

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:

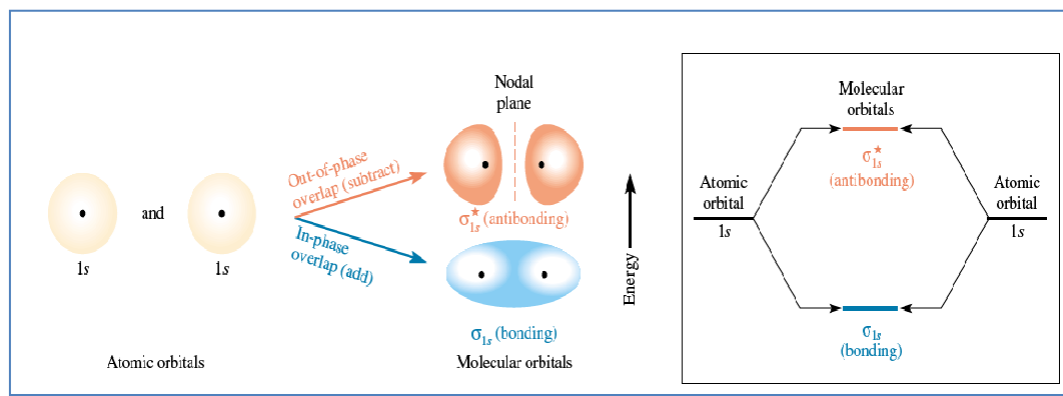
- Orbitals of lowest energy are filled up first.
- Each orbital will hold a maximum of two electrons, provided that they have opposite signs.

Pauli Exclusion Principle

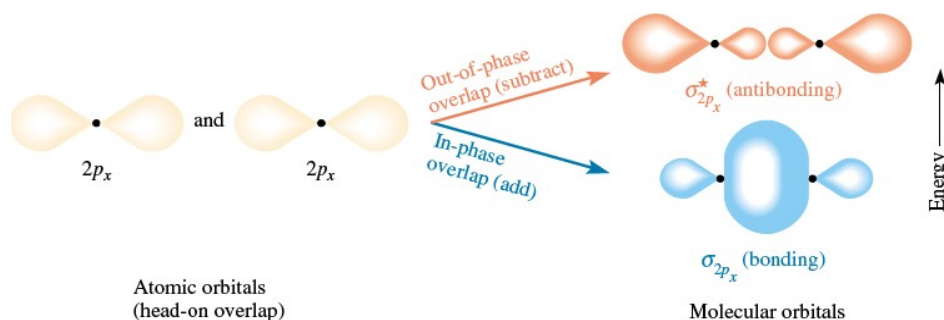
- in a given atom, no two electrons can have all four quantum numbers the same.
- when applied for MO, the principle states that no two electrons in the same molecule can have all four quantum numbers the same.

Hund's rule:

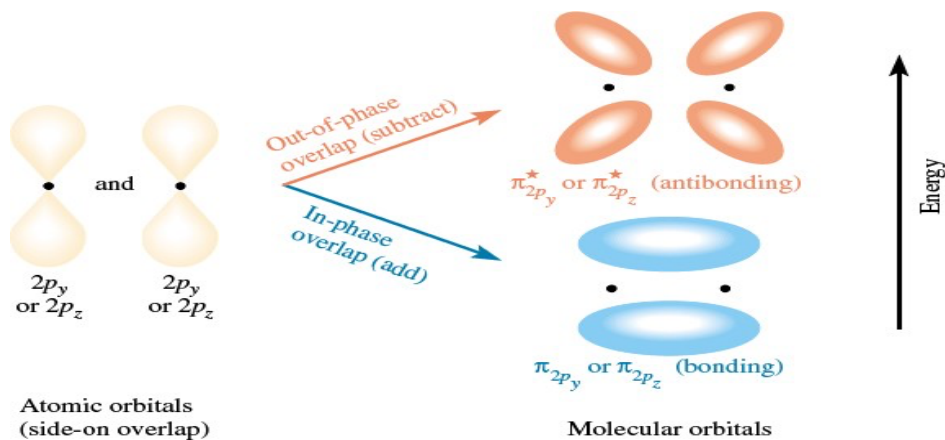
- Several orbitals have the same energy (degenerate orbitals of d, f)
- Electrons will be arranged so as to give maximum number of unpaired spins.



(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.



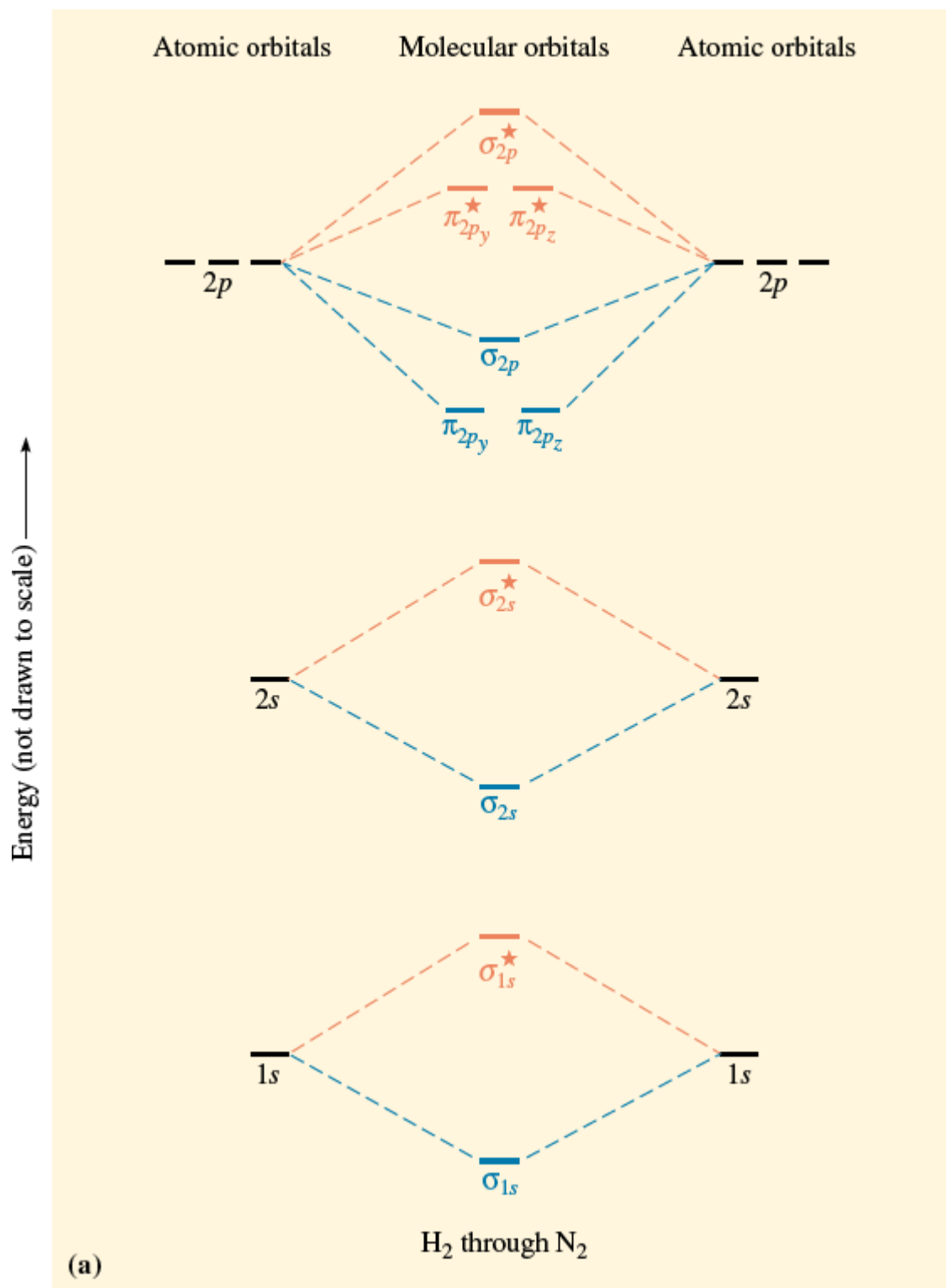
Production of σ_{p_x} and $\sigma^*_{p_x}$ MO by overlap of σ_{p_x} AO on two atoms.



