Valence Shell Electron Pair Repulsion (VSEPR)

This theory was developed by **Gillespie** and **Nyholm**. It is based on the effect of electron repulsion on the bond angles. The shape of the molecule or ion depends upon the number of bonding electron pairs (bp's) and nonbonding electron pairs or lone pairs (lp's) in the central atom.

During the formation of simple covalent molecule, the central atom forms covalent bond with other atoms. The central atom is oriented in such a way that there is minimum repulsion (maximum stability) between them. The molecule has a definite shape because; there is only one orientation of orbitals corresponding to minimum energy.

Postulates of VSEPR

1. If the central atoms in a molecule are surrounded by only bonding electron pairs (bp) [electron pairs involved in covalent bonding] and not by non-bonding electron pairs or lone pairs (lp's) [electron pairs not involved in bonding] it will have regular geometry or shape. The shape of such molecules is given in Table.

VSEP (Total electron pairs)	Number of bond pair of electrons	Number of lone pair of electrons	Shape/Geometry	Bond angle	Example
2	**2**	**0**	**Linear**	**180°**	**BeF_2**
3	**3**	**0**	**Trigonal planar**	**120°**	**BCl_3**
4	**4**	**0**	**Tetrahedral**	**109.5°**	**CH_4**
5	**5**	**0**	**Trigonal bipyramidal**	**90/120°**	**PF_5**
6	**6**	**0**	**Octahedral**	**90°**	**SF_6**

2. If the central atom in a molecule is surrounded by both bp's, and lp's it will have distorted or irregular geometry or shape, because, the lp's repel adjacent bonding electron pairs more strongly than do bonding electron pairs which increases as:

    (bp – bp) < (bp – lp) < (lp – lp)

    Due to this reason the bond angle decrease in the order of

    CH_4 (109.5°) > NH_3 (107.5°) > H_2O (104.5°)

    And the number of lp's increases as:

    CH_4 (0 lp) < NH_3 (1 lp) < H_2O (2 lp)

    In other words we can say that as the number of lp's increases, repulsion increases and bond angle decrease or distortion increases.

3. Repulsion between electron pairs in filled shell is greater than that in incomplete shell. So as repulsion increases, bond angle decreases.

    Here we take the hydrides of 16th group elements of the periodic table with their bond angles:

    H_2O (104.5°) >> H_2S (92.2°) > H_2Se (91°)

4. If the electronegativity of the central atom decreases, bond angle decreases, at the same time if the electronegativity of the surrounding atoms decreases (central atom remains the same) the bond angle increases

 PI_3 (102°) > PBr_3 (101.5°) > PCl_3 (100°)

Limitations of VSEPR Theory

     a) It does not explain the shapes of polar molecules e.g. Li_2O and H_2O should have same structure but Li_2O is linear while H_2O is angular.
     b) It does not explain the shapes of the molecules or ions which are extensive by delocalized π-electron system.
     c) It does not explain the shapes of some molecules which have an inert pair of electrons.
     d) It does not explain the shapes of certain compounds of transitional metals e.g. the shape of the compound p^8 electronic configuration of the central atom, is square planar and not tetrahedral as predicted by this theory.

➢ The number of electron pairs around the central atom and its corresponding shape is determined as follows:
     a. Decide which is the central atom in a molecule
     b. Count up the valence (outer shell) electrons on the central atom.
     c. Count up the electrons used by the outer atoms to make bonds with the central atom.
     d. The sum of (b) + (c) divided by two gives the Valence Shell Electron Pair (VSEP) count.
     e. The predicted geometry of the molecule is based on the number of VSEP as follows:

A. Examples of covalent molecule where lone pairs are absent:
1. CH_4

     a. Central atom is C; outermost electrons in C = 4
     b. electrons used by C atoms to make bonds with H = 4; VSEP = 8/2 = 4
     c. Bond pair=4, lone pair=0, shape of CH_4 is tetrahedral having a H-C-H of 109.5°
   The shape of this molecule, however, is not planar. The four bond pairs are arranged about the C atom, pointing toward the corners of a regular tetrahedron. This shape minimizes the repulsion between the bond pairs.
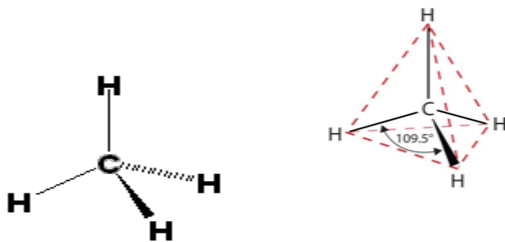
        (shape: tetrahedron; bond angle = 109.5°)

B. **Examples of covalent molecule where lone pairs and bond pairs are present**
   1. NH_3
     a. Central atom is N; outermost electrons in N = 5
     b. electrons used by N atoms to make bonds with H = 3
     c. Total Valence shell electrons (VSE) = 8; VSEP = 8/2 = 4
     d. Since VSEP is 4, predicted shape of NH_3 is tetrahedral having a H-N-H of 109.5°
     e. But 3 VSEP are involved in bonding and 1 VSEP is lone pair and not involved in bonding. Lone pair-bond pair repulsion > bond pair-bond pair. Hence its actual shape is trigonal pyramidal having bond angle of 107° which is less than 109.5°.
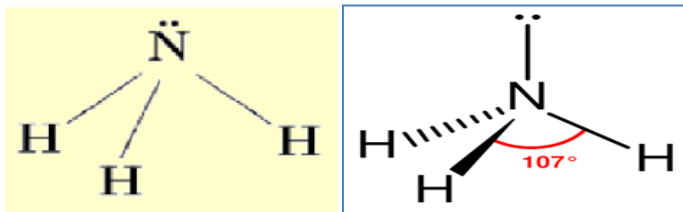
(shape: trigonal pyramidal; bond angle = 107°)

2. **H_2O**
   a. Central atom is O; outermost electrons in O = 6
   b. electrons used by O atoms to make bonds with H = 2
   c. Total Valence shell electrons (VSE) = 8; VSEP = 8/2 = 4
   d. Since VSEP is 4, predicted shape of H_2O is tetrahedral having a H-O-H of 109°
   e. But 2 VSEP are involved in bonding and 2 VSEP is lone pair and not involved in bonding. Lone pair-bond pair repulsion > bond pair-bond pair. Hence its actual shape is is V-shape having bond angle of 104.5.
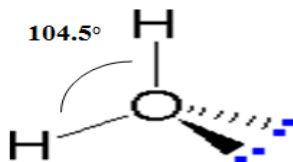

(shape: V; bond angle = 104.5°)

3. **XeF_4**
   a. Central atom is Xe
   b. outermost electrons in Xe = 8
   c. electrons used by Xe atoms to make bonds with F = 4
   d. Total Valence shell electrons (VSE) = 12
   e. VSEP = 12/2 = 6
   f. Since VSEP is 6, predicted shape of XeF_4 is octahedral
   g. But 4 VSEP are involved in bonding and 2 VSEP is lone pair and not involved in bonding.
   h. Lone pair-bond pair repulsion > bond pair-bond pair. Hence its actual shape is is square planar having bond angle of 90°. Lone pairs are on opposite sides of the molecule (180° from each other) to minimize lone-pair-lone-pair interactions.
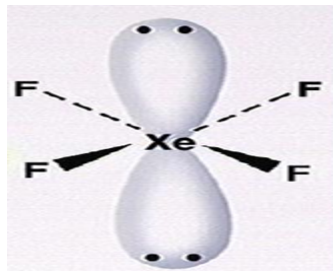

(shape: square planar; bond angle = 90°)

4. **SO_2**
   a. Central atom is S
   b. outermost electrons in S = 6
   c. electrons used by S atoms to make bonds with O = 4
   d. Total Valence shell electrons (VSE) = 10
   e. VSEP = 10/2 = 5
   f. 4 VSEP are involved in 2 double bonds and 1 VSEP is the lone pair.
   g. Predicted shape is trigonal planar but the actual shape is bent or V having a bond angle of <120°. The lone pair of electrons occupies a relatively large volume, since they are held by only one atom. They compress the bond angle between the oxygens and sulfur to less than 120°. The actual O-S-O bond angle is 119.5°.


