INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 1

DATE:- 26, FEBRUARY, 2021

TIME: (9.00A.M.)

Octet rule:

Covalent bond: Sharing of electrons,

Single bond: e. g. H_2, CH_4

Double bond: e. g. O_2

Triple bond: e. g. N_2

Ionic bond: e. g. NaCl

Coordinate bond: e. g. $NH_3 \longrightarrow BF_3$

Metallic bond: e. g. Na metal

Limitations of octet rule: Incomplete and Expanded octet, energy, stability, Direction of bond, forces.

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 2

DATE:- 24, MARCH, 2021

TIME: (10.00A.M.)

Octet rule:

Covalent bond: Sharing of electrons,

Single bond: e. g. H_2, CH_4

Double bond: e. g. O_2

Triple bond: e. g. N_2

Ionic bond: e. g. NaCl

Coordinate bond: e. g. $NH_3 \longrightarrow BF_3$

Metallic bond: e. g. Na metal

Limitations of octet rule: Incomplete and Expanded octet, energy, stability, Direction of bond, forces.
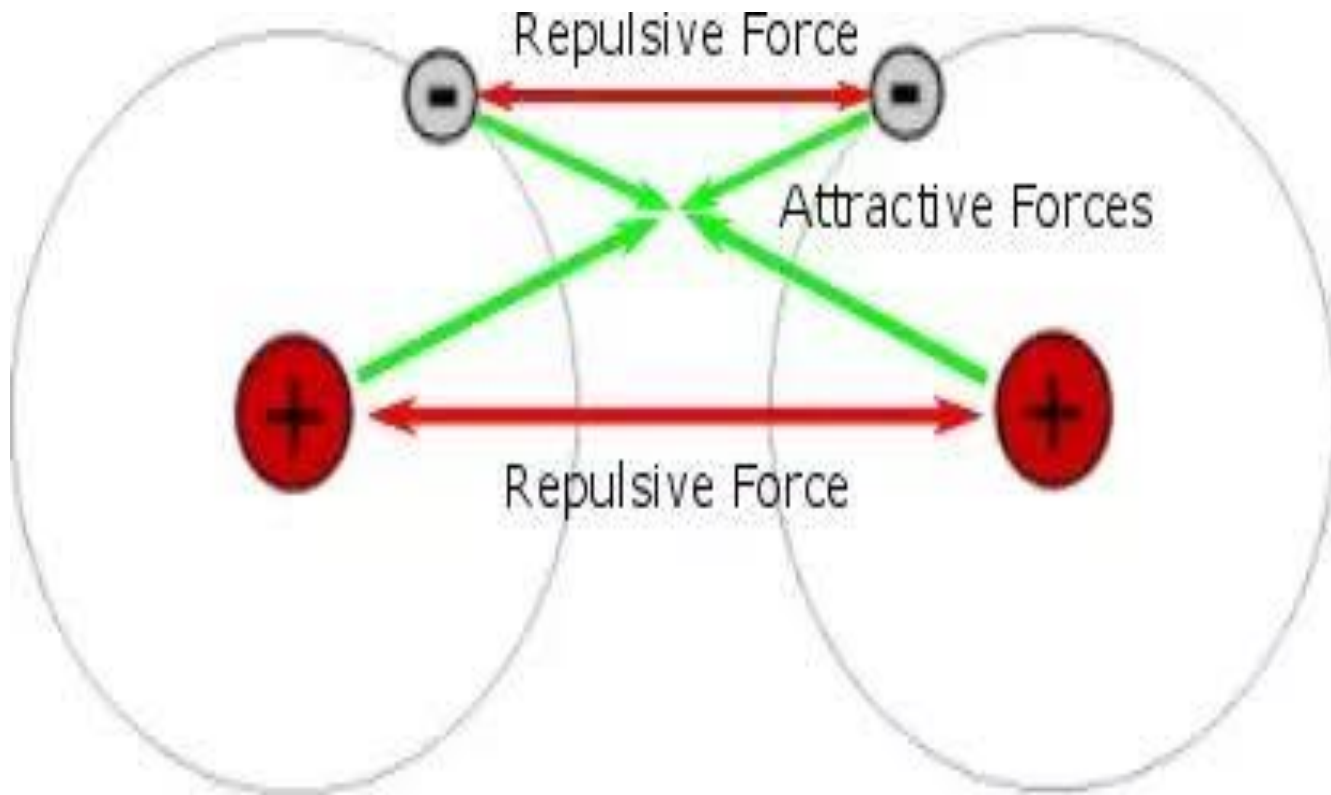
Theories of covalent bond: -