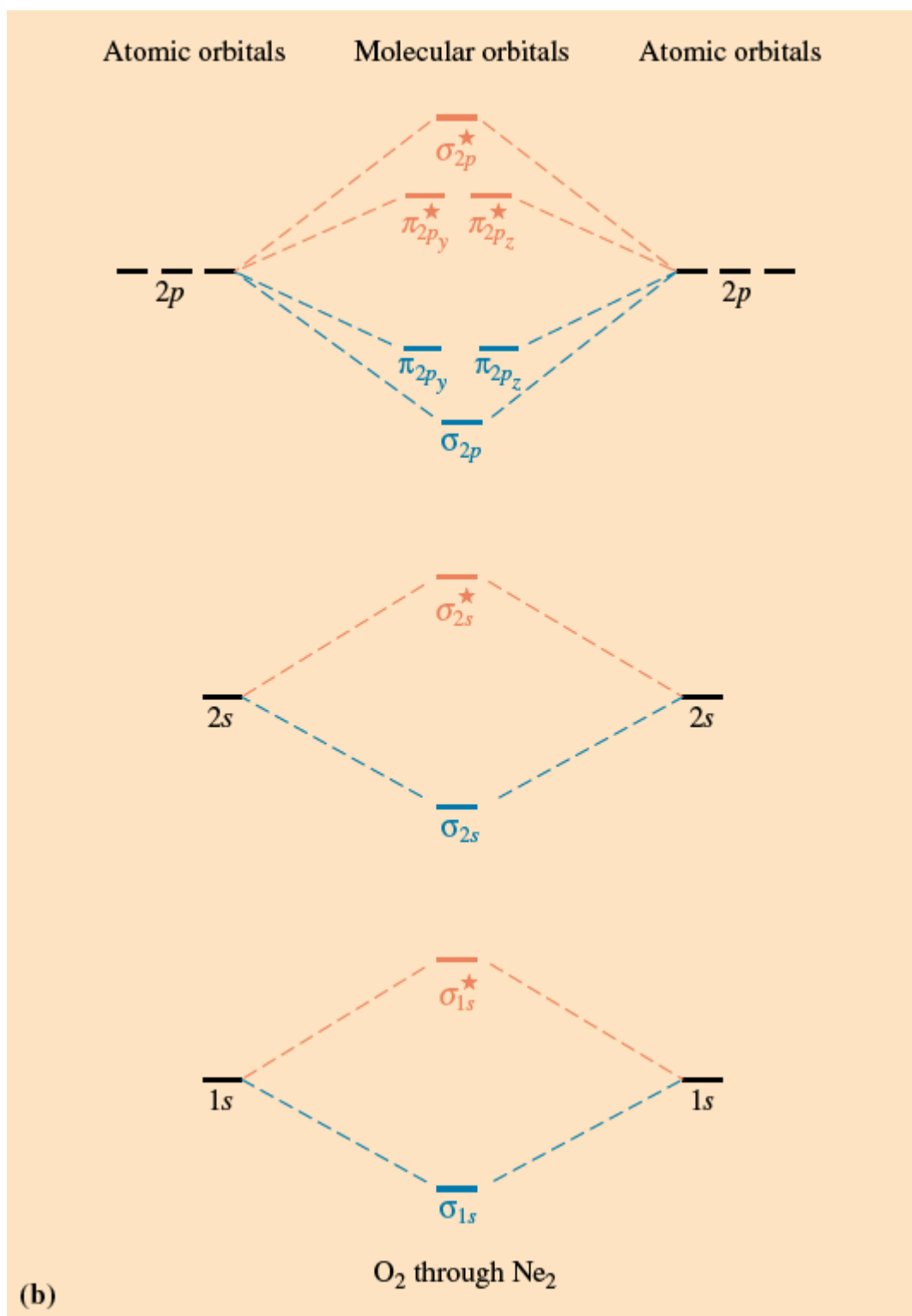
The Π_{2p} and Π^*_{2p} MO from overlap of one pair of $2p$ AO (for instance, $2p_y$ orbitals)

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



$(\sigma_{1s}), (\sigma_{1s}^*), (\sigma_{2s}), (\sigma_{2s}^*), (\pi_{2p_y}) = (\pi_{2p_z}), (\sigma_{2p}), (\pi_{2p_y}^*) = (\pi_{2p_z}^*), (\sigma_{2p}^*)$



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.

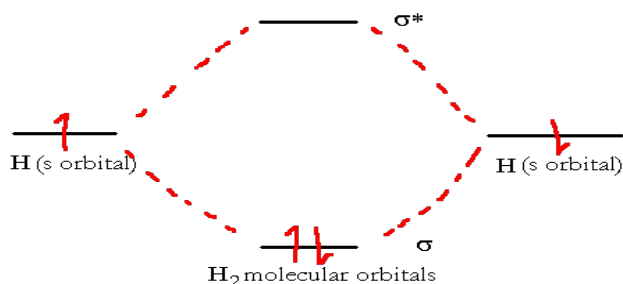
Then Bond Order (BO) $\equiv \frac{N_b - N_a}{2}$

- If $BO > 1$; i.e. $BMO > ABMO$; then the molecule is stable
- If $BO < 1$; then the molecule is unstable
- If $BO = 0$; the molecule is unstable.
- 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.
- Bond length is found to be inversely proportional to the bond order. Greater the bond order, shorter is the bond length.

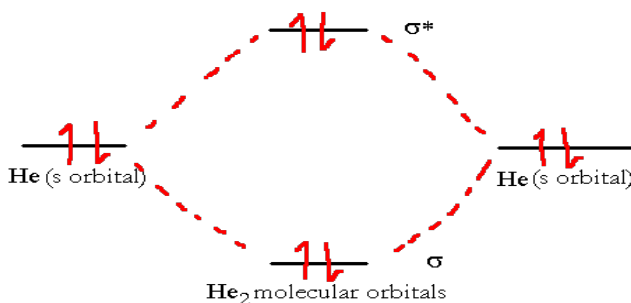
8. Diamagnetic and paramagnetic nature of the molecules

If all the electrons in the molecule are paired, it is diamagnetic in nature.

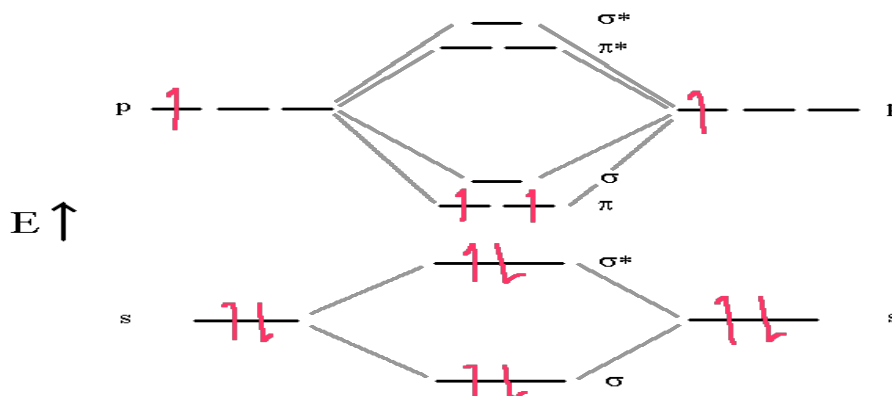
On the other hand, if the molecule has some unpaired electrons, it is paramagnetic in nature.

Molecular orbital diagrams of homonuclear diatomic molecules**1. H_2** 

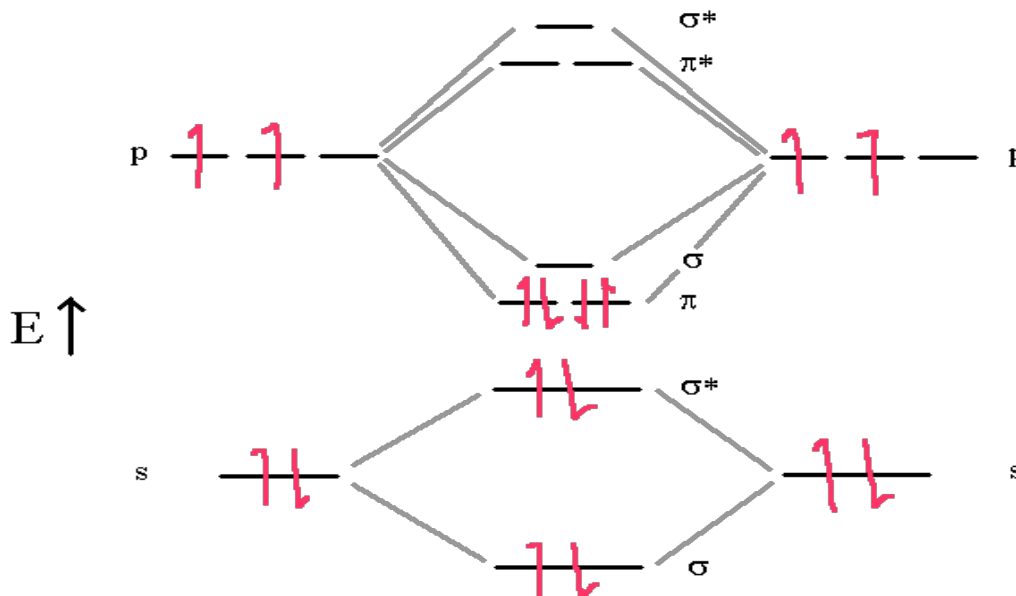
- The Molecule H_2 has an electron configuration $(\sigma_{1s})^2$.
- Bond order = $[\text{bonding electrons} - \text{Anti-bonding electrons}] / 2 = 2 / 2 = 1$.