(shape: V; bond angle = 119.5°)
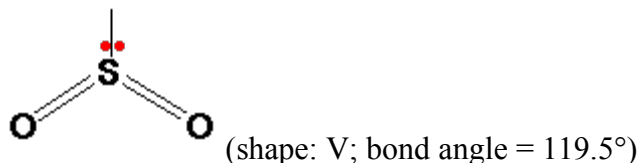
C. **Examples of charged covalent molecule**
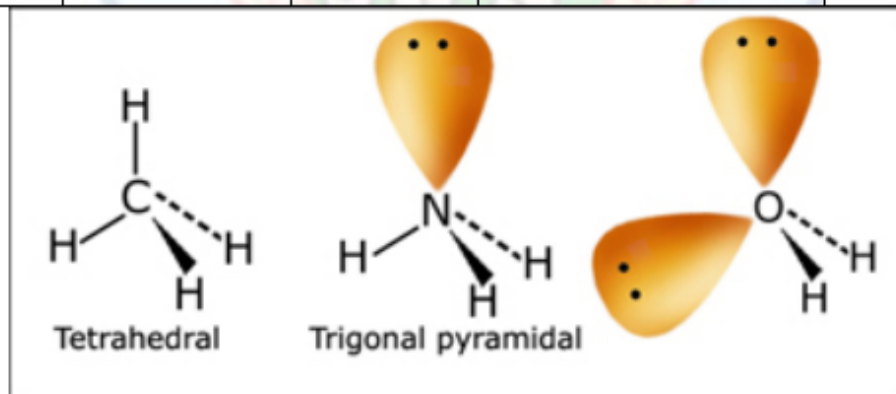   1. NH_4^+
      a. Central atom is N; outermost electrons in N = 5
      b. electrons used by N atoms to make bonds with H = 4
      c. + charge = 1
      d. Total Valence shell electrons (VSE) = 9-1 = 8; VSEP = 8/2 = 4
      e. Since VSEP is 4, predicted shape of NH_4^+ is tetrahedral which is its actual shape having a bond angle of 109.5°
      f. Shape:
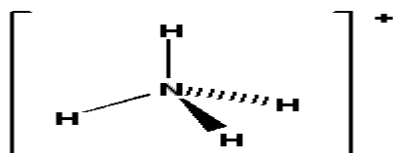
   2. H_3O^+
      a. Central atom is O; outermost electrons in O = 6
      b. electrons used by O atoms to make bonds with H = 3
      c. + charge = 1
      d. Total Valence shell electrons (VSE) = 9-1 = 8; VSEP = 8/2 = 4
      e. Since VSEP is 4, predicted shape of H_3O^+ is tetrahedral but its actual shape is pyramidal having a bond angle of 106°
      f. Shape:
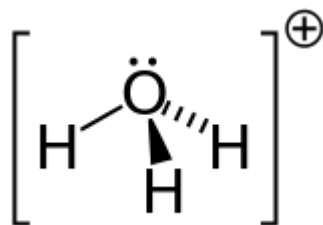
Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Bond angles
Molecular geometries of molecules with four electron pairs with different combinations of lone pairs and bond pairs resulting into irregular geometry.				
CH_4	4	0	Tetrahedral	109.5°
NH_3	3	1	Trigonal pyramidal	107°
OH_2	2	2	Angular	104.5°

Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs resulting into irregular geometry.

Molecular Orbital Theory

Postulates:
1. When nuclei of two atoms come close to each other, their atomic orbitals combine leading to the formation of molecular orbitals (MO) and electrons in them belong to the molecule as a whole.
2. The atomic orbitals of same energy and symmetry will combine to form molecular orbitals (MO).
3. The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals that are combined. The MO thus formed is associated with a definite energy level and the total energy of the molecule is the sum of energies of occupied molecular orbitals.
   When two atomic orbitals are combined, one of the resulting MOs is at a lower energy than the original atomic orbitals; this is a bonding orbital (BMO). The other MO is at a higher energy than the original atomic orbitals; this is an antibonding orbital (ABMO).
   Difference between a BMO and an ABMO
      a. BMO is formed by addition overlap of atomic orbitals (AO). ABMO is formed by subtraction overlap of AOs.
      b. BMO has lower energy and hence greater stability than the AOs from which it is formed. ABMO has a higher energy and lower stability than the AOs.
      c. The electron charge density in between the nuclei is high resulting in lesser repulsion between the nuclei and this causes greater stability of the BMO. In ABMO, the electron charge density is low in between the nuclei which causes greater repulsion and hence destabilizes the ABMO.

4. The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of MOs.
5. Electrons fill the molecular orbitals in the same way as they fill the atomic orbitals, following the Aufbau principle, Pauli Exclusion Principle and the Hund's rule of maximum multiplicity.
   Aufbau principle:
      ➢ Orbitals of lowest energy are filled up first.
      ➢ Each orbital will hold a maximum of two electrons, provided that they have opposite signs.
   Pauli Exclusion Principle
      ➢ in a given atom, no two electrons can have all four quantum numbers the same.
      ➢ when applied for MO, the principle states that no two electrons in the same molecule can have all four quantum numbers the same.
   Hund's rule:
      ➢ Several orbitals have the same energy (degenerate orbitals of d, f)
      ➢ Electrons will be arranged so as to give maximum number of unpaired spins.
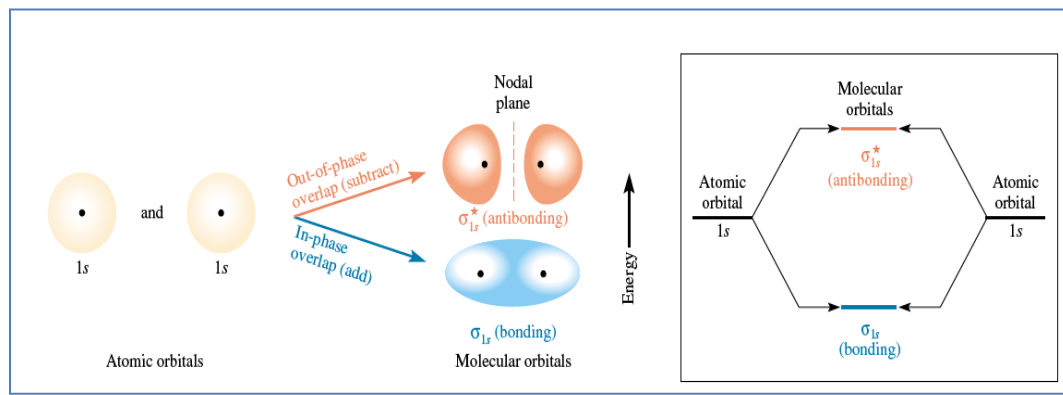
(MO) diagram for the combination of the 1s atomic orbitals on two identical atoms (*at the left*) to form two MOs: a *bonding* orbital, 1s (*blue*), resulting from addition of the 1s orbitals. The other is an *antibonding* orbital, 1s* (*red*), at higher energy resulting from subtraction of the combining 1s orbitals. Nuclei are represented by dots.
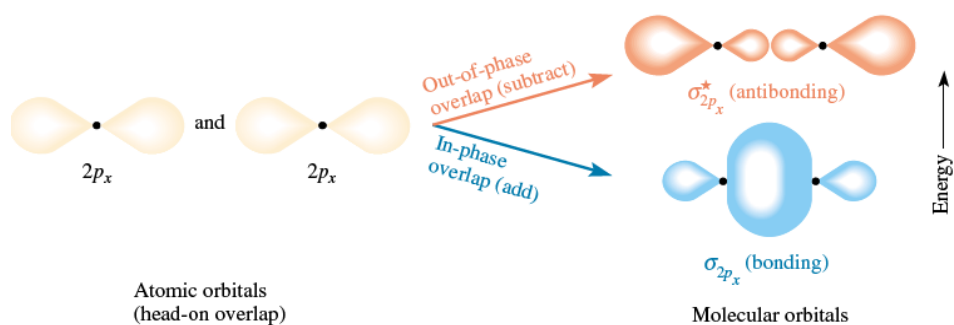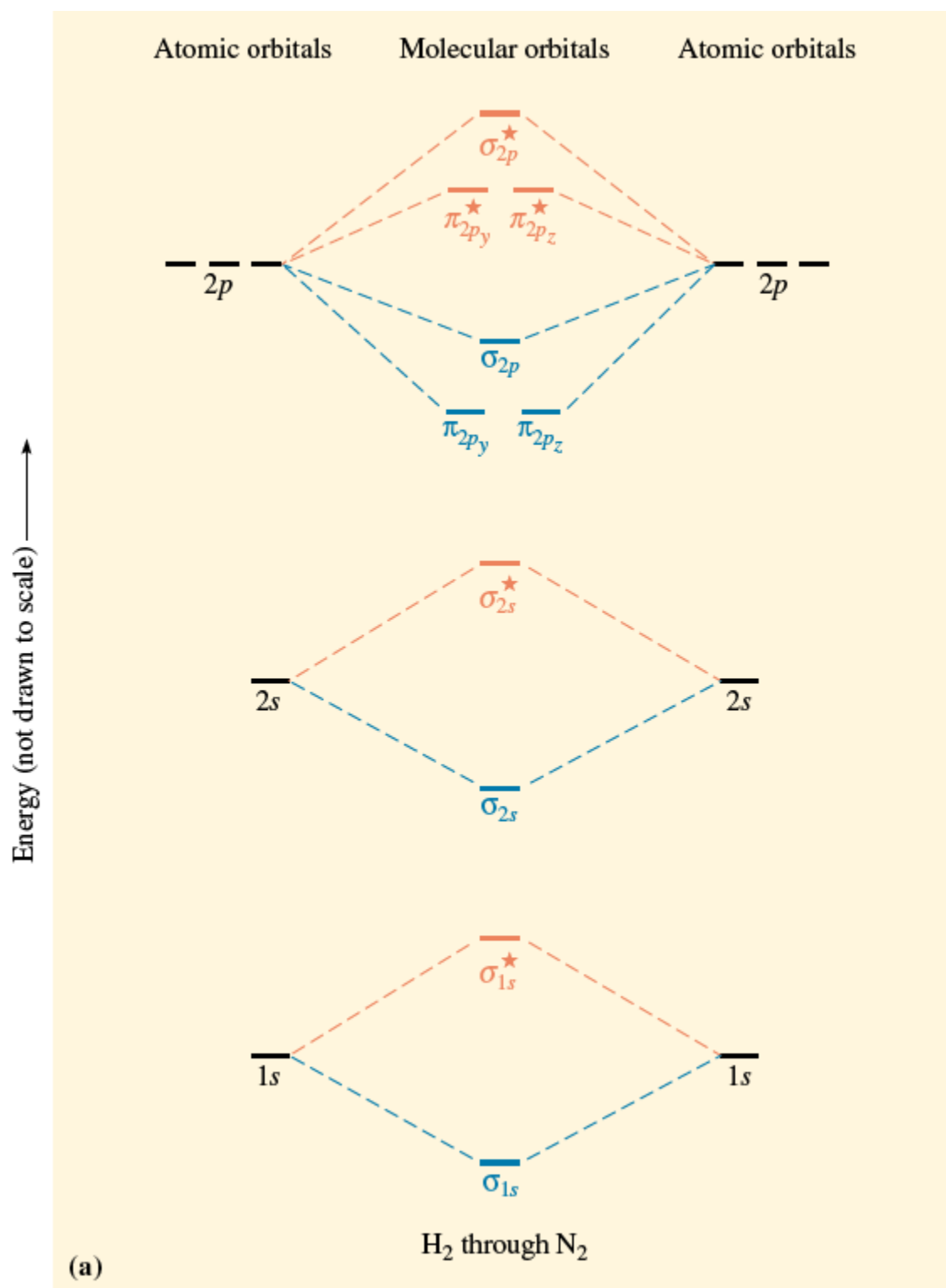

