition metal ion d- orbital's in square planar geometry.

11. Explain the band structure of conductors, semiconductors and insulators.

12. Explain effects of doping on conductance?

Descriptive Questions:

1. Explain Molecular energy level diagrams of N_2.

2. Describe the Molecular energy level diagrams of O_2.

3. Explain π molecular orbital's of benzene.

4. Describe crystal field splitting of transition metal ion d- orbitals in octahedral geometry.

5. What is crystal Field splitting of transition metal ion d- orbital's in tetrahedral geometry.

6. What is crystal Field splitting of transition metal ion d- orbital's in square planar geometry.

7. Explain doping in semi conductors.

Objective Questions:

1. Which of the following d-orbitals are in *Between the axis*?   [a]
   a. d_{xy}, d_{xz} and d_{yz} b. d_z^2 and $d_{x^2-y^2}$ c. d_{xz} and d_{yz} d. d_{xy}, and d_{xz}

2. According to the molecular orbital theory magnetic nature of the *Fluorine* is.   [b]
   a. Paramagnetic   b. Diamagnetic c. Ferromagnetic d. Anti-ferromagnetic.

3. What is the coordination number of *octahedral geometry*?   [b]
   a. 4   b. 6   c. 5   d. 7

4. In which type of doping creates +ve holes in semiconductor.   [a]
   a. p-type   b. n-type   c. Both a & b   d. s-type

5. Which of the following d-orbitals are along the axis?   [b]
   a. d_{xy}, d_{xz} and d_{yz} b. d_z^2 and $d_{x^2-y^2}$
   c. d_{xz} and d_{yz} d. d_{xy}, and d_{xz}

6. According to the molecular orbital theory magnetic nature of the Nitrogen is.   [b]
   a. Paramagnetic   b. Diamagnetic
   c. Ferromagnetic   d. Anti-ferromagnetic.

7. According to the crystal field theory what is the force between metal and ligand. [a]
   a. Electrostatic force   b. Vanderwall force
   c. Gravitational force   d. Potential force.

8. Which of the following are semiconductors?   [a]
   a. Si and Ge   b. Li and Na
   c. Fe and Co   d. O_2 and N_2.

Fill in the blanks:

1. Molecular orbital is ----------------centric?

2. The shape of the *d-orbital* is ----------------------------.

3. According to the molecular orbital theory magnetic nature of the Oxygen is -----------------.

4. Energy gap between valence band and conduction band maximum in ------------------------.

5. Atomic orbital is ----------------centric?

6. The shape of the *p-orbital* is ------------------.

7. According to the molecular orbital theory magnetic nature of the *Nitrogen* is ----------------

8. Energy gap between Valence band and Conduction band is minimum in --------------------.