2. He_2 

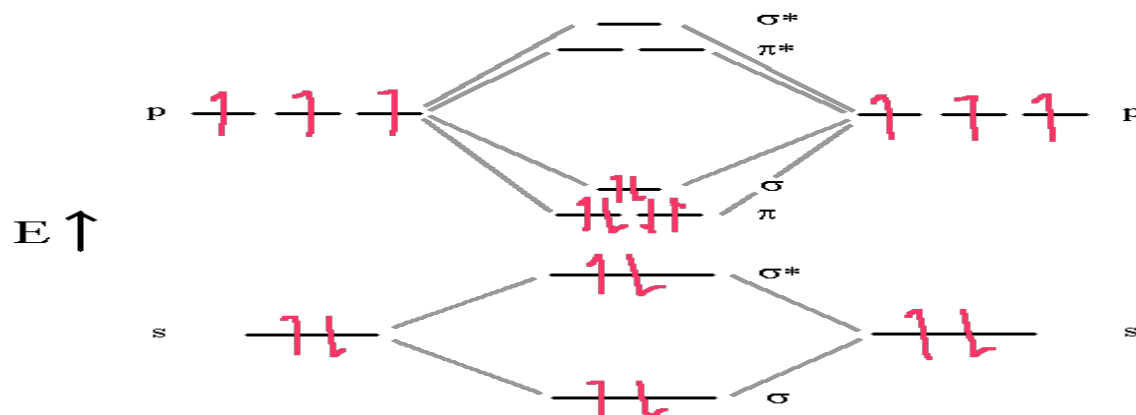
- The MO electronic configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^2$, i.e., one bonding orbital having 2 electrons and one antibonding orbital having 2 electrons.
- Bond order = $[2 - 2] / 2 = 0$
- Thus the He_2 molecule does not exist.

3. B_2 

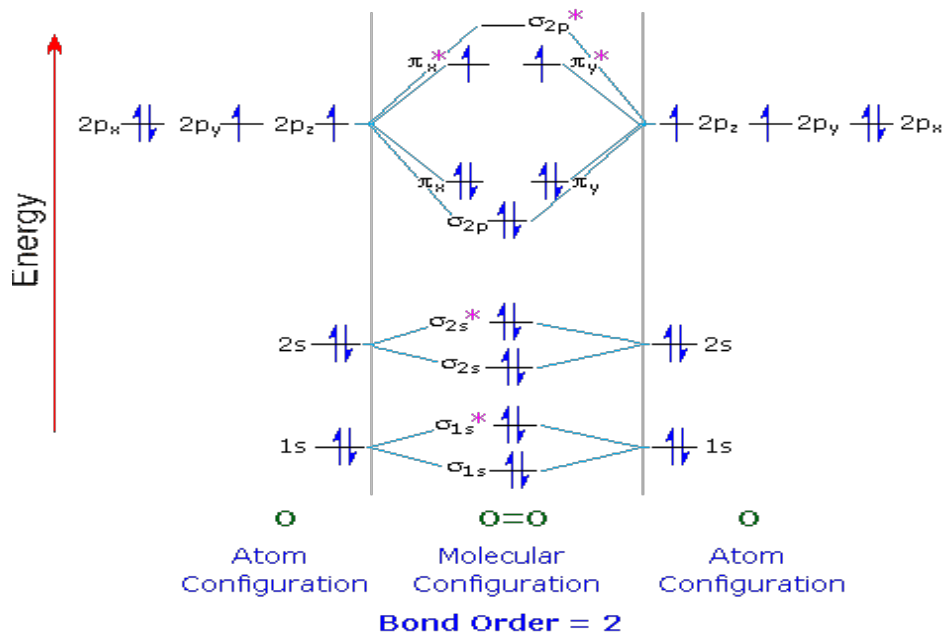
- Atomic Number of B = 5; Number of electrons in Boron molecule = 10
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2[(\pi 2p_y)^1(\pi 2p_z)^1]$, **$\pi 2p$ orbitals have lower energy than $\sigma 2p_x$ orbital.**
- Since the π_{2py} , π_{2pz} orbitals are 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 B_2 exists

4. C_2 

- Atomic Number of C = 6; Number of electrons in C_2 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 C_2 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
Increasing energy (not to scale)											
σ_{2p}^*	—	—	—	—	—	—	—		—	—	$\uparrow\downarrow$
$\pi_{2p_y}^*, \pi_{2p_z}^*$	—	—	—	—	—	—	—		$\uparrow\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2p}	—	—	—	—	$\uparrow\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	π_{2p_y}, π_{2p_z}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
π_{2p_y}, π_{2p_z}	—	—	—	—	$\uparrow\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2p}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}^*	—	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{1s}^*	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{1s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
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	—

^aElectron 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.

^bExists only in the vapor state at elevated temperatures.

Mixing of Molecular Orbitals

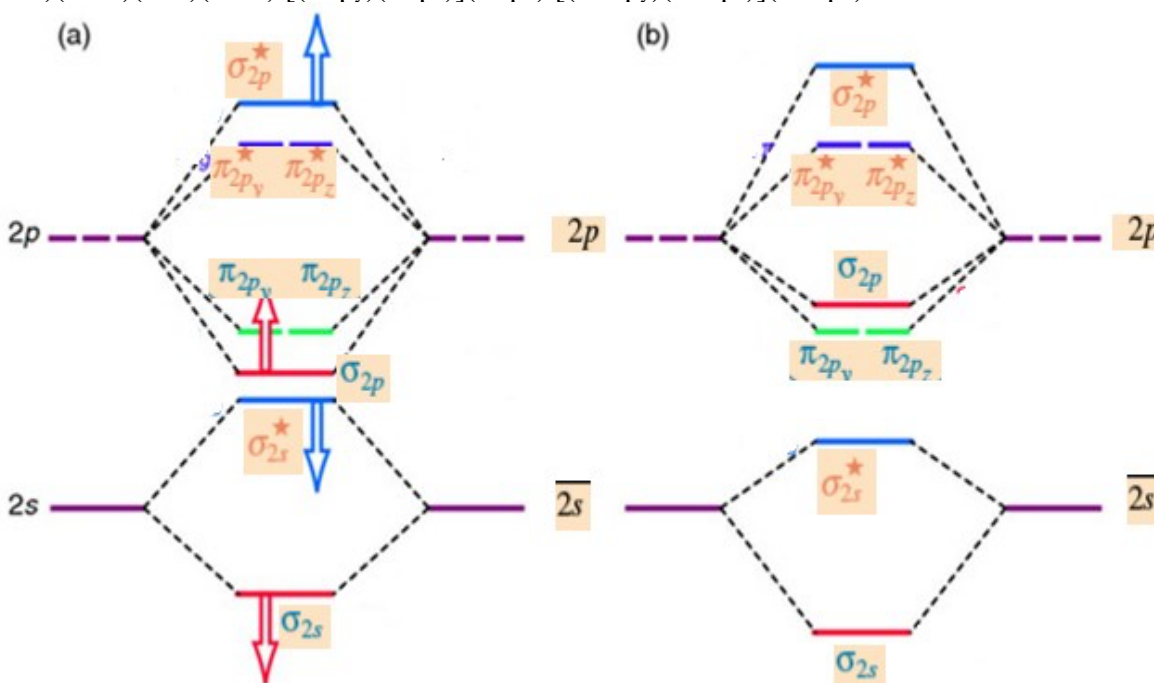
Molecular Orbitals of similar but unequal energies can interact or mix provided they have similar symmetry.

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 σ_{2s} and σ_{2p_x} MO mix as a result of which the final energy level of σ_{2s} is lowered while that for σ_{2p_x} is raised. Similarly, after mixing of σ^*_{2s} and $\sigma^*_{2p_x}$ MO, the final energy of σ^*_{2s} is lowered and that for $\sigma^*_{2p_x}$ is raised. The π_{2p_y} and π_{2p_z} MO are not involved in mixing and hence their energy levels remain the same.

The for molecules Be₂, B₂, C₂, N₂; MO thus attained after mixing are:

$(\sigma 1s)(\sigma^* 1s)(\sigma 2s)(\sigma^* 2s) [(\pi 2p_y)(\pi 2p_z)](\sigma 2p_x) [(\pi^* 2p_y)(\pi^* 2p_z)](\sigma^* 2p_x)$



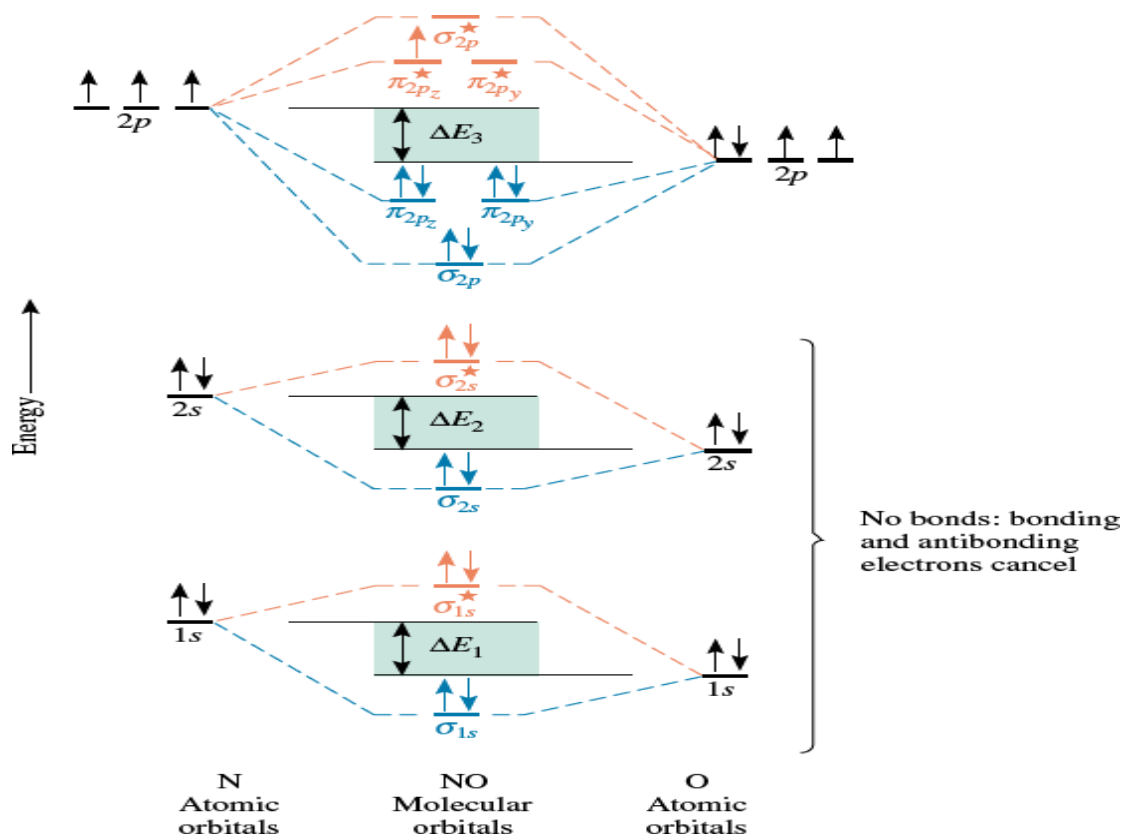
Whereas, in the case of O, F and Ne, the energy difference between the 2s and 2p_x atomic orbitals is very high (> 1000kJ/mol); thereby no mixing is observed between the MO and the MO levels as arranged for O₂ and F₂ are:

$\sigma 1s)(\sigma^* 1s)(\sigma 2s)(\sigma^* 2s) \sigma 2p_x [(\pi 2p_y)(\pi 2p_z)][(\pi^* 2p_y)(\pi^* 2p_z)](\sigma^* 2p_x)$

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.

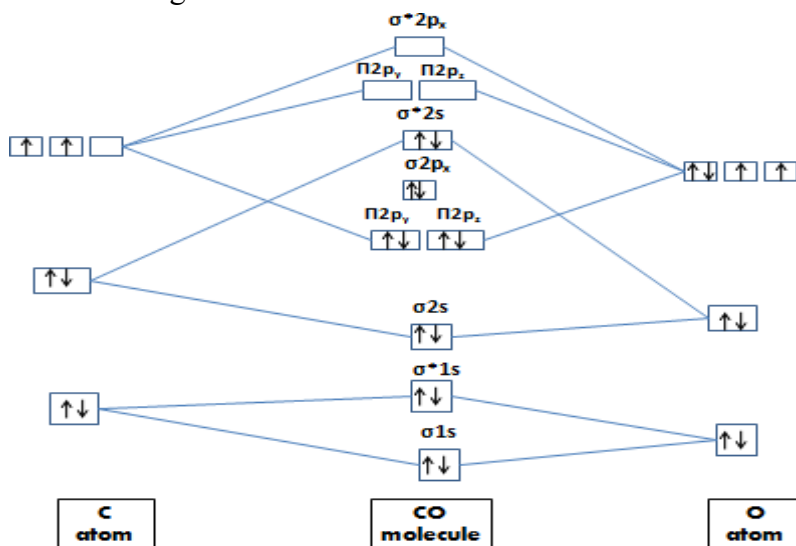
2. CO

- 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 1.115\AA while that for CO was 1.128\AA , 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 ($\sigma^* 2s$). This could happen when the energy gap between the $\sigma 2s$ and $\sigma^* 2s$ 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

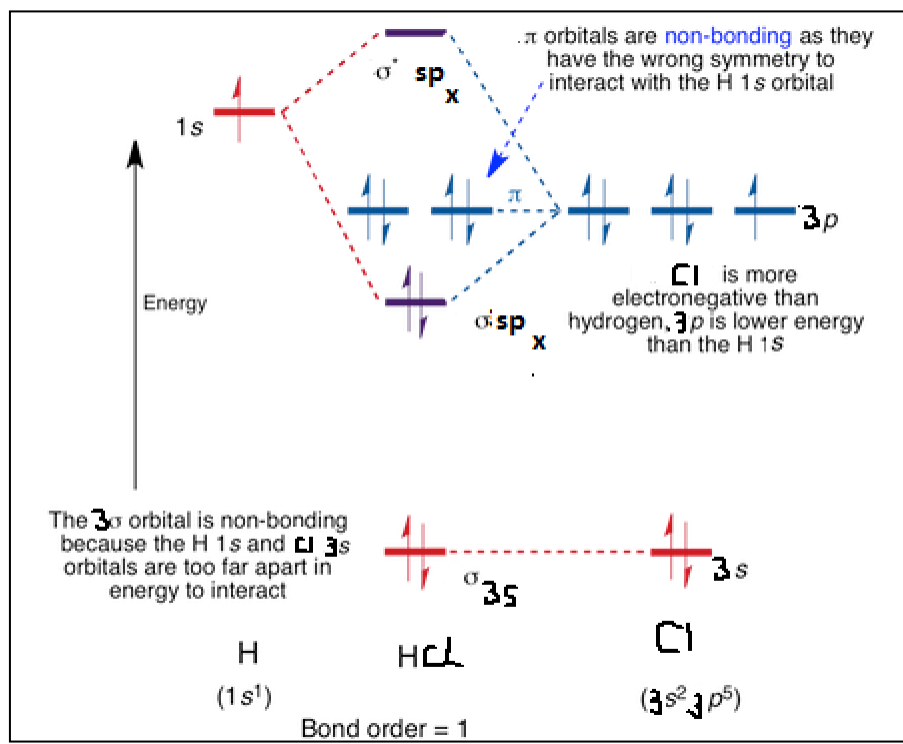
Two atomic orbitals are capable of combining provided they have same symmetry; the extent to which they will actually combine depend upon whether their energies are comparable. If their energy levels are vastly different, they will not mix.

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 (σ_{sp_x}) and an antibonding molecular orbital ($\sigma^*_{sp_x}$). The 3p_y and 3p_z 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 = $\frac{2-0}{2} = 1$

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.

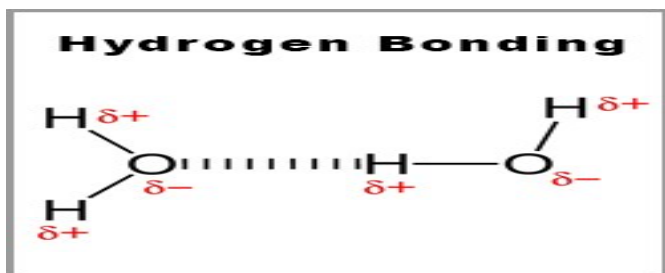
The strength of a hydrogen bond varies from 10-40kJ/mol while that of a covalent bond is 400kJ/mol.

Thus hydrogen bond is much weaker than a covalent bond

Example of molecules exhibiting hydrogen bonding are HF, H₂O, NH₃

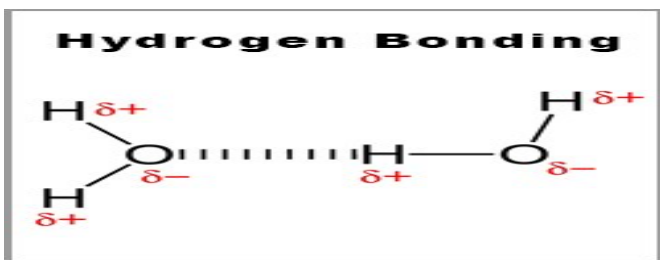
In HF, F atom is highly electronegative; hence it pulls the covalently bonded electron pair towards the nucleus and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge and the F atom with a slight negative charge. This phenomenon of charge separation makes the HF 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)

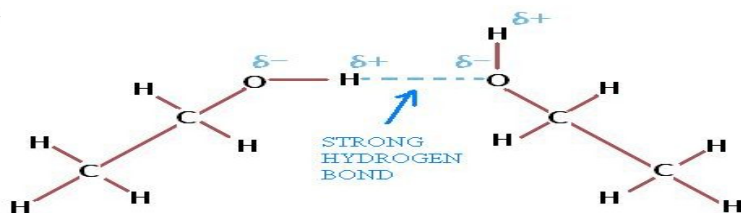
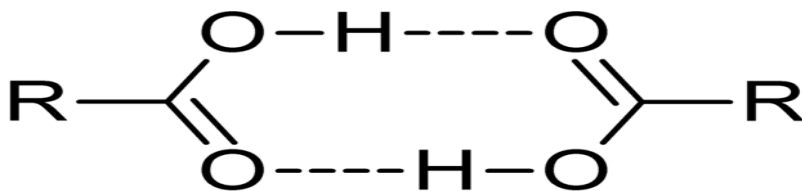


Hydrogen bonding in H₂O (dotted line shows hydrogen bonding)

H₂O 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)**Ethanol****Hydrogen bonding in carboxylic acids (dotted line shows hydrogen bonding)****Types of hydrogen bonds**