Production of σp_x and $\sigma^* p_x$ MO by overlap of σp_x AO on two atoms.
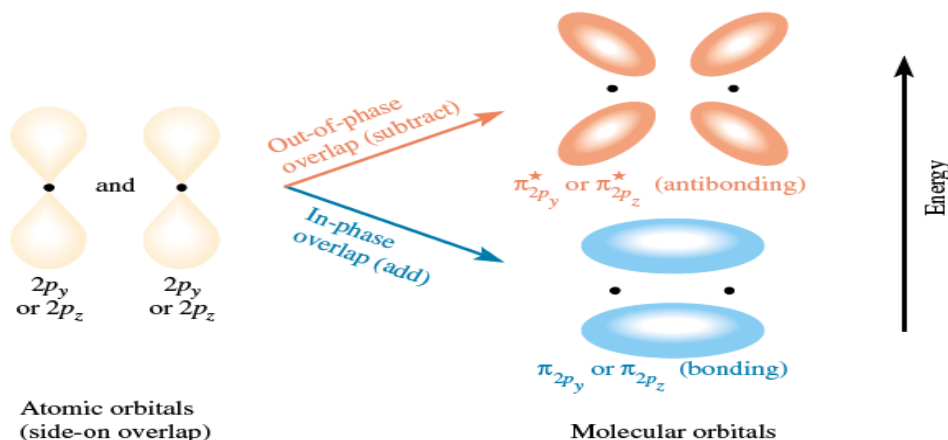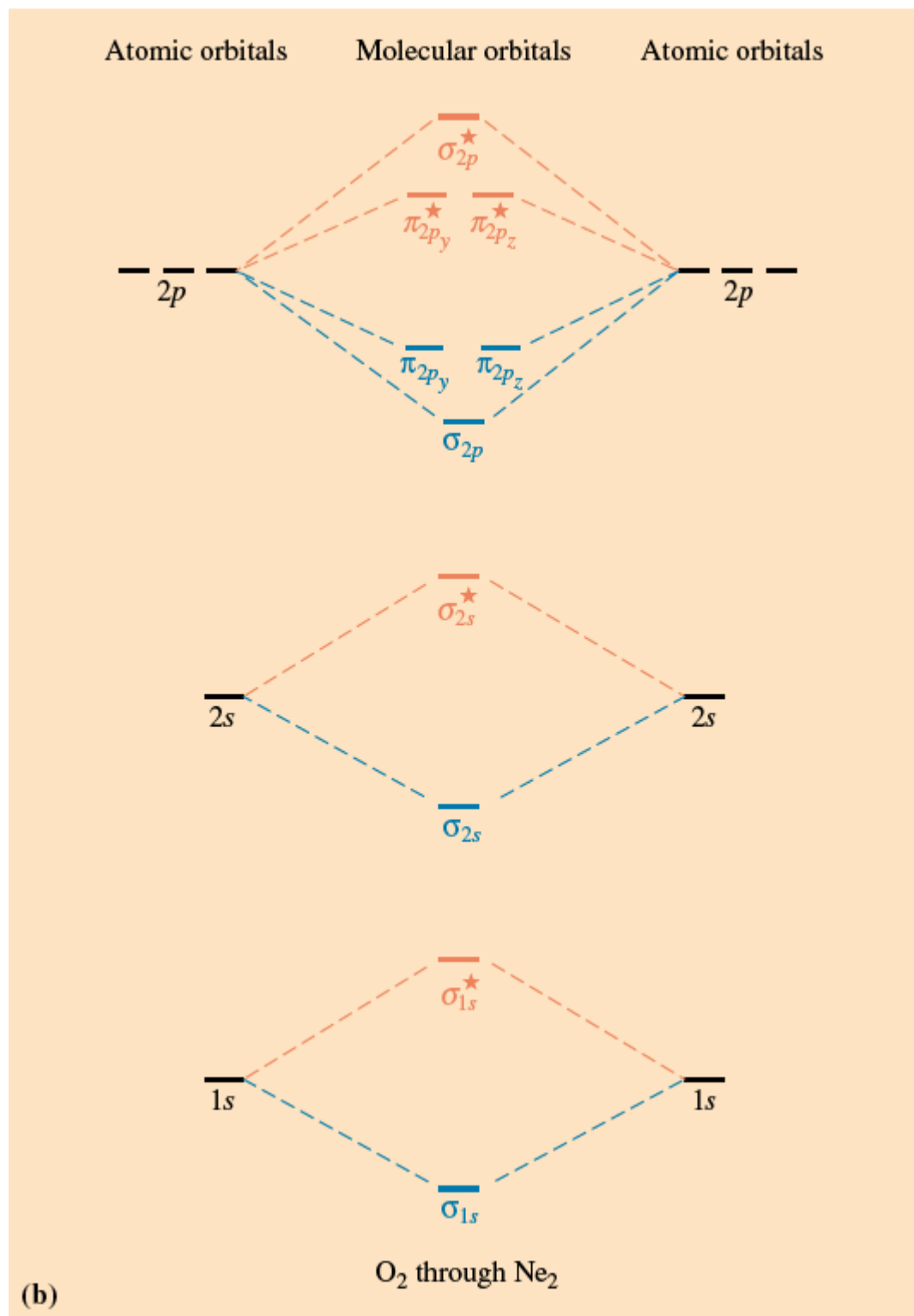

The $\Pi 2p$ and $\Pi^* 2p$ MO from overlap of one pair of 2p AO (for instance, 2p_y orbitals)

6. **The order of energy of molecular orbitals**
   In simple homonuclear diatomic molecules (H_2, He_2, Li_2, Be_2, B_2, C_2, N_2) the order is

Atomic orbitals   Molecular orbitals   Atomic orbitals

Energy (not drawn to scale) →

$\sigma_{2p}^{\star}$

$\pi_{2p_y}^{\star}$ $\pi_{2p_z}^{\star}$

$2p$ ... $2p$

σ_{2p}

π_{2p_y} π_{2p_z}

$\sigma_{2s}^{\star}$

$2s$ ... $2s$

σ_{2s}

$\sigma_{1s}^{\star}$

$1s$ ... $1s$

σ_{1s}

H_2 through N_2

(a)

($\sigma 1s$), ($\sigma^* 1s$), ($\sigma 2s$), ($\sigma^* 2s$), ($\pi 2p_y$) = ($\pi 2p_z$), ($\sigma 2p_z$), ($\pi^* 2p_y$) = ($\pi^* 2p_z$), ($\sigma^* 2p_z$)

Atomic orbitals   Molecular orbitals   Atomic orbitals

$\sigma_{2p}^{\star}$

$\pi_{2p_y}^{\star}$ $\pi_{2p_z}^{\star}$

$2p$ $2p$

π_{2p_y} π_{2p_z}

σ_{2p}

$\sigma_{2s}^{\star}$

$2s$ $2s$

σ_{2s}

$\sigma_{1s}^{\star}$

$1s$ $1s$

σ_{1s}

O_2 through Ne_2

(b)

For diatomic molecules like O_2, F_2 and hypothetical Ne_2, the order is
($\sigma 1s$), ($\sigma^* 1s$), ($\sigma 2s$), ($\sigma^* 2s$), ($\sigma 2p_x$), ($\pi 2p_y$) = ($\pi 2p_z$), ($\pi^* 2p_y$) = ($\pi 2p_z$) ($\sigma^* 2p_x$)

7. **Bond order and stability**:
   If N_b represents the number of electrons present in the BMO and N_a the number of electrons present in the ABMO.
   Then Bond Order (BO) $= \dfrac{[\text{BMO} - \text{ABMO}]}{2}$
   a. If BO > 1; i.e BMO > ABMO; then the molecule is stable
   b. If BO < 1; then the molecule is unstable
   c. If BO = 0; the molecule is unstable.
   d. For diatomic molecules, the stability is directly proportional to the bond order. Thus a molecule with a bond order 3 is more stable than a molecule with a bond order 2.
   e. Bond length is found to be inversely proportional to the bond order. Greater the bond order, shorter is the bond length.
8. **Diamagnetic and paramagnetic nature of the molecules**
   If all the electrons in the molecule are paired, it is diamagnetic in nature.
   On the other hand, if the molecule has some unpaired electrons, it is paramagnetic in nature.