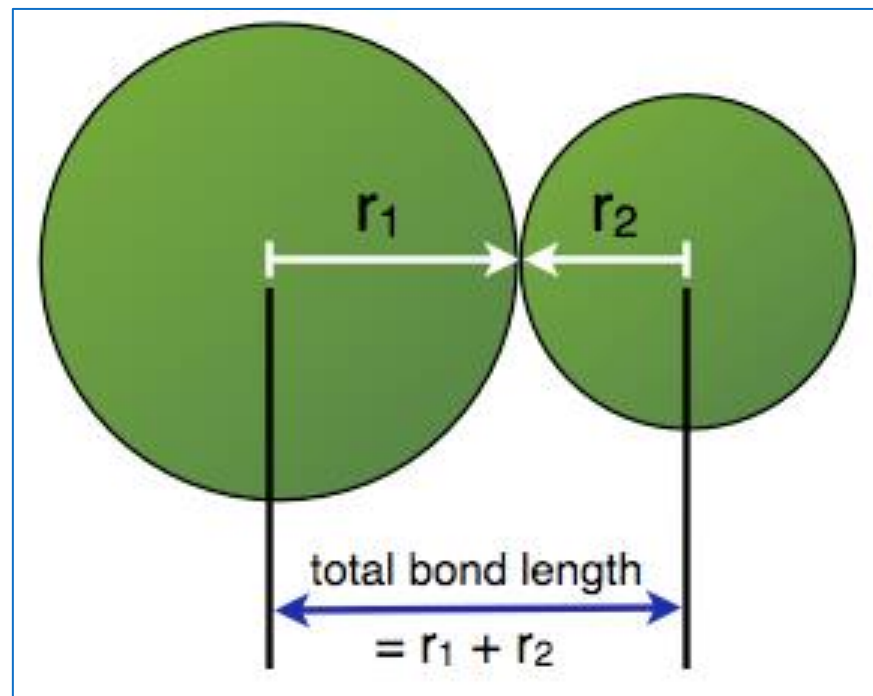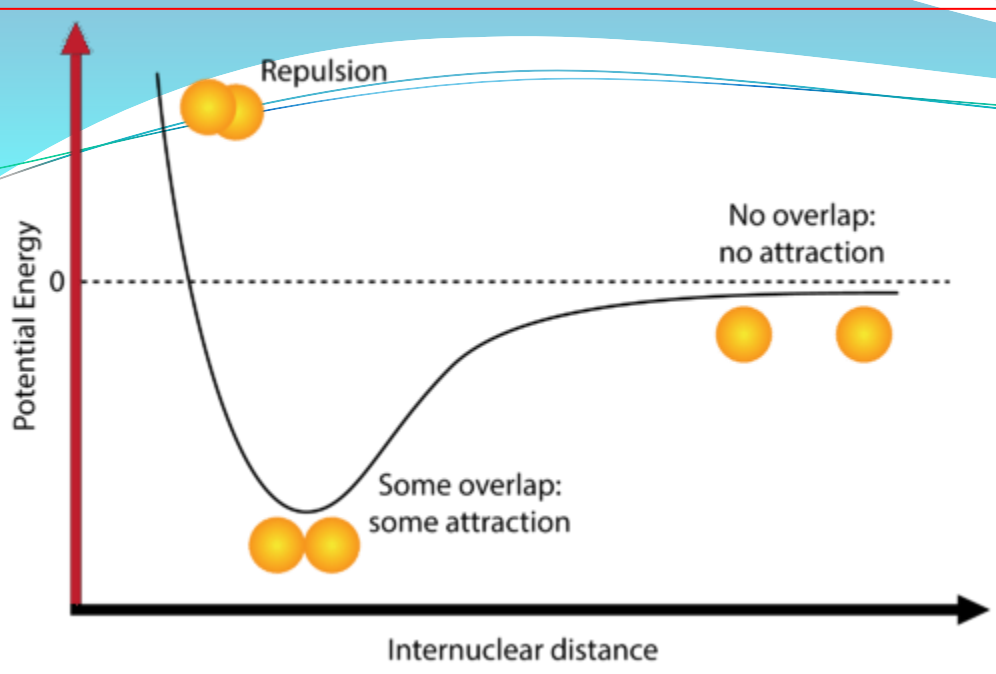There are two theories of chemical bonding:

Valence Bond Theory (Orbital overlap concept of covalent bond) (VBT): -

This theory was proposed by Heitler and London in 1927 on the basis of wave mechanics of electron and it was further extended by Pauling and Slater in 1931, to explain directional character of covalent bond and geometry of molecules.

Assumptions of valence bond theory:-

1) Covalent bond is formed between the two atoms, when orbitals of two atoms having unpaired electrons overlap.

2) Each overlapping atomic orbital should contain an unpaired electron with opposite spin. The electron spins are neutralized and electrons get paired on overlapping of atomic orbitals.

3) Each overlapping atomic orbital should have comparable energy.

Repulsion

Potential Energy

0

No overlap:
no attraction

Some overlap:
some attraction

Internuclear distance

r_1

r_2

total bond length
$= r_1 + r_2$

4) During overlapping of atomic orbitals, the electron density between two nuclei increases and therefore repulsion between the two nuclei of the bonded atoms decreases. This results in liberation of energy.

5) The equilibrium distance between the atoms where both attractive and repulsive forces get balanced is called as Bond length.

6) The electron pair is localized (fixed) between the bonded atoms in the molecule.

7) Individual atoms retain their identity in the molecule.

8) The strength of covalent bond depends upon the extent of overlapping between the two atoms.

9) Greater the overlap of atomic orbitals, stronger is the bond formed.

10) The number of covalent bonds formed by an atom is equal to the number of unpaired electrons in the atom.

11) The direction of the bond depends upon the direction of overlapping.