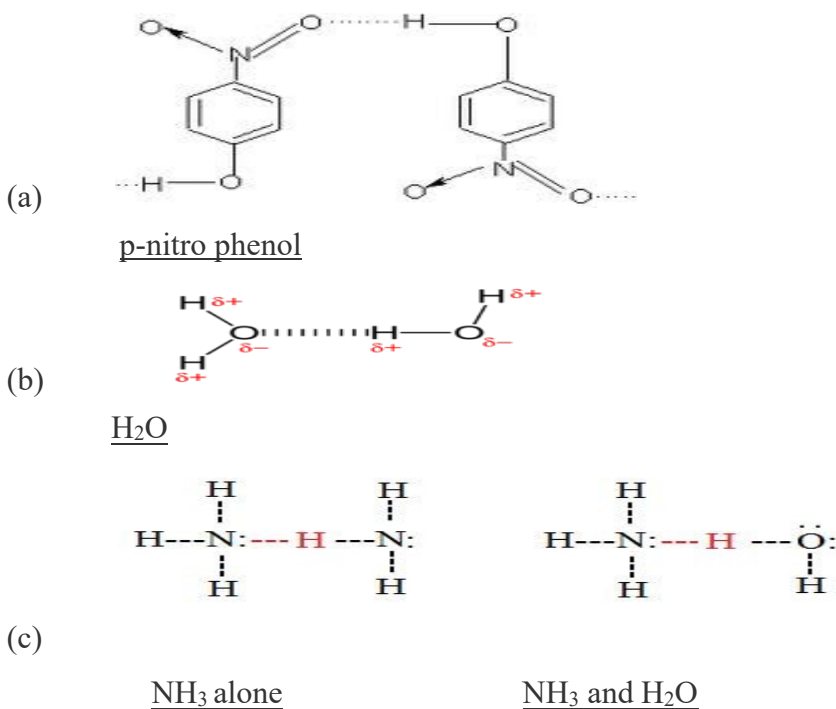
Hydrogen bonds can occur within one single molecule, between two like molecules, or between two unlike molecules.

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

**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.



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. CH₃OCH₃ (dimethyl ether) is completely miscible in water but CH₃SCH₃ (dimethyl sulphide) is partially miscible. This is because dimethyl ether is capable of hydrogen bonding with H₂O 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 H₂O 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 H₂O is liquid but H₂S?
Water is liquid because it is inter-molecularly hydrogen bonded and the force of attraction is strong. H₂S 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

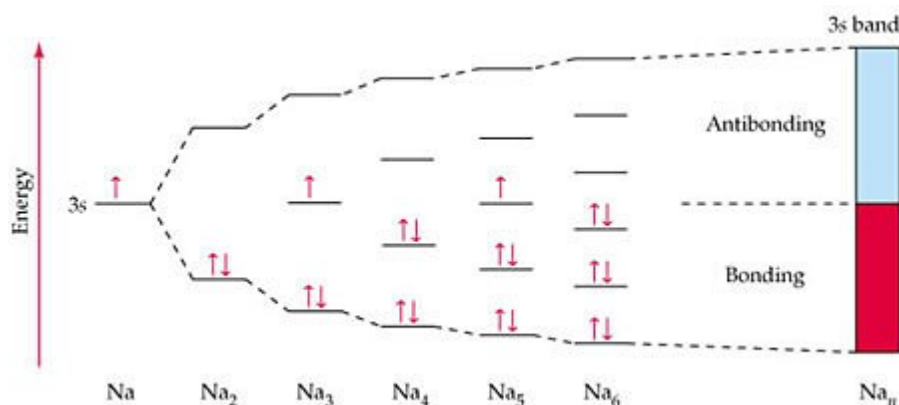
Metallic Bonding

- 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)

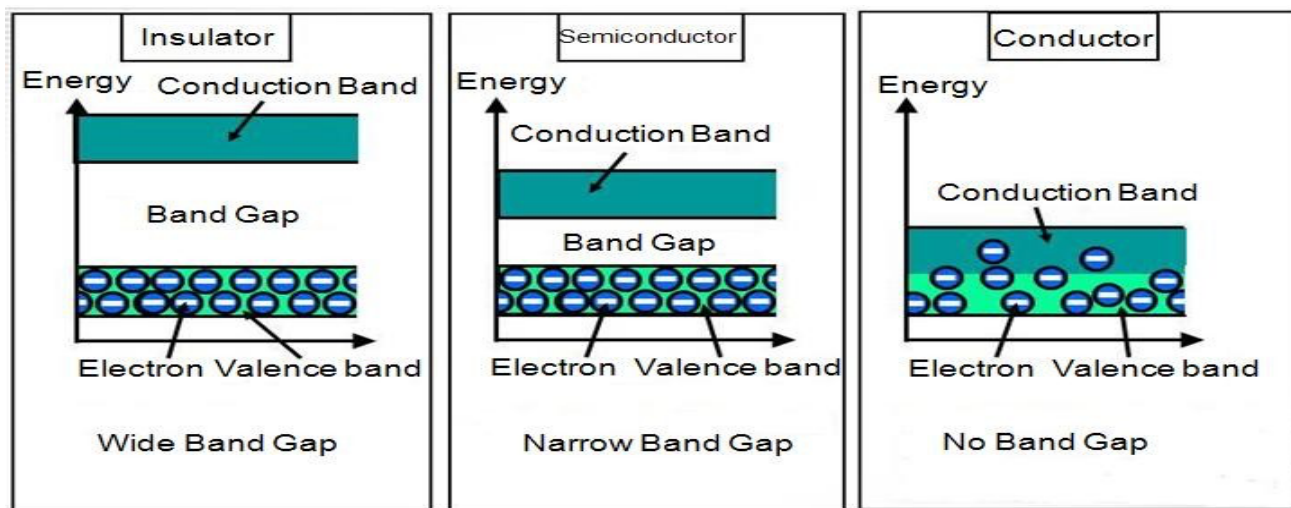
A. Molecular Orbital theory in metals or Band Theory

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 $[\text{Ne}] 3s^1$.
 - a. In Na_2 , the 3s orbitals of the two Na atoms combine to give a bonding MO ($\sigma 3s$) and an antibonding MO ($\sigma 3s^*$). 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 bonding and anti-bonding MO. The three valence electrons from the 3 Na atoms 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].

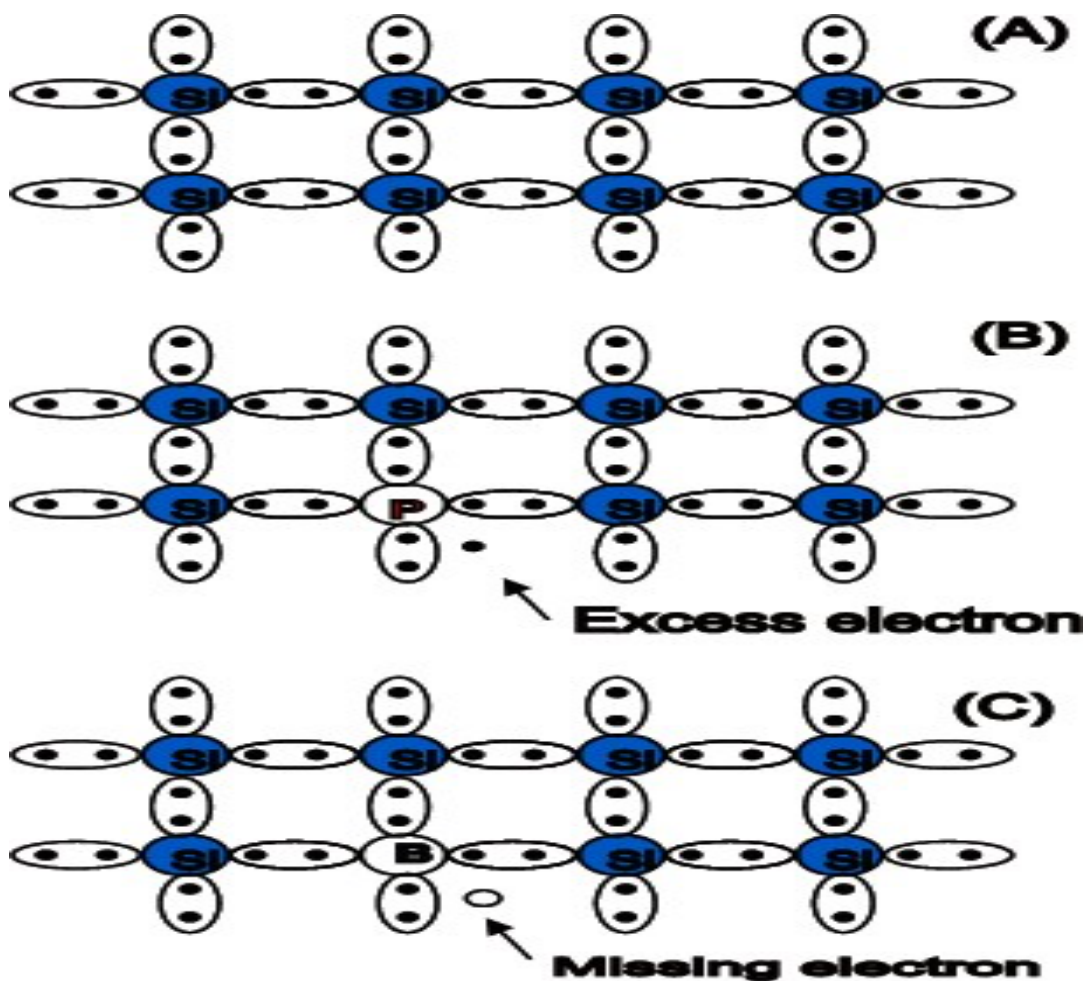
n-type doping

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.