Molecular orbital diagrams of homonuclear diatomic molecules

1. **H₂**
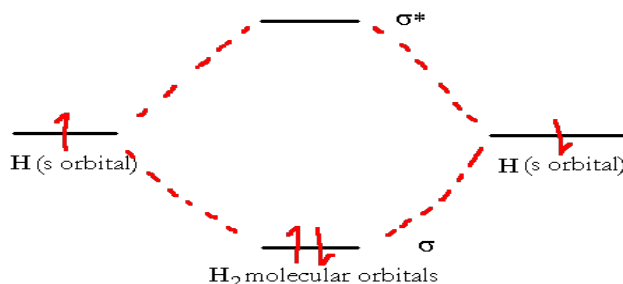
➤ The Molecule H_2 has an electron configuration $(\sigma_{1s})^2$.
➤ Bond order = [bonding electrons-Anti-bonding electrons]/2 = 2/2 = 1.

2. **He₂**
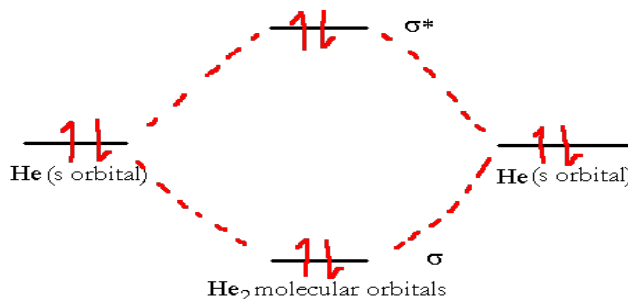
➤ The MO electronic configuration is $(\sigma_{1s})^2(\sigma^*_{1s})^2$, i.e., one bonding orbital having 2 electrons and one antibonding orbital having 2 electrons.
➤ Bond order = [2-2]/2 = 0
➤ Thus the He₂ molecule does not exist.

3. **B₂**
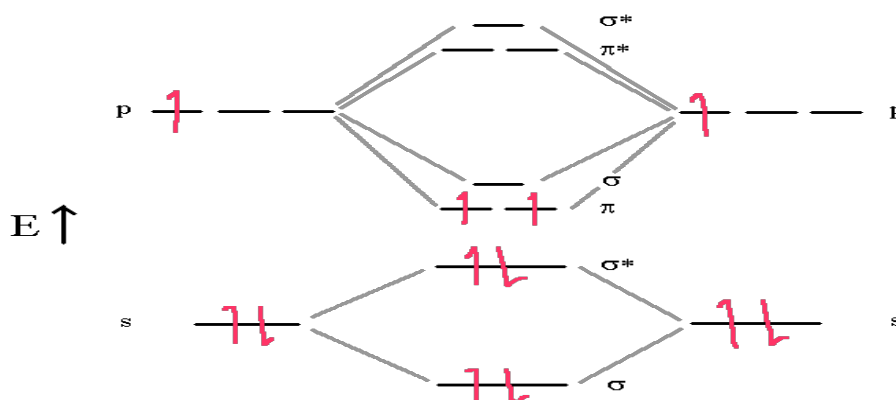
- Atomic Number of B = 5; Number of electrons in Boron molecule = 10
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^*1s)^2\ (\sigma 2s)^2(\sigma^*2s)^2\ [(\pi 2p_y)^1(\pi 2p_z)^1]$, **$\pi 2p$ orbitals have lower energy than $\sigma 2p_x$ orbital.**
- Since the $\pi_{2py},\ \pi_{2pz}$ orbitals are degenerate (identical energy) Hund's rule applies and each orbital is singly filled.
- The inner shell does not participate in bonding. Stability occurs due to filling of π_{2p} orbitals
- Bond order = [6-4]/2 = 1; hence B₂ exists

4. **C₂**
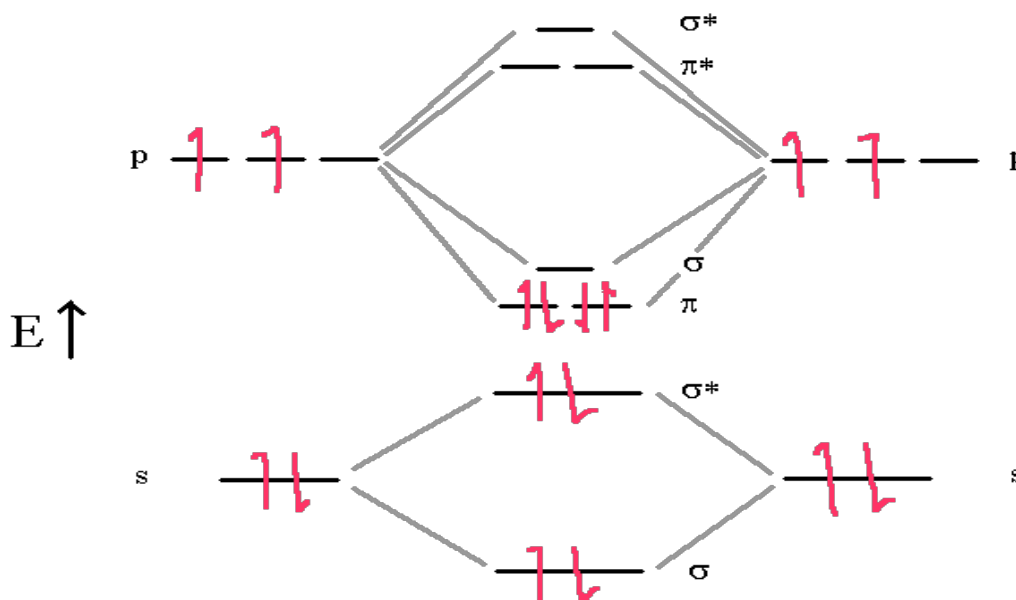
- Atomic Number of C = 6; Number of electrons in C₂ molecule = 12
- The MO electronic configuration is $(\sigma_{1s})^2(\sigma^*_{1s})^2\ (\sigma_{2s})^2(\sigma^*_{2s})^2\ [(\pi_{2py})^2(\pi_{2pz})^2]$
- Bond order = [8-4]/2 = 2; hence C₂ exists

5. **N_2**
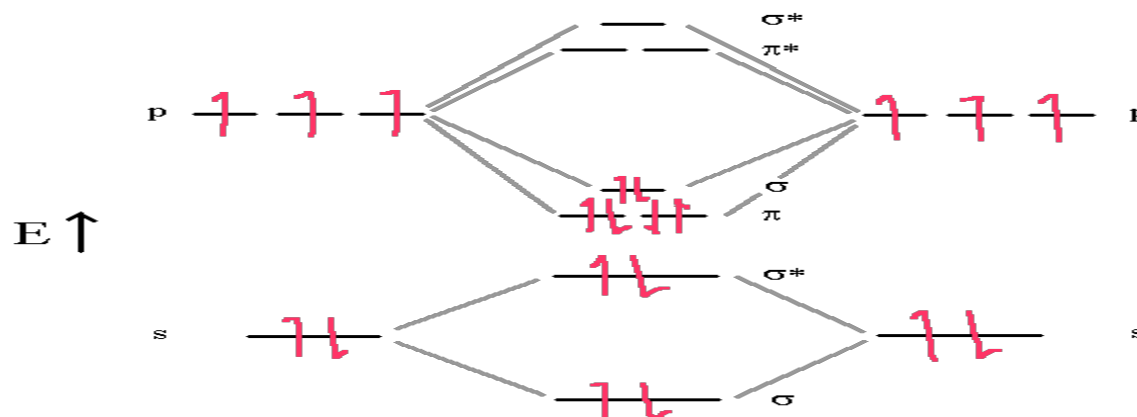
- Atomic Number of N = 7; Number of electrons in N_2 molecule = 14
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2 (\sigma 2s)^2(\sigma^* 2s)^2 [(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2$
- The inner shell do not participate in bonding, the bonding and antibonding 2s orbitals cancel each other, so only one $\sigma 2p_x$ and 2 $\pi 2p$ orbitals remain giving a
- Bond order = [10-4]/2 = 3; hence 3 bonds exist in N_2 molecule

