

DIGITALIZATION OF LESSON PLAN

Department of Chemistry

VSSUT Burla

Course - B.Tech (Chemistry)

For all branches

Syllabus

B.Tech, CHEMISTRY- 1

Module-1

(To develop basic concept of quantum mechanics and its applications in bonding and spectroscopy)

1. Structure Bonding: Failure of classical mechanics, uncertainty principle, wave nature of particles, Schrödinger equation (need not be derived), interpretation of wave functions, Molecular Orbital theory of diatomic molecules and metallic bonding. (No of lectures-7)

2. Spectroscopy and photochemistry: Interaction and radiation with matter, microwave, IR and UV-VIS spectroscopy: Basic Concepts of selection rules and application to molecular structure determination.

(No of lectures-5)

Module – 2

(To develop the basic concepts of thermodynamics and its application to chemical systems)

1. Thermodynamics and chemical equilibrium: variables of states: 1st law of thermodynamics and applications to ideal gas, enthalpy and heat capacity, Measurement of enthalpy and heat capacity, thermo-chemical calculation 2nd law of thermodynamics concepts of entropy, entropy in physical and chemical changes, molecular interpretation of entropy. The free energy concepts: application to gases: Gibbs Helmholtz equation: free energy change and criterion of spontaneity of chemical equation; free energy change and criterion of spontaneity of chemical reactions and chemical equilibrium. Physical, ionic and chemical equilibrium. (No of lecturers- 9)

2. Phase rule: one and two component systems H₂O , S, Cd-Bi and Fe-C systems

(No of lecturers- 3)

Module - 3

(To develop basic concepts about the rates of reactions Basic idea on homogeneous and heterogeneous catalysis process)

1. Reaction Kinetics and catalysis: collision theory; order and molecularity of reaction kinetics of zero, 1st and 2nd order reactions; activation energy, theory of absolute reaction rates, homogeneous and heterogeneous catalysis. (No of lectures-6)

Module-4

(To develop concepts of electrochemistry and solid state)

1. Electro chemistry: Electro chemical cells, EMF and free energy change of electrochemical reactions, electrode potentials and measurements with reference to standard hydrogen electrode and their

application to redox processes, Measurement of EMF, determination of pH, Dry cells , fuel cells and storage cells (No of lectures – 6)

2. Solid state: crystal systems , Bravais lattices, closed packed structures, ionic solids, crystal defects including Schottky and Frankel defects (No of lectures-4)

BOOKS:

1. Physical chemistry by G.M.Barrow, 5th edition, Tata McGraw Hill, New Delhi 1992
2. Physical Chemistry by P.W. Atkins, 6th edition, oxford
3. Textbook of Chemistry –I, Kalyani Publisher
4. Principles of Physical chemistry by Puri, Sharma and Pathania (Bishal publishing and Co).
5. K. L. Kapoor, *Text Book of Physical Chemistry*, MACMILLAN, 2006
6. Physical Chemistry Through Problems : Dogra & Dogra
7. Fundamentals of Molecular Spectroscopy : C.N. Banwell
8. Matrix educare Pvt.Ltd. by Dr. Priya Mohapatra, Dr. Debapriya De.

Module	Lesson	Author's Name
Module-1	1. Structure Bonding	Dr. Ramakrishna D. S.
	2. Spectroscopy and photochemistry	Dr. Ramakrishna D. S.
Module -2	1. Thermodynamics and chemical equilibrium	Dr. Aruna Kumar Barick
	2. Phase rule	Dr. Aruna Kumar Barick
Module -3	1. Reaction Kinetics and catalysis	Dr. P R Mohapatra / B N Ghosh
Module-4	1. Electro chemistry	Dr. P R Mohapatra / B N Ghosh
	2. Solid state	Dr. Ramakrishna D. S.

Module-1

(To develop basic concept of quantum mechanics and its applications in bonding and spectroscopy)

1. **Structure Bonding:** Failure of classical mechanics, uncertainty principle, wave nature of particles, Schrödinger equation (need not be derived), interpretation of wave functions, Molecular Orbital theory of diatomic molecules and metallic bonding. (No of lectures-7)

Classical Mechanics:

1. It speaks energy to be emitted continuously.
2. It predicts a precise trajectory with precisely specified locations and momentum at each instant.
3. It allows the translational, rotational and vibrational modes of motion to be excited to any energy level simply by controlling the applied source.
4. It treats particle nature and wave nature as quite distinct concepts.