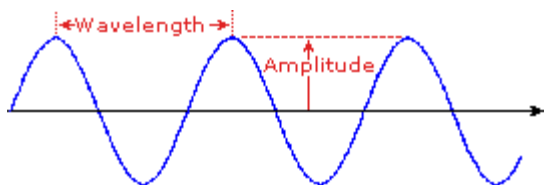
Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiation as determined by quantum mechanical selection rules. It is the study of electromagnetic radiation scattered, absorbed or emitted by molecules.

The structure of organic compounds can be determined by the study of their interaction with light (electromagnetic radiation). Spectroscopic techniques are non-destructive and generally require small amounts of sample. They help in fast analysis of sample.

Light is uniform or homogeneous in color, it is actually composed of a broad range of radiation having wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum.

Different regions of the electromagnetic spectrum provide different kinds of information as a result of such interactions. Light may be considered to have both wave-like and particle-like characteristics. Like all wave characteristics, it is characterized by a wavelength or frequency.

Wavelength is defined, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters).



- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

Frequency is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz).

Frequency and wavelength are inversely related but has a direct relationship to energy.

$$\nu = c/\lambda \quad \nu = \text{frequency}, \lambda = \text{wavelength}, c = \text{velocity of light} (c = 3 \cdot 10^{10} \text{ cm/sec})$$

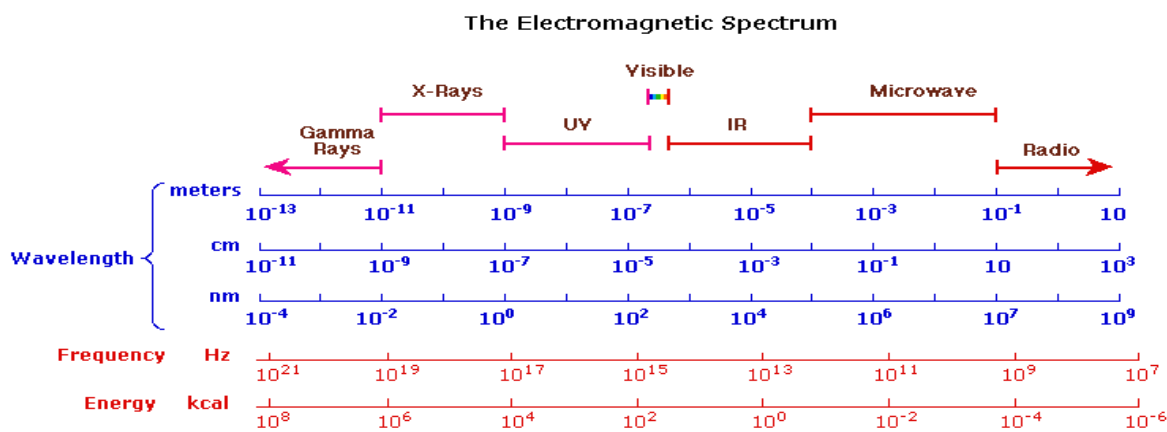
$$\Delta E = h\nu \quad E = \text{energy}, \nu = \text{frequency}, h = \text{Planck's constant} (h = 6.6 \cdot 10^{-27} \text{ erg sec})$$

Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet.

The Electromagnetic Spectrum

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the

radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This electromagnetic spectrum ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency.



$\nu = c/\lambda$ ν =frequency, λ =wavelength, c =velocity of light ($c=3 \cdot 10^{10}$ cm/sec)

$\Delta E = h\nu$ E =energy, ν =frequency, h =Planck's constant ($h=6.6 \cdot 10^{-27}$ erg sec)

Effect of electromagnetic radiation on molecules

	Wavelength (λ)		Energy	Molecular effects
	cm		kcal/mol	
higher frequency shorter wavelength	10 ⁻⁹	gamma rays	10 ⁶	ionization
	10 ⁻⁷	X rays	10 ⁴	
		vacuum UV	10 ²	
	10 ⁻⁵	near UV		electronic transitions
	10 ⁻⁴	visible	10	
	10 ⁻³	infrared (IR)	1	molecular vibrations
			10 ⁻²	
	10 ⁻¹	microwave	10 ⁻⁴	rotational motion
	10 ²			nuclear spin transitions
lower frequency longer wavelength	10 ⁴	radio	10 ⁻⁶	

Spectra	Transitions	Region of electromagnetic spectrum
Infrared	Between the vibrational energy levels	Infrared (500-4000cm ⁻¹)
UV-Vis	Between the electronic energy levels	Visible (12,500-25,000cm ⁻¹) UV (25,000 – 70,000cm ⁻¹)
NMR	Between the magnetic energy levels of nuclei	Radiofrequency

UV-Vis. Spectroscopy

- It involves transitions of electrons within a molecule from a lower to higher energy level or vice-versa by the absorption or emission of energy or radiations.
- The frequency of the radiations fall in the UV-Visible range of the electromagnetic spectrum. The Visible range is 12,500-25,000cm⁻¹ (400-750nm) and the UV region is 25,000-72,000 cm⁻¹ (190-400 nm)
- They have limited use in sample identification but are highly useful in quantitative measurements.

For quantitative measurement,

The concentration of an analyte in solution can be determined by measuring the absorbance at a specific wavelength and applying the Beer Lambert law.

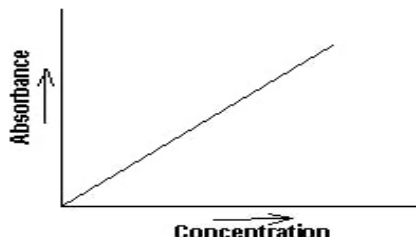
When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength.

Beer Lambert law: $A = \epsilon C l$

Where A= absorbance (no units, since $A = \log_{10} P_0 / P$); C= sample concentration in mole/L, l= length of light passing through the sample in cm; ϵ is the molar absorptivity with units of L mol⁻¹ cm⁻¹

The law tells us that absorbance depends on the total quantity of the absorbing compound in the

light path through the cuvette. If we plot absorbance against concentration, we get a straight line passing through the origin (0,0).



Principle of UV-Vis Spectroscopy:

Electronic transitions

The absorption of UV or visible radiation corresponds to the excitation of outer most

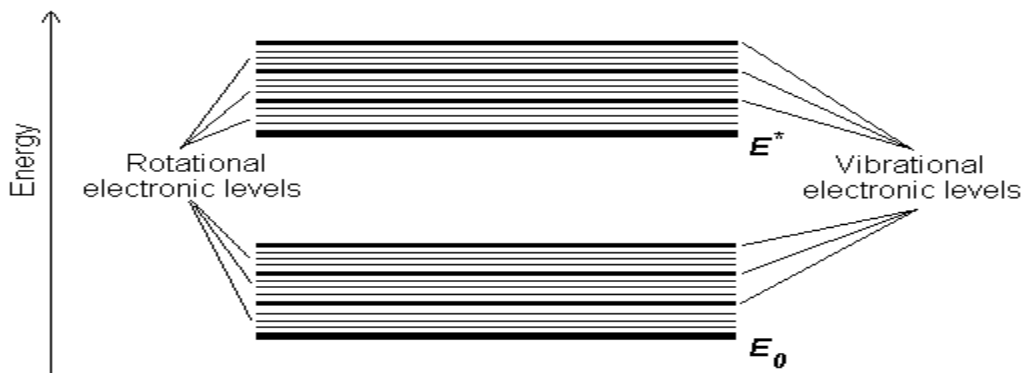
valence electrons. When an atom or molecule absorbs energy, electrons are promoted

from their ground state to an excited state. In a molecule, the atoms can rotate and

vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level. Thus

each electronic level in a molecule is associated with a number of vibrational sub-level (with smaller energy separation) and each vibrational sub-level is again associated with a number of rotational sub-levels (with still smaller energy separation).

Thus in its transition to a higher energy level, an electron can go from any of the sub-levels (corresponding to various vibrational and rotational states) in the ground state to any of the sub-levels in the excited state (diag below). The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band.



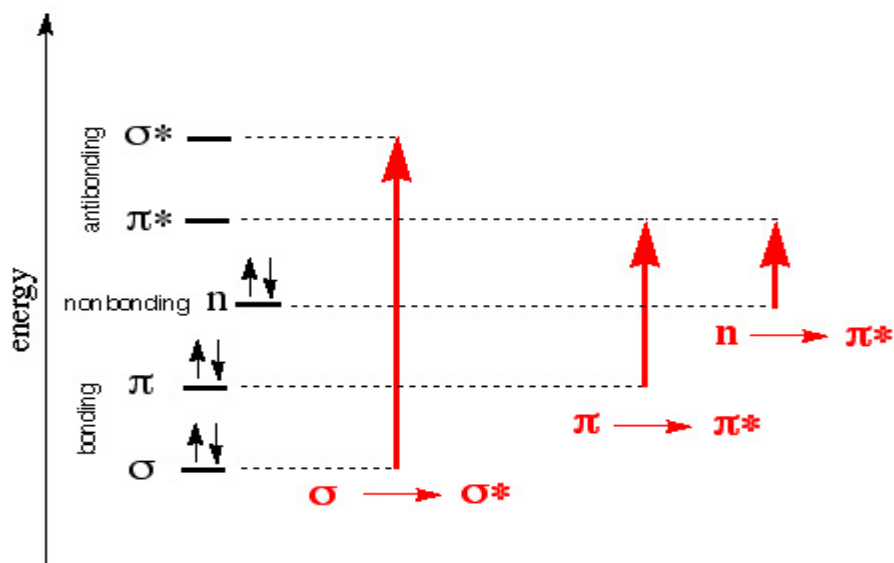
Absorbing species containing π , σ , and n electrons

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy.