O_2
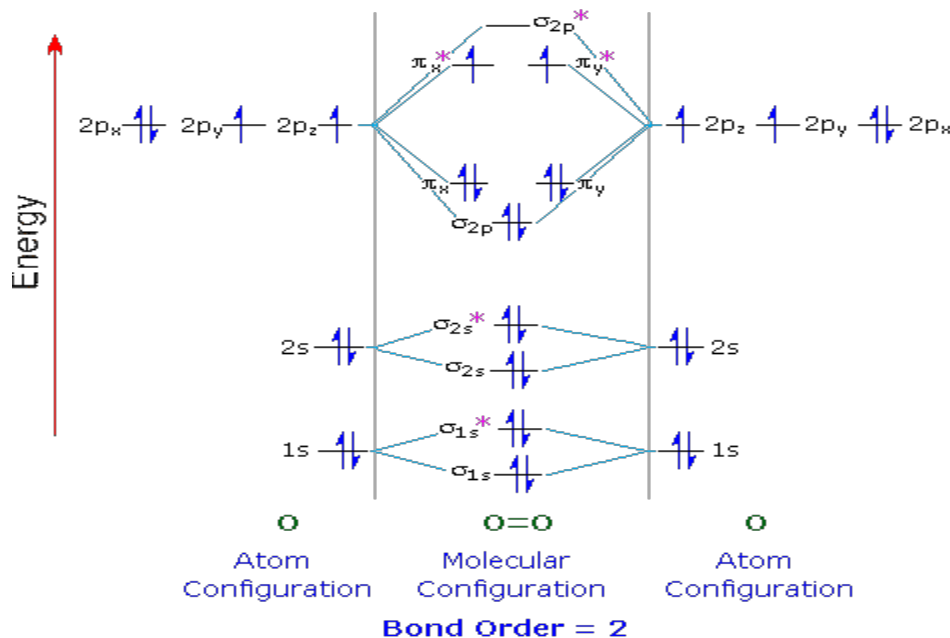
- Atomic Number of O = 8; Number of electrons in O_2 molecule = 16
- The MO electronic configuration is

$(\sigma 1s)^2(\sigma^*1s)^2 \; (\sigma 2s)^2(\sigma^*2s)^2 \; [(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2[(\pi^*2p_y)^1(\pi^*2p_z)^1]$
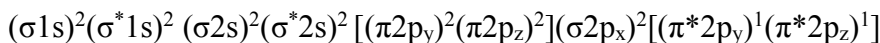
➢ The antibonding π^*_{2py} and π^*_{2pz} orbitals are singly occupied in accordance to Hund's rule.

➢ Unpaired electrons give rise to paramagnetism. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic.

➢ Bond order = [10-6]/2 = 2; hence a double bonds exist in O_2 molecule

Molecular Orbitals for First- and Second-Period (Row) Diatomic Molecules[a]

	H_2	He_2[c]	Li_2[b]	Be_2[c]	B_2[b]	C_2[b]	N_2		O_2	F_2	Ne_2[c]
Paramagnetic?	no	no	no	no	yes	no	no		yes	no	no
Bond order	1	0	1	0	1	2	3		2	1	0
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09		1.21	1.43	—
Observed bond energy (kJ/mol)	436	—	110	9	≈270	602	945		498	155	—

[a]Electron distribution in molecular orbitals, bond order, bond length, and bond energy of homonuclear diatomic molecules of the first- and second-period elements. Note that nitrogen molecules, N_2, have the highest bond energies listed; they have a bond order of three. The species C_2 and O_2, with a bond order of two, have the next highest bond energies.

[b]Exists only in the vapor state at elevated temperatures.

Mixing of Molecular Orbitals

Molecular Orbitals of similar but unequal energies can interact or mix provided they have similar symmetry.

This phenomenon is observed for Be, B, C, N where the energy difference between the 2s and $2p_x$ atomic orbitals is very less.

The $\sigma2s$ and $\sigma2p_x$ MO mix as a result of which the final energy level of $\sigma2s$ is lowered while that for $\sigma2p_x$ is raised. Similarly, after mixing of $\sigma*2s$ and $\sigma*2p_x$ MO, the final energy of $\sigma*2s$ is lowered and that for $\sigma*2p_x$ is raised. The $\pi2p_y$ and $\pi2p_z$ MO are not involved in mixing and hence their energy levels remain the same.

The for molecules Be_2, B_2, C_2, N_2; MO thus attained after mixing are:

$(\sigma1s)(\sigma^*1s)(\sigma2s)(\sigma^*2s)\,[(\pi2p_y)(\pi2p_z)](\sigma2p_x)\,[(\pi^*2p_y)(\pi^*2p_z)](\sigma^*2p_x)$
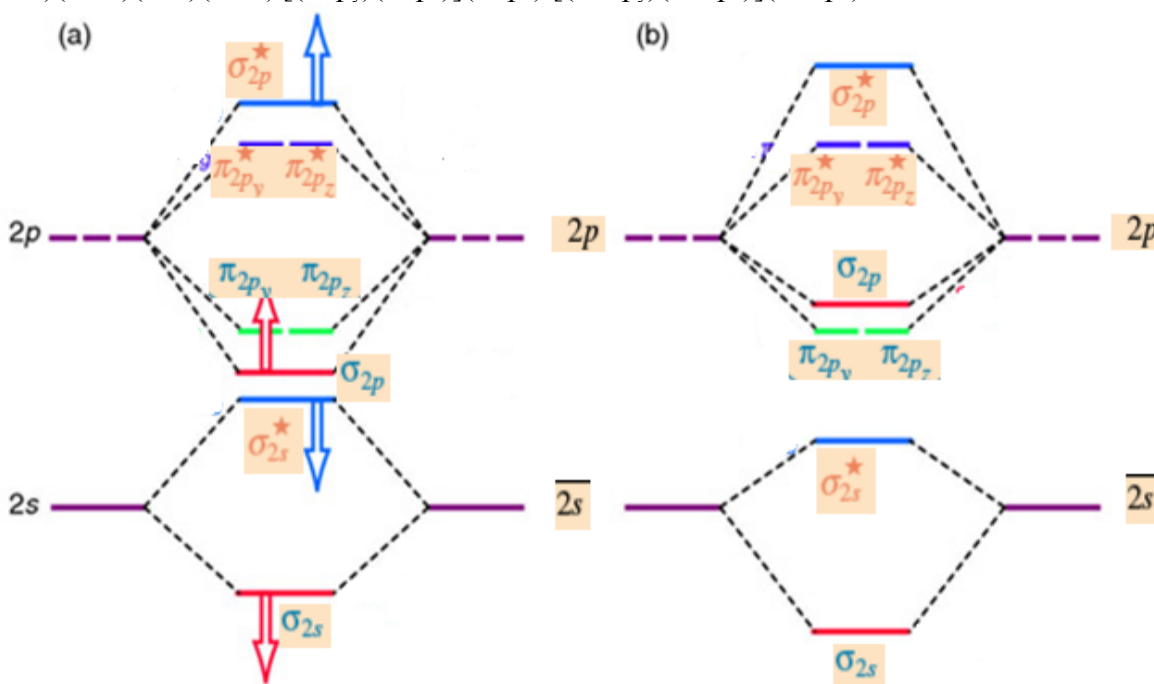

Whereas, in the case of O, F and Ne, the energy difference between the 2s and 2px atomic orbitals is very high (> 1000kJ/mol); thereby no mixing is observed between the MO and the MO levels as arranged for O_2 and F_2 are:

$\sigma1s)(\sigma^*1s)(\sigma2s)(\sigma^*2s)\,\sigma2p_x\,[(\pi2p_y)(\pi2p_z)][(\pi^*2p_y)(\pi^*2p_z)](\sigma^*2p_x)$