12) Axial (End to end) overlapping of atomic orbitals forms sigma bond, while, lateral overlap forms π-bond.
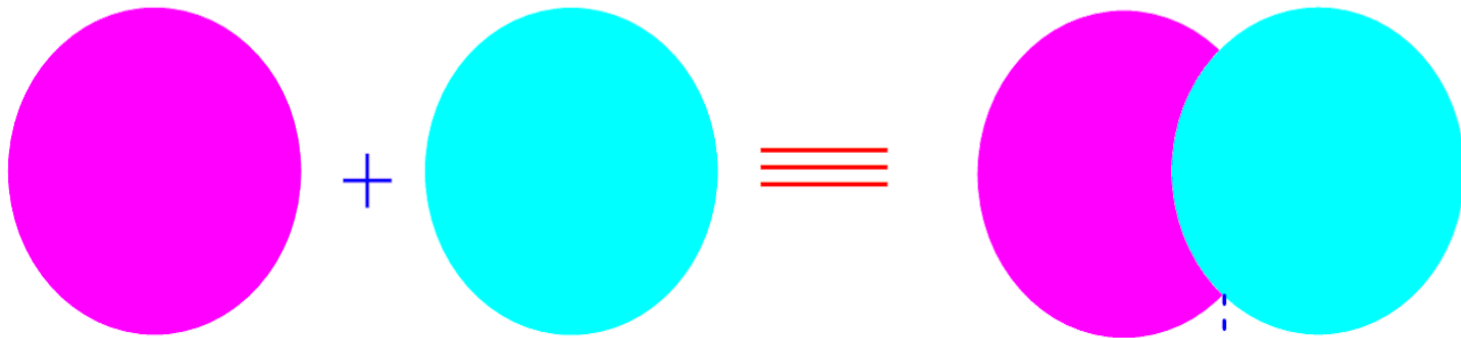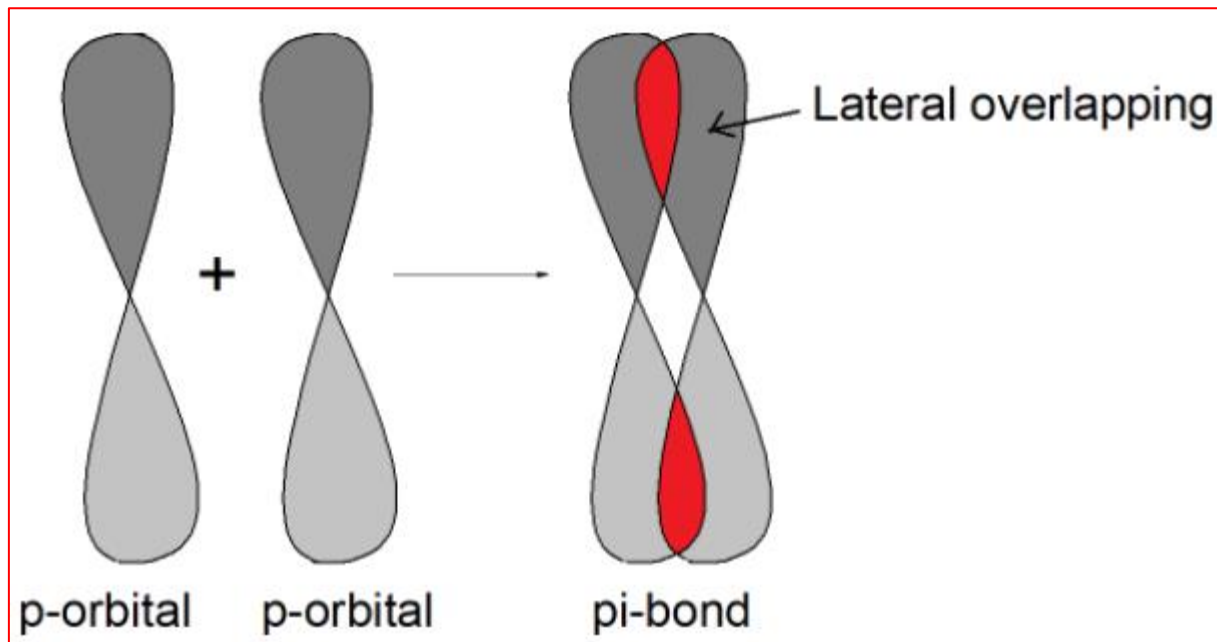
1s
orbital

1s
orbital

Formation of sigma bond
by the overlapping between
two 's'-orbital.

P$_X$
orbital

P$_X$
orbital

face to face over-lapping
Sigma bond formation
between 'p'-orbital.

p-orbital   p-orbital   pi-bond

Limitations of valence bond theory:

1) It fails to explain the bond order and stabilization energy in the formation of molecule.

2) It fails to explain the formation of odd molecular ions like H_2^+, He_2^+ etc.

3) It fails to explain the paramagnetic property of oxygen molecule.

4) It fails to explain the bonding in electron deficient molecules. e.g. BH_3, $AlBr_3$, etc.