Classification of electronic transitions:

1. **$\sigma \rightarrow \sigma^*$ transition:** As (σ) electrons are held more firmly in the molecule, this transition takes place in the UV region.
2. **$\pi \rightarrow \pi^*$ transition:** This transition takes place in the near UV and the Vis region.
3. **$n \rightarrow n^*$ transition:** This transition takes place in the Vis region.

The relative energies of the molecular orbitals showing such transitions are shown:



The position of bands for different electronic transitions is summarized:

Organic compound	Electronic transitions	Position of bands
------------------	------------------------	-------------------

Alkanes	$\sigma \rightarrow \sigma^*$ transition	150 nm (requires high energy which does not lie in the UV region)
Alkenes	$\pi \rightarrow \pi^*$ transition	170-190nm
Aliphatic ketones	$n \rightarrow \pi^*$ transition	280 nm (forbidden and of low intensity)
	$n \rightarrow \sigma^*$ transition	185 nm (allowed and of high intensity)
	$\pi \rightarrow \pi^*$ transition	160 nm (allowed and of high intensity)
Conjugated dienes	$\pi \rightarrow \pi^*$ transition	217 nm (transition is of low energy and is due to conjugation)

Chromophores: A chromophore is the part of a molecule responsible for its color. The color arises when a molecule absorbs certain wavelengths of visible light and transmits or reflects others. The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state.

Auxochrome: An auxochrome is a group of atoms attached to a chromophore which modifies the ability of that chromophore to absorb light. They themselves fail to produce the colour; but when present along with the chromophores in an organic compound intensifies the colour of the chromogen.

Examples include the hydroxyl group (-OH), the amino group (-NH₂), and an aldehyde group (-CHO).

Terminology for absorption shifts

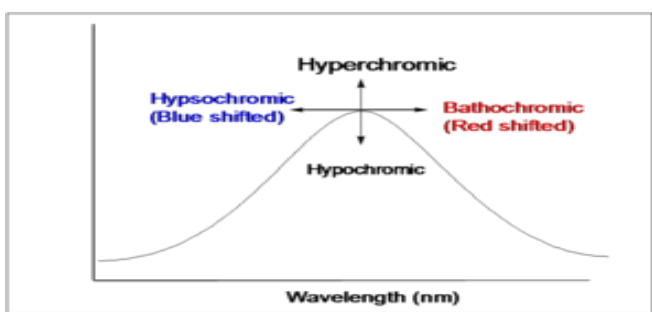
The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n \rightarrow \pi^*$ transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Often (but *not* always), the reverse (i.e. *red shift*) is seen for $\pi \rightarrow \pi^*$ transitions. This is caused by attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences $n \rightarrow \pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

Bathochromic: a shift of a band to lower energy or longer wavelength (often called a red shift).

Hypsochromic: a shift of a band to higher energy or shorter wavelength (often called a blue shift).

Hyperchromic: an increase in the molar absorptivity.

Hypochromic: a decrease in the molar absorptivity.



Applications of UV-Vis. Spectroscopy

1. For the identification of aromatic compounds and conjugated dienes or other olefins.
2. Detection of impurities
3. Quantitative determination of analyte
4. Determination of molecular weight
5. Study of kinetics of chemical reaction
6. Dissociation constant for weak acids and bases can be determined.

Infra-Red Spectroscopy

Theory or Principle of Infrared Absorption Spectroscopy

- a. IR photons have low energy (1-15kcal/mol); hence are not large enough to excite electrons (electronic transitions do not occur) but may induce vibrational excitation of covalently bonded atoms and groups in organic molecules.
- b. The covalent bonds in molecules are not rigid sticks or rods, but are more like stiff springs that can be stretched and bent. Thus, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their

component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations.

c. There are three types of molecular transitions that occur during IR irradiation:

- 1) Rotational transitions:
- 2) Vibrational-rotational transitions
- 3) Vibrational transitions

d. **Conditions for IR absorbance to occur:**

- The frequency of vibration must satisfy the equation: $E=h\nu$.
- The intensity of absorption must be proportional to square of the rate of change of dipole.
- The natural frequency of vibration of the molecule must be equal to the frequency of incident radiation.
- Changes in the vibration must stimulate changes in the dipole moment of the molecule. Hence Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.

Thus Infra red inactive molecules-

- a. do not show vibrational spectra.
- b. Do not have a permanent dipole moment
- c. Do not exhibit a change in dipole moment
- d. Eg - O_2 , H_2 , N_2 etc

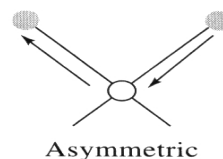
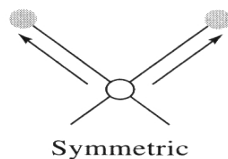
Infra red active molecules –

- a. Show vibrational spectra
- b. Have a permanent dipole moment
- c. Exhibit a change in the dipole moment
- d. CO_2 is a molecule which does not have a permanent dipole moment but still is IR active.

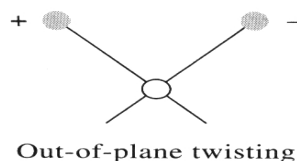
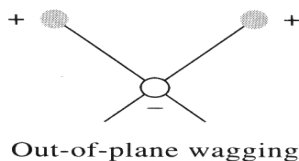
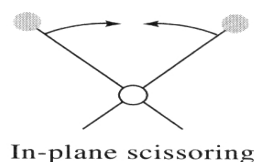
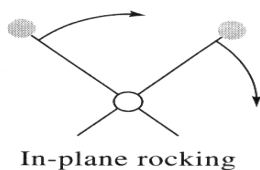
e. The IR region is divided into three regions: the near, mid, and far IR. The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between 3×10^{-4} and 3×10^{-3} cm. In wave numbers, the mid IR range is $4000\text{--}400\text{ cm}^{-1}$. An increase in wave number corresponds to an increase in energy.

f. The different Vibrational Modes occurring as a result of IR absorption:

- i. **Stretching** -the rhythmic movement along a bond axis with a subsequent increase and decrease in bond length



- ii. **Bending** - a change in bond angle or movement of a group of atoms with respect to the rest of the molecule.



- g. It is not necessary that all fundamental vibrations will exist in the IR spectrum. Some vibrations are inadequate and are called degenerate bonds. Since different bonds and functional groups absorb at different wavelengths, an IR spectrum is used in the identification of a compound or establishing the structure of an unknown substance.

Regions of IR spectra

1. **Functional group region**: is the high frequency region between **5000-1300cm⁻¹**. It is particularly useful in the identification of important functional groups present in the organic molecule.
2. **Finger print region**: is the middle frequency region between **1300-650cm⁻¹**. This region helps in the identification of unknown organic substance. No two compounds, however closely related can have identical or superimposable bands in this region.

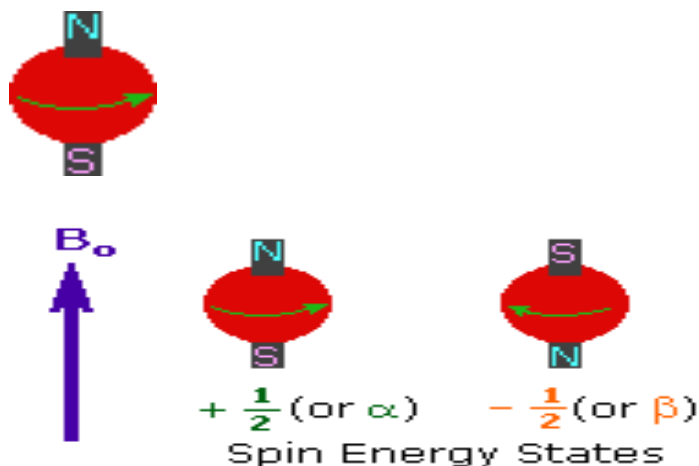
Applications of IR Spectroscopy

1. Identification of an unknown compound
2. Identification of functional groups in organic molecules.
3. To distinguish between inter and intra molecular hydrogen bonding

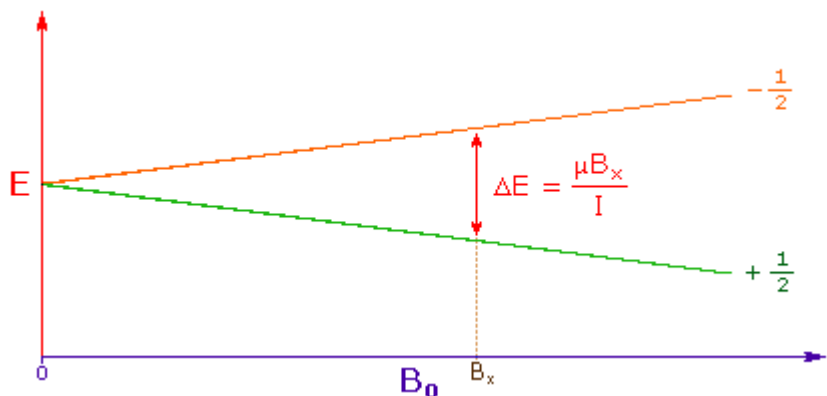
4. To determine the structure of an organic compound**NMR-Spectroscopy (Nuclear Magnetic Resonance Spectroscopy)**

- The nuclei of many elemental isotopes have a characteristic spin (I).
- Some nuclei have integral spins (e.g. $I = 1, 2, 3 \dots$), some have fractional spins (e.g. $I = 1/2, 3/2, 5/2 \dots$), and a few have no spin, $I = 0$ (e.g. ^{12}C , ^{16}O , ^{32}S , \dots).
- Isotopes of particular interest and use to organic chemists are ^1H , ^{13}C , ^{19}F and ^{31}P , all of which have $I = 1/2$.