Molecular orbital diagrams of heteronuclear diatomic molecules

In the case of heteronuclear diatomic molecules, the same postulates of MOT are applicable during the combination between atomic orbitals from two different atoms.
But if there is a difference in electronegativity between the two involved atoms, the atom with highest electronegativity will be assigned the lower energy level.
1. **NO**
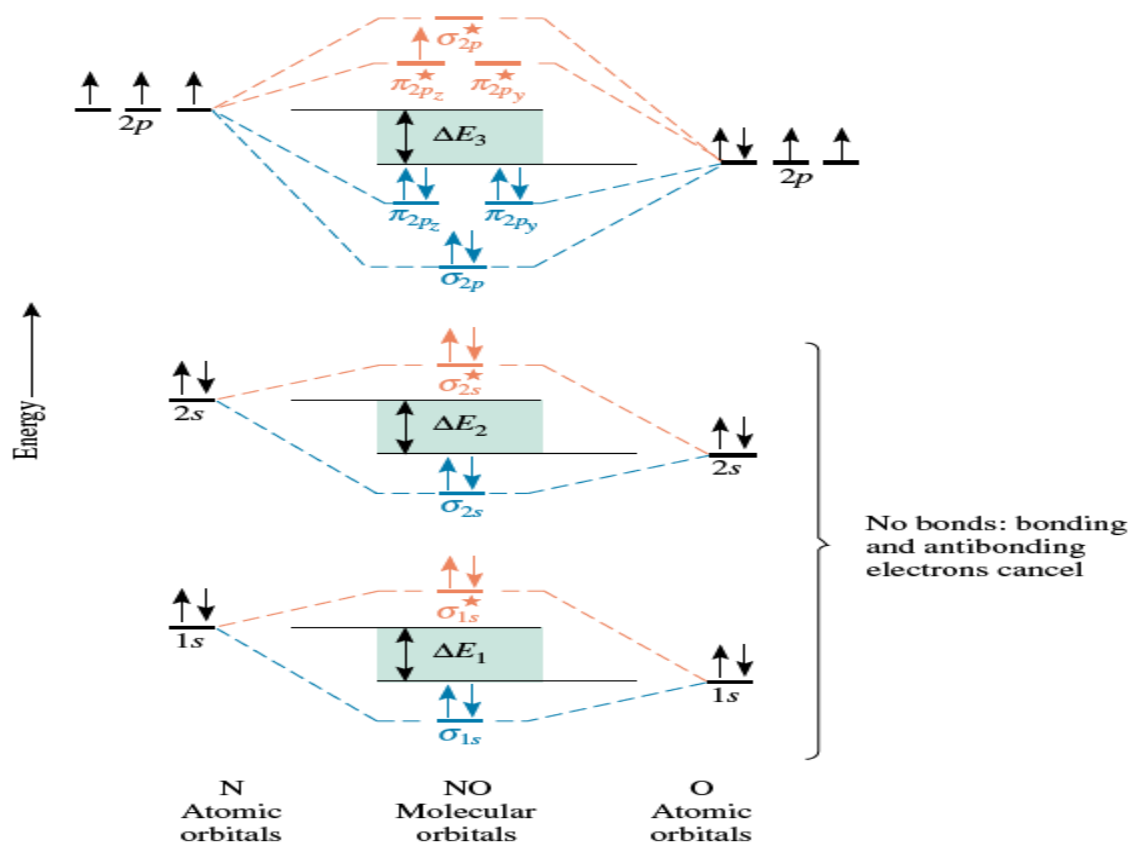
MO energy level diagram for nitrogen oxide, NO, a slightly polar heteronuclear diatomic molecule

➢ The AO of oxygen, the more electronegative element, are a little lower in energy than the corresponding AOs of nitrogen, the less electronegative element.
➢ Atomic Number of N = 7; Atomic Number of O = 8; Number of electrons in NO = 15
➢ The MO electronic configuration is
$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2 [(\pi^* 2p_y)^1 (\pi^* 2p_z)^0](\sigma^* 2p_x)$
➢ Bond order = [10-5]/2 = 2.5; hence NO is stable.
➢ NO is paramagnetic since it contains one unpaired electron.
➢ In the case of NO^+, The MO electronic configuration is:
$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2 [(\pi^* 2p_y)^0 (\pi^* 2p_z)^0](\sigma^* 2p_x)^0$
Bond order = [10-4]/2 = 3; hence NO^+ is also stable.

- ➤ NO^+ is diamagnetic since it contains no unpaired electron.
- ➤ Compared to NO, NO^+ has a higher bond order; hence it will have a lesser bond length and more stability.

2. **CO**
   - ➤ Atomic Number of C = 6; Atomic Number of O = 8; Number of electrons in CO = 14
   - ➤ The MO electronic configuration is:
     $(\sigma 1s)^2(\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2 [(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2[(\pi^*2p_y)^0(\pi^*2p_z)^0](\sigma^*2p_x)^0$
   - ➤ The AO of oxygen are a little lower in energy than the corresponding AOs of Carbon, the less electronegative element.
   - ➤ Bond order = [10-4]/2 =3; thus CO contains a triple bond.
   - ➤ CO is diamagnetic because there are no unpaired electrons.
     In the case of CO^+, the bond order calculated was 2.5, since one electron was removed from $\sigma 2p_x$, as per the MO electronic configuration: $(\sigma 1s)^2(\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2[(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^1$
Thus, it is assumed that CO^+ will have a greater bond length and hence lesser stability as compared to CO.
But experimental data of the bond length of CO^+ was found to be 1.115Å while that for CO was 1.128 Å, this reveals the more stability of CO^+ as compared to CO.
The more stability of CO^+ can happen only when the electron was released from an antibonding molecular orbital (σ^*2s). This could happen when the energy gap between the $\sigma 2s$ and σ^*2s MO is very large as seen from the MOT diagram below:
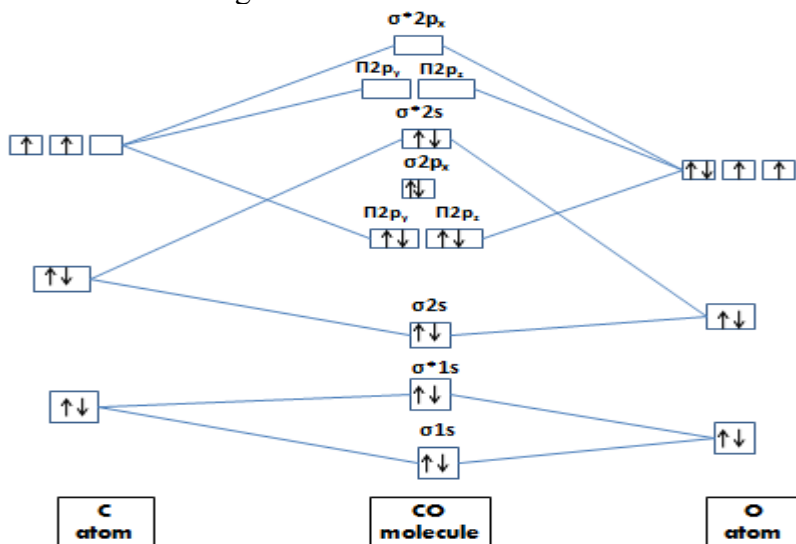
- ➤ As per the above diagram, the MOT electronic configuration of CO is:
  $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2 [(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2(\sigma^*2s)^2 [(\pi^*2p_y)^0(\pi^*2p_z)^0](\sigma^*2p_x)^0$
- ➤ The bond order thus calculated was = (10-4)/2 = 3
- ➤ Whereas, the MOT electronic configuration of CO^+ is:
  $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2 [(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2(\sigma^*2s)^1 [(\pi^*2p_y)^0(\pi^*2p_z)^0](\sigma^*2p_x)^0$
- ➤ The bond order of CO^+ thus calculated was = (10-3)/2 = 3.5
- ➤ Thus, higher bond order of CO^+ explains its higher stability as compared to CO.
- ➤ This also explains the shorter bond length of CO^+

3. **HCl**

Atomic Number of H = 1; Atomic Number of Cl = 17; Number of electrons in HCl = 18
Two atomic orbitals are capable of combining provided they have same symmetry; the extent to which they will actually combine depend upon whether their energies are comparable. It their energy levels are vastly different, they will not mix.
In HCl molecule, the 1s AO of hydrogen atom and $3p_x$ AO of chlorine are the only orbitals of comparable energy and symmetry. So these orbitals combine fairly effectively to form a bonding (σsp_x) and an antibonding molecular orbital ($\sigma^* sp_x$). The 3py and 3z orbitals are non bonding because they neither help nor hinder in bonding to a significant extent.
The 2 valence electrons occupy the bonding molecular orbital, and the antibonding molecular orbital is empty.
Bond order= 2-0/2 = 1
The HCl molecule is diamagnetic because it does not have any unpaired electrons.
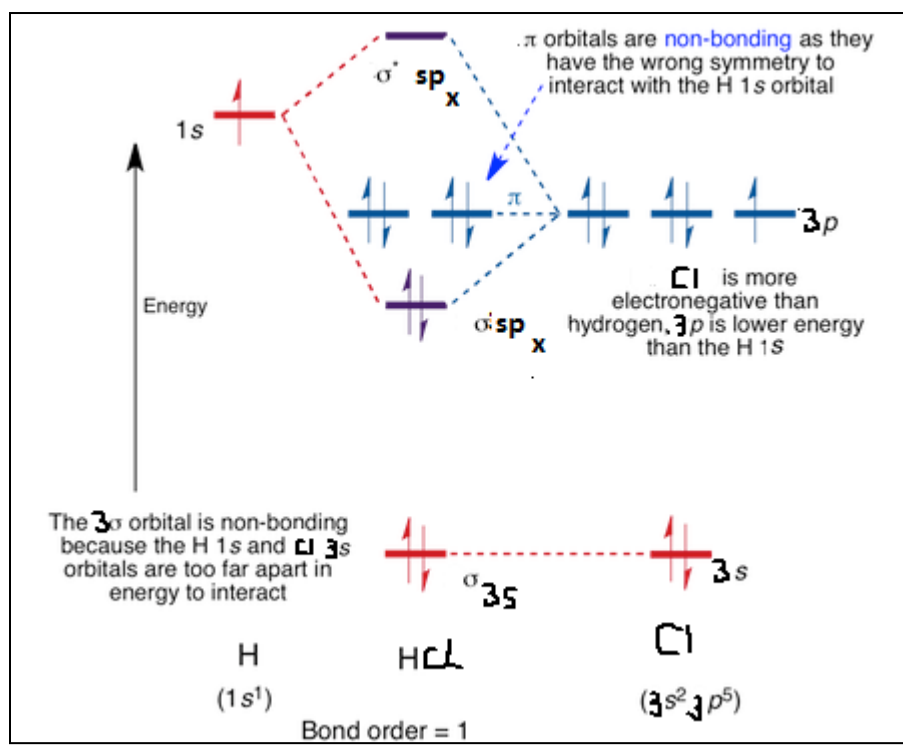
Hydrogen Bonding

The attractive electrostatic force which binds hydrogen atom (positive end) of one molecule with an electronegative atom (F, O, N) (negative end) of another molecule is known as hydrogen bond.