The phenomena associated with large size objects moving at speeds much below the speed of light e.g., falling stones planetary motions etc. could be explained by classical mechanics (or also called as Newtonian mechanics). But the phenomena associated with small size objects moving at speeds of light e.g., motions of electrons, atoms, molecules etc. could not be explained satisfactorily by classical mechanics

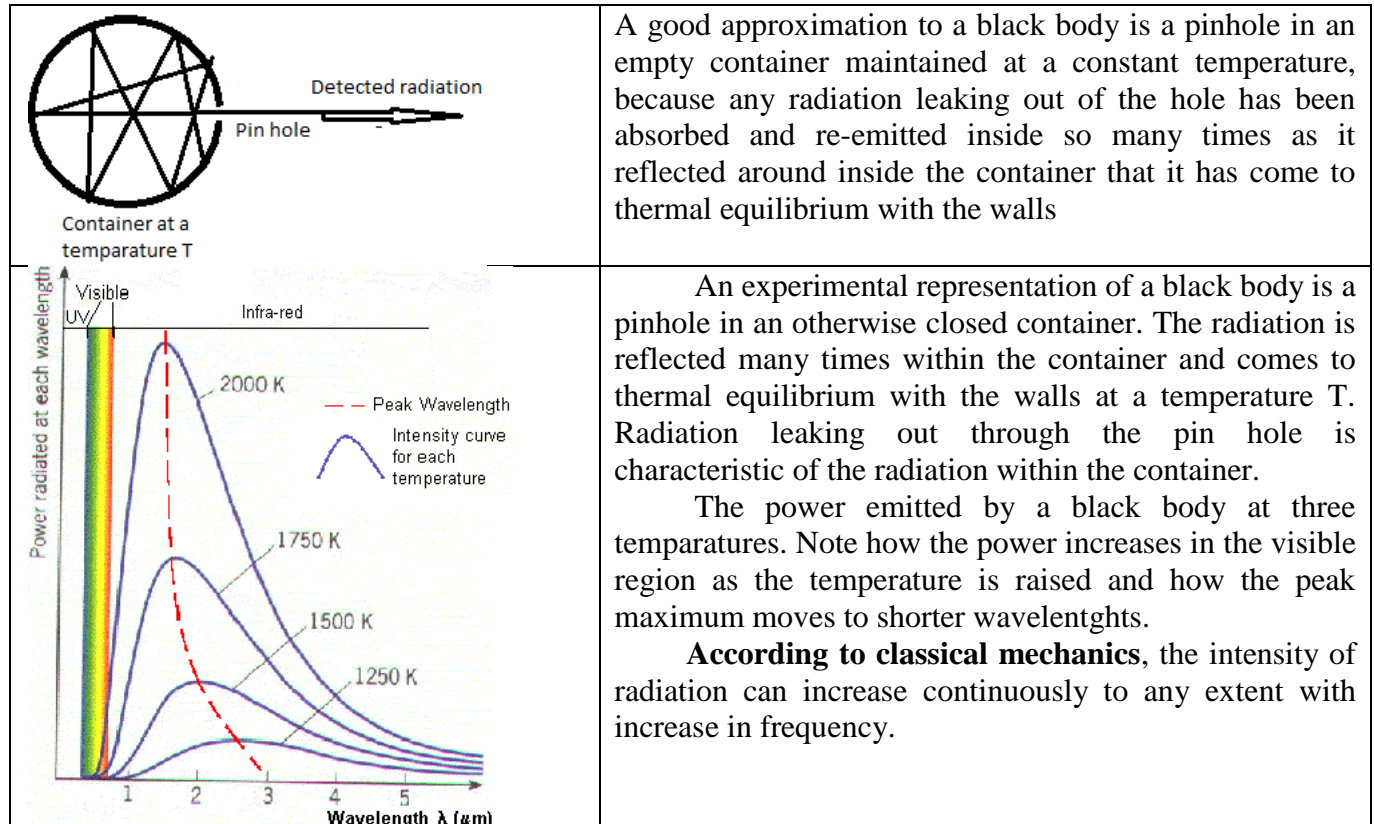
FAILURES OF CLASSICAL MECHANICS:

1. The nature of emission of radiation from hot bodies Ex: (black body radiation)
2. Ejection of electrons from metal surface when radiation strikes it (Photo electric effect)
3. Variation of heat capacity of solids as a function of temperature.
4. Line spectra of atoms with special reference to hydrogen atoms.
5. It fails when applied to small particles such as electrons, atoms, molecules etc.

For example, according to classical mechanics, it should be possible to determine both position and velocity (or momentum) of all moving particle but for microscopic particles such as electrons, atoms, molecules etc, it was impossible.

6. The nature of bonding in molecules is not explained satisfactorily.

BLACK BODY: Black body is an ideal body and is defined as an object, which is capable of absorbing all radiations incident upon it. It is not only a perfect absorber but also a perfect radiator. It is a blackened metallic hollow sphere, blackened inside with a pin hole. All the incident radiations that fall