5) It fails to explain the formation of metallic bond and formation of coordinate bond.

6) It fails to explain the observed valency, bond equivalence and geometry of the molecules.

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CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 3

DATE:- 31, MARCH, 2021

TIME: (10.00A.M.)

Limitations of valence bond theory:

1) It fails to explain the bond order and stabilization energy in the formation of molecule.

2) It fails to explain the formation of odd molecular ions like H_2^+, He_2^+ etc.

3) It fails to explain the paramagnetic property of oxygen molecule.

4) It fails to explain the bonding in electron deficient molecules. e.g. BH_3, $AlBr_3$, etc.

5) It fails to explain the formation of metallic bond and formation of coordinate bond.

6) It fails to explain the observed valency, bond equivalence and geometry of the molecules.

1) To explain observed Valency

$C(6) \rightarrow 1s^2, 2s^2, 2px^1, 2py^1$
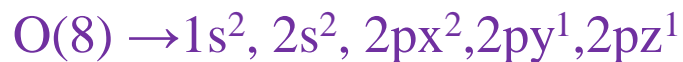
Formation of excited state

$C(6) \rightarrow 1s^2, 2s^1, 2px^1, 2py^1, 2pz^1$

2) To explain bond equivalence

Valence shell $\rightarrow 2s^1, 2px^1, 2py^1, 2pz^1$

Hybridization

3) To explain observed geometry (VSEPR theory)

Even Filled orbital of vacant orbital can be involved in hybridization.

$O(8) \rightarrow 1s^2, 2s^2, 2px^2, 2py^1, 2pz^1$

In H_2O, molecule, the bond angle is $104^0 28'$

In NH_3 molecule, the bond angle is $107^0 28'$

In AlBr3 molecule, Al $(13) \rightarrow 1s^2, 2s^2, 2px^2, 2py^2, 2pz^2, 3s^2 \ 3px^1$

Excited state $\rightarrow 3s^1 \ 3px^1, 3py^1 \ 3pz^0 (SP^3 \text{hybridization})$

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 4

DATE:- 2, APRIL, 2021

TIME: (9.00A.M.)

Molecular orbital Theory (MOT): -

This theory is also called as electron pair theory. It was developed by F. Hund and R. S. Mulliken in 1932 and was later extended by J. E. Lenard Jones and Charles Coulson.

Assumptions of Molecular orbital theory:

1) The molecule is formed by linear combination of atomic orbitals of different atoms.

2) The atomic orbitals from valence shell of one atom combine with corresponding valence shell atomic orbitals of other atom. The inner atomic orbitals do not take part in bonding.

3) The atomic orbitals overlap and combine to form new polycentric orbitals, called as molecular orbitals.

4) The valence electrons of the combining atoms are now under the influence of all the nuclei in the molecule. i.e. delocalized over all the nuclei in the molecule.

5) In the formation of molecule, atoms lose their identity.

6) Like atomic orbitals, the molecular orbitals also possess different energies and shapes.

7) The number of molecular orbitals produced will be equal to the number of atomic orbitals combined.

8) The atomic orbitals of the two or more atoms combine to form molecular orbitals only when they have i) Close distance ii) Similar energy iii) Matching symmetry iv) Matching geometry

9) As the wave function ψ is used to describe the electron density in the particular orbital of the atom, the same ψ describes the electron density in the particular molecular orbital.

10) As atoms possess atomic orbitals such as s,p,d,f similarly molecules possess molecular orbitals such as σ π, δ, σ*, π* etc. (The asterisk indicates higher energy anti-bonding molecular orbital).

11) As atoms possess energy levels such as 1s, 2s, 2p, 3s, 3p similarly molecules possess molecular energy levels as σ1S, σ*1S, σ2S, σ*2S, σ2P, π2P, etc.