The strength of a hydrogen bond varies from 10-40kJ/mol while that of a covalent bond is 400kJ/mol. Thus hydrogen bond is much weaker than a covalent bond

Example of molecules exhibiting hydrogen bonding are HF, H_2O, NH_3

In HF, F atom is highly electronegative; hence it pulls the covalently bonded electron pair towards the nucleus and away from the hydrogen atom. **The hydrogen atom is then left with a partial positive charge and the F atom with a slight negative charge.** This phenomenon of charge separation makes the HF molecule polar and the molecule behaves as a dipole. The electrostatic force of attraction causes one molecule of HF to get attached to another HF molecule. This attractive force between H atom of HF molecule and F atom of another HF molecule is hydrogen bond.

hydrogen bonding in HF (dotted line shows hydrogen bonding)
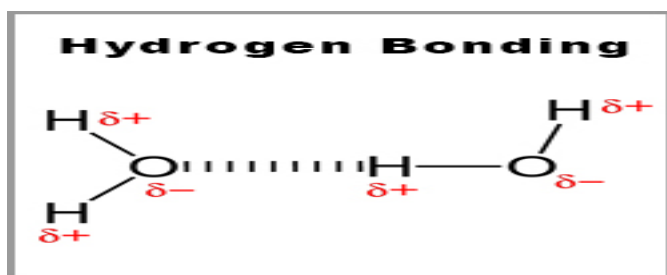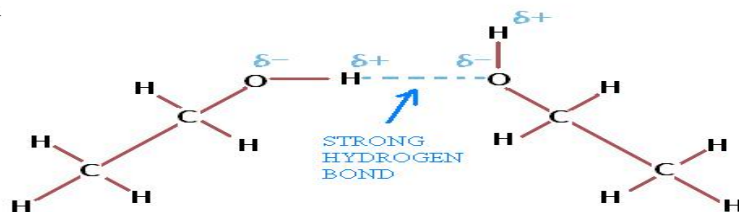

Hydrogen bonding in H_2O (dotted line shows hydrogen bonding)

H_2O molecule too exhibits hydrogen bonding because it is polar molecule and because of its bent shape, is also a dipole; Oxygen end carrying a negative charge and hydrogen end carrying a positive charge.
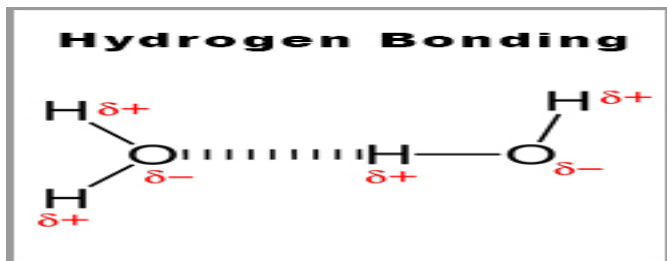
Hydrogen bond exists in alcohols and carboxylic acids.

Hydrogen bonding in alcohols (dotted line shows hydrogen bonding)

Hydrogen bonding in carboxylic acids (dotted line shows hydrogen bonding)
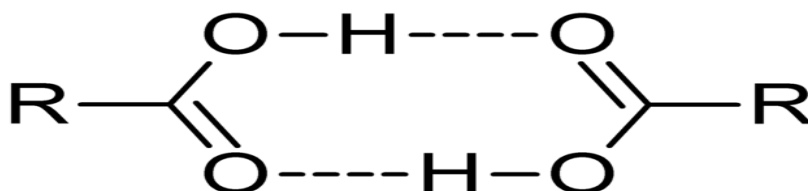
Types of hydrogen bonds

Hydrogen bonds can occur within one single molecule, between two like molecules, or between two unlike molecules.

1. **Intramolecular hydrogen bonds**:
   - Intramolecular hydrogen bonds are those which occur within one single molecule.
   - This occurs when hydrogen and an electronegative element like O, N, F is present in the same molecule.
   - Example is o-nitro phenol, o-Cl-phenol

Ortho nitrophenol   Ortho nitrobenzoic acid   Salicyldehyde (o-hydroxy benzaldehyde)

2. **Intermolecular hydrogen bonds**
   - Intermolecular hydrogen bonds occur between hydrogen atom of one molecule and an electronegative atom of another molecule of the same substance.
   - Example, NH_3, H_2O molecules alone, or between NH_3 and H_2O molecules.

(a)

p-nitro phenol

(b)

H_2O

(c)

NH₃ alone   NH₃ and H₂O
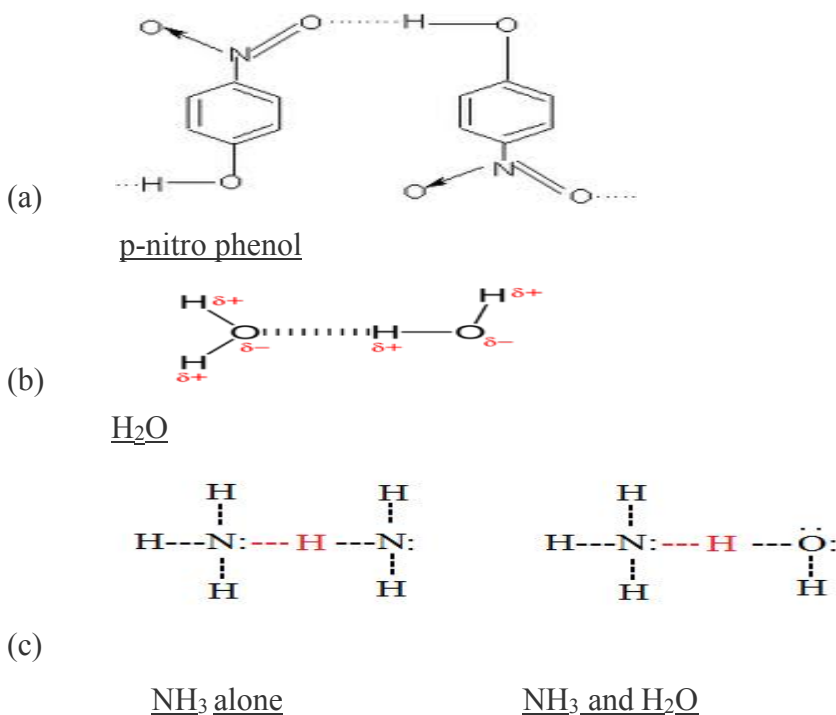
Consequences of hydrogen bonding

1. **Melting and boiling points**:

   Compounds exhibiting hydrogen bonding have strong intermolecular force of attraction and hence require high energy to break the bonds in order to separate the molecules. Consequently such molecules have high melting point and boiling point.

   Also, boiling point of liquids increases because hydrogen bonding leads to increase in intermolecular attractions which lead to increase in heat of vaporization.

   The abnormal boiling point of water is due to hydrogen bonding.

2. **Association of molecules**:

   Due to hydrogen bonding, two or more molecules of a compound get associated to form bigger units. For example, 2 molecules of carboxylic acid get associated to form a dimer.

3. **Solubility**

   The solubility of organic compounds in water is attributed to hydrogen bonding.

   For example, a. CH_3OCH_3 (dimethyl ether) is completely miscible in water but CH_3SCH_3 (dimethyl sulphide) is partially miscible. This is because dimethyl ether is capable of hydrogen bonding with H_2O molecule.

   The high solubility of sugar in water is due to hydrogen bonding.

4. **Viscosity**:

   Intermolecular hydrogen bonding increases attraction between molecules in different layers of hydrogen bonded liquids. This results in increase in viscosity. Compounds exhibiting strong hydrogen bonding are highly viscous and have high surface tension.

   Example: concentrated sulphuric acid, glycerol etc are highly viscous due to extensive hydrogen bonding

5. **Unique properties of water**:

➢ Density of water in solid state is less than that in liquid state. This is unusual because

   in most substances, density in solid state is more than in liquid state. This is due to intermolecular hydrogen bonding.

➢ Water contracts when heated between 0°C and 4°C. This is again unusual because most substances expand when heated in all temperature ranges.

➢ Water is liquid over wide temperature range (0-100°C)

➢ known as universal solvent: can dissolve many substances

➢ water has high heat of evaporation thereby sweating leads to cooling

➢ adhesion and cohesion: strong forces of attraction between molecules allows water to rise up inside plants from roots to leaves

➢ water conducts heat more easily than any other liquid except mercury

   Typical questions on hydrogen bonding

1. Melting and boiling point of para isomer is greater than that of ortho isomer. This is because in ortho isomer, intermolecular hydrogen bonding is reduced.
2. Solubility of nitro phenols in polar solvents like H_2O is para isomer > ortho isomer because para isomer shows intermolecular hydrogen bonding in water.
3. Ortho nitro phenol is more volatile than para nitro phenol because of intra molecular hydrogen bonding in o-isomer.
4. Explain why H_2O is liquid but H_2S?
   Water is liquid because it is inter-molecularly hydrogen bonded and the force of attraction is strong. H_2S is gas due to absence of hydrogen bonding and the force of attraction is less.
5. arrange the following types of interactions in order of decreasing stability: Dipole attraction, hydrogen bonding, covalent bond, Van der waal
   Covalent bond > Hydrogen bond > dipole > Van der Waal

Metallic Bonding

- The force of attraction which binds a metal atom to a number of electrons within its sphere of influence is known as metallic bond
- The attractive force that holds the atoms of two or more metals together in a metal crystal or in an alloy is known as metallic bond.
- Characteristics of metals:
  1. They are good conductors of heat
  2. They are good conductors of electricity.
  3. They have high density
  4. they have high melting point and high boiling point
  5. They have metallic luster
  6. they are hard and have high elasticity
  7. They have the tendency to crystallize
  8. They form alloys with other metals easily
  9. They can be drawn into wires (ductility) and can be hammered into sheets (malleability)

A. **Molecular Orbital theory in metals or Band Theory**
1. Band theory is a quantitative model of applying the MO theory to bonding in metals.
2. Postulates:
   - Each atomic orbital of two metal atoms interact giving rise to two molecular orbital.
   - Atomic orbitals combining to form MO need to have same energy and same symmetry.
   - Each MO is associated with a separate energy level and each has capacity to accommodate 2 electrons.
   - Bonding molecular orbitals result from constructive interference.
   - Antibonding molecular orbitals result from destructive interference.
   - Bonding orbitals are at a lower energy level than the antibonding MO
   - The number of molecular orbitals formed equals the number of atomic orbitals involved.
   - For every bonding molecular orbital formed, one antibonding molecular orbital is also formed.
   - For odd number of bonding atoms, a nonbonding molecular orbital is formed.
   - The molecular orbitals formed belong to the entire set of atoms
   - As the number of atoms increase in a metallic crystal, more will be the number of atomic orbitals which may overlap to give more MO each having a distinct energy level. The energy separation between any two adjacent MO energy levels would go on decreasing with increase in the number of overlapping atomic orbitals.
- Consequently if the overlapping atomic orbitals are very large, there is virtually no energy difference from one MO to the next. At this point, the MO has merged into a band of continuous energy, and this is the origin of the term band theory.
3. **Let's consider sodium metal**: The electronic configuration of Na atom is [Ne] $3s^1$.
   a. In Na_2, the 3s orbitals of the two Na atoms combine to give a bonding MO (σ3s) and an antibonding MO (σ3s*). Each sodium atom has just one $3s$ valence electron, so the lower-energy bonding orbital is filled and the higher-energy antibonding orbital is empty.

b. Suppose there are 3 Na atoms joined to form Na_3. Three 3s atomic orbitals combine to form 3 MOs-one bonding, one non bonding and one antibonding. The energy of non-bonding MO is in between that for bending and anti-bonding MO. The three valence electrons from the 3 Na toms would occupy the bonding and non-bonding MO.

c. In Na_4, 4 atomic orbitals combine to form four MOs- two bonding and two anti-bonding. The 4 valence electrons would occupy the two lowest bonding MOs.
   Thus half of the total number of MO is vacant.

d. As the number of atoms increase, the spacing between the energy levels of various orbitals decrease. And when the number of atoms is very large, the energy levels of the orbitals are so close that a band of closely spaced MO is formed. This band which is half full with valence electrons and constituting the bonding MO is called the valence band (VB). The anti-bonding MO constituting the other half of the band and which is empty is called the conduction band (CB).
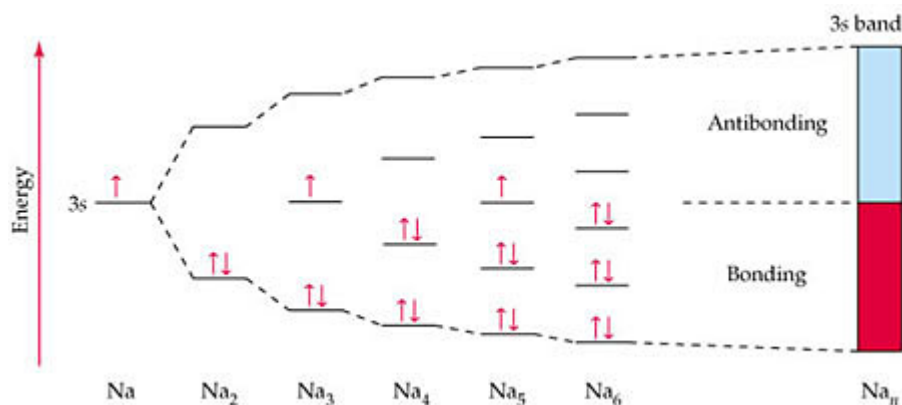
➤ In the case of Na metal, the gap between the valence band and conduction band is negligible and the band is half filled, slight excitation can move the valence electrons from valence band to conduction band. Hence sodium metal has high thermal and electrical conductivity.

4. Band theory helps to explain the properties of metals but also helps to classify metals into 3 categories: conductors, insulators and semi-conductors depending on the energy gap between the valence and conduction band.
   a. Conductors: Either the valence band and conduction band overlap (Magnesium metal) or there is half filled valence band (sodium metal).
   b. Insulator: there is large gap between the filled valence band and empty conduction band (diamond). There is hence no electron movement of electrons from valence band to conduction band.
   c. Semiconductors: when there is a small gap between the valence band and conduction band (Si or Ge) sufficient to promote an electron from VB to CB thereby contributing to conductivity.
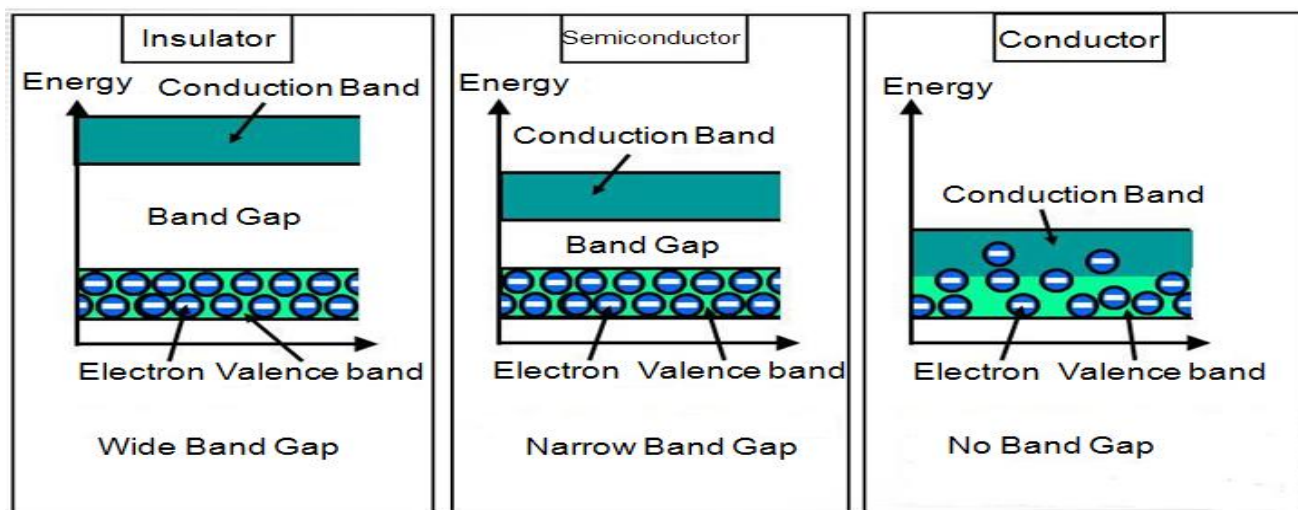
Semiconductors are of two types:

Intrinsic semiconductors

Intrinsic semiconductors are basically insulators at zero temperatures, but their conductivity increases with increase in temperature.

Extrinsic semiconductors

Semiconductors are produced by doping an insulator with a suitable impurity. Such types are called as extrinsic semiconductors. These are of two types: n-type and p-type semiconductor.

Let us take our well-known silicon as an example. We know that silicon is covalently bonded with four silicon atoms. It suggests that there are no free electrons available for conduction [A].

n-type doping

Group 15 elements in the periodic table are, in general, considered for n-type doping. Typically, Phosphorous, Arsenic and Antimony are the elements from group V [B]. They have five electrons in the outermost shell and if it replaces an intrinsic silicon atom, one electron will remain as excess. Such kind of elements are called Donors. This excess (additional) electron is loosely bounded, and therefore it behaves more like a free-electron. In the band diagram, the energy levels of these donor atoms lie in the forbidden gap, slightly below the conduction band of intrinsic semiconductor.

p-type doping

Group 13 of periodic table elements is suitable for p-type doping. They are Boron, Gallium and Indium so on. The outermost shell contains three electrons, if such elements replace a Silicon atom;

one bonding remains vacant. Hence the dopant is ready to accept one electron and thus called an Acceptor [C]. The Acceptor energy level are close to valence band.