The theory behind NMR comes from the spin, I of a nucleus. Just as electrons have a $+1/2, -1/2$ spin, certain nuclei also experience charged spins that create a magnetic field (called the magnetic moment), which allows chemists to study them using NMR. Nuclei with even numbers of both neutrons and protons experience NO spin and nuclei with odd numbers of both neutrons and protons have integer spins. Nuclei that have the sum of protons and neutrons equal to an odd number (like ^1H and ^{13}C) have half-integer spins. When there is no external or applied magnetic field (B_0), the nuclear spins orient randomly; however, when there is an applied magnetic field, the nuclei orient themselves with or against the larger applied field. The α -spin state is parallel to the applied force and has lower energy than the β -spin state that is antiparallel to the applied force. The energy difference (ΔE) between the α - and β -spin states depends on the strength of the applied magnetic field. The greater the strength of the applied magnetic field, the greater is the ΔE between the between the α - and β -spin states. This (ΔE) is $\sim 0.02 \text{ cal mol}^{-1}$, which lies in the radio frequency region. The emitted energy in this region produces an NMR signal.



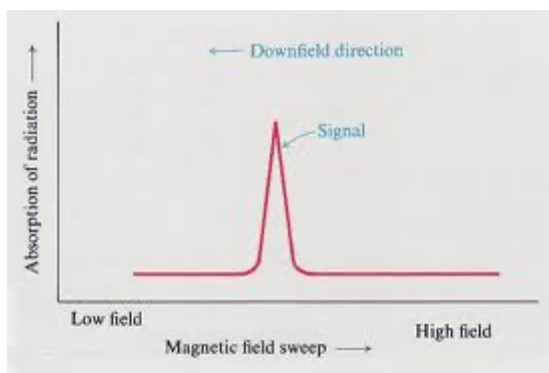
Addition of energy results in a spin flip



As the applied magnetic field increases, so does the energy difference between α - and β -spin states

NMR Spectrum

The NMR spectrum is a plot of the intensity of NMR signal versus the magnetic field (frequency) in reference to a standard (TMS).



NMR Applications

Today, NMR has become a sophisticated and powerful analytical technology that has found a variety of applications in many disciplines of scientific research, medicine, and various industries. Modern NMR spectroscopy has been emphasizing the application in biomolecular systems and plays an important role in structural biology. With developments in both methodology and instrumentation in the past two decades, NMR has become one of the most powerful and versatile spectroscopic techniques for the analysis of

biomacromolecules, allowing characterization of biomacromolecules and their complexes. Together with X-ray crystallography, NMR spectroscopy is one of the two leading technologies for the structure determination of biomacromolecules at atomic resolution. In addition, NMR provides unique and important molecular motional and interaction profiles containing pivotal information on protein function. The information is also critical in drug development.

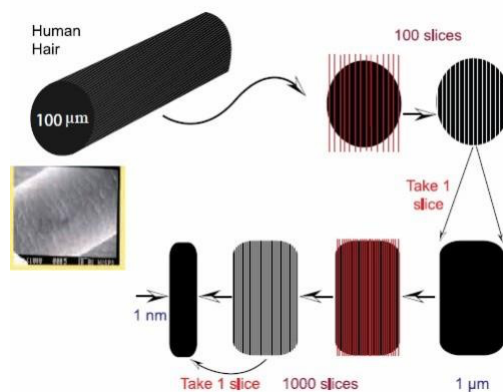
NANOMATERIALS

- A. Basics
- B. Classification of nanomaterials
- C. Properties of nanomaterials

A. Basics of nano-materials and nano-chemistry

- Nanoscience: Scientific study of nanomaterials or objects having size in the 1 – 100 nm range in at least one dimension.
- Nanotechnology: Technology of using nanomaterials to develop products with possible practical application.

The term nano is derived from the Greek word for dwarf. It is used as a prefix for any unit (sec or meter). A nano represents a billionth of a unit. A Nanoscale is considered to span from 1nm to 100 nm.

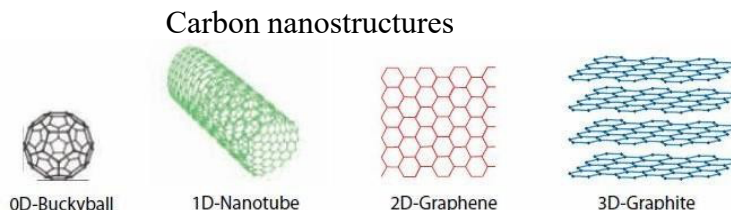


Cross-sectional area of human hair

Nanomaterials are typically categorized as zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D). This classification is based on the number of dimensions which are not confined to the nanoscale range (1- 100nm). This means that in 0D nanomaterials, no dimensions are outside the nanoscale range. In 1D nanomaterial, 1 dimension is outside the nanoscale. In 2D and 3D, two and three dimensions are outside the nanoscale range respectively.

Common examples of 0D nanomaterials are nanoparticles. 1D nanomaterial includes nanotubes, nanorods and nanowires. 2D nanomaterials include nanofilms, nanolayers, and nanocoatings. 3D nanomaterials are known as bulk nanomaterials; none of its dimension exists in the nanoscale range. The reason for their inclusion in the nanomaterials is because: such materials possess a nanocrystalline structure or involve the presence of features at the Nanoscale. Bulk nanomaterials can be composed

of a multiple arrangement of nanosized crystals in different orientations. 3D nanomaterials can contain dispersed nanoparticles, bundles of Nanowires, nanotubes as well as multi nanolayers. The different nanostructures existing in carbon nanomaterials are 0D- Buckyball, 1D-nanotube, 2D-graphene and 3D-graphite



B. Difference between nanomaterials and bulk materials (micro-sized)

1. Surface effects (Surface-to Volume Ratio versus Shape)

One of the fundamental differences between nanomaterials and large-scale materials is that nanoscale materials have an extraordinary ratio of surface area to volume. The large surface area of nanomaterials as compared to their volumes plays a significant role in dictating their properties.

2. Quantum effects

In bulk crystalline materials, the electrons are delocalized within the entire particle. The atomic energy levels spread out into continuous valence and conduction bands. While band gap is minimal in conductors, the same is maximum in insulators. In semiconductors, the band gap is very small resulting in requirement of a minimum energy to excite the valence band electrons to conduction band. This overall behavior changes when the dimension of the bulk materials are reduced to Nanoscale.

For 0D nanomaterials, where all the dimensions are in Nanoscale, the electrons are confined in 3D space. Therefore no electron displacement occurs. For 1D, electron confinement is restricted to 2D, whereas delocalization takes place across the long axis of nanowire/nanorod/nanotube. In the case of 2D nanomaterials, the conduction electrons are confined to the 1d, whereas delocalization takes place across the plane of the sheet.

Thus, for 0D nanomaterials, the electrons are fully confined. For 3D nanomaterials, the electrons are fully delocalized. In 1D and 2D nanomaterials, electron confinement and delocalization coexist.

With decrease in the size of the material to nanoscale, electron movement is restricted within the dimension of the nanostructure. Also, the atomic energy levels within valence and conduction band become discrete. The band gap is also shifted to higher energy levels.



C. Properties of nanomaterials as compared to bulk materials

1. Mechanical properties: Increased hardness, yield strength, elastic modulus, toughness
2. Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetism disappears and transfers to superparamagnetism in the nanometer scale due to the huge surface energy.
3. Reduced Melting Point -- Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants (spacing between atoms is reduced), due to a huge fraction of surface atoms in the total amount of atoms.
4. Metal nanoparticles have unique light scattering properties and exhibit Plasmon resonance
5. Optical properties of nanomaterials can be significantly different from bulk crystals.
 - Semiconductor Blue Shift in absorption and emission due to an increased band gap
 - Metallic Nanoparticles Color Changes in spectra due to Surface Plasmons Resonances
6. Electrical conductivity decreases with reduced dimension
7. Self-purification is an intrinsic thermodynamic property of nanostructures and nanomaterials due to enhanced diffusion of impurities/defects/dislocations to the nearby surface.
8. Increased perfection enhances chemical stability.

Bulk (e.g. Gold)	Nano (e.g. Gold)
<ol style="list-style-type: none">1. Is a pure metal having metallic properties Like metallic lustrous, malleability, ductility, better heat and electrical conductivity, high density, high melting point (1080°C), high tensile strength and is chemically inert2. Yellow or golden color when in a mass	<ol style="list-style-type: none">1. Is not a metal but is a semiconductor2. Color is never yellow or golden3. Color depends on its size and shape For example; Gold particles in glass: 25 nm — Red reflected 50 nm — Green reflected4. Are very good catalysts.5. Melts at relatively low temperature (~940° C).6. Unexpected visible properties & they are small enough to scatter visible light rather than absorb)