12) As atomic orbitals can be arranged in their increasing order of energies as $1S < 2S < 2P < 3S < 3P,$……..etc. The molecular orbitals are also arranged in their increasing order of energies such as $σ1S < σ*1S < σ2S < σ*2S < $……..etc.

13) Aufbau principle, Hunds rule and Paulis exclusion principle are used for filling electrons in different molecular orbitals.

14) The combination of atomic orbitals forms two types of molecular orbitals namely bonding molecular orbital (BMO) and antibonding molecular orbital (ABMO).

15) The bonding molecular orbital has lower energy while antibonding molecular orbital has higher energy than parent atomic orbitals.

16) When the overlapping lobes of combining orbitals have same sign (+ + or - -), then bonding molecular orbital is formed and when the signs of overlapping lobes are of different sign(+ - or - +), then antibonding molecular orbital is formed.

17) The combination of atomic orbitals between two atoms gives sigma and pi molecular orbitals. The axial overlap of orbitals gives sigma MO's while lateral overlap gives Pi MO's.

Linear combination of atomic orbitals: (LCAO method):

Consider the two similar atoms H and H. These atoms are denoted as 1 and 2. Atomic orbital of atom 1 has wave function ψ_1 and atomic orbital of atom 2 has wave function ψ_2. When these atoms form a bond, the electrons originally in the atomic orbitals now occupy molecular orbitals. The molecular orbital is formed by a linear combination of the atomic orbitals ψ_1 and ψ_2 as

$$\Psi = N\,[C_1\,\psi_1 + C_2\,\psi_2]$$

Where Ψ is the wave function for the molecular orbital. N is the normalizing constant. The value of N is so selected that the probability of finding the electron in the whole space of the molecule is unity. C_1 and C_2 are the constants, whose values are so selected that they give a minimum energy for the molecular orbital wave function Ψ.

A wave function Ψ describes the probability of finding the electron and Ψ^2 describes the electron density. The two ways of combinations are

$\Psi_{(g)} = N\,[\psi_1 + \psi_2]$ and

$\Psi\,(u) = N\,[\psi_1 + (-\psi_2)]\ = N\,[\psi_1 - \psi_2]$

Thus, when a pair of atomic orbitals ψ_1 and ψ_2 combines they produce a pair of molecular orbitals $\Psi_{(g)}$ and $\Psi\,(u)$. Hence, the number of molecular orbitals produced must always be equal to the number of atomic orbitals taking part in combination. i.e. orbitals are not destroyed. Thus, such type of addition and subtraction of the wave functions of the atomic orbitals is called as LCAO principle.

In the MOT, wave functions are designated $\Psi_{(g)}$ and $\Psi\,(u)$. The letter 'g' stands for gerade (even) and the letter 'u' stands for ungerade (odd). The symbols g and u refer to the symmetry of the orbitals about its centre. The wave function is gerade, if the sign of Ψ remains unchanged when the orbital is reflected about its centre. While, the wave function is called ungerade, when the sign of Ψ is changed on the reflection of orbital about its centre.

The electron distribution in a MO can be obtained by squaring the wave function.

$$\Psi^2 (g) = \Psi_1{}^2 + \Psi_2{}^2 + 2\,\Psi_1\,\Psi_2$$

$$\Psi^2 (u) = \Psi_1{}^2 + \Psi_2{}^2 - 2\,\Psi_1\,\Psi_2$$

These two molecular orbitals differ by $2\,\Psi_1\,\Psi_2$. The wave function $\Psi_{(g)}$ increases the electron density between the nuclei by an amount $2\,\Psi_1\,\Psi_2$ and is therefore a bonding MO of lower energy. The wave function $\Psi_{(u)}$ decreases the electron density in between the nuclei by an amount $2\,\Psi_1\,\Psi_2$ and is therefore an anti-bonding MO of higher energy.

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ONLINE LECTURE NO. 5

DATE:- 16 APRIL, 2021

TIME: (9.00A.M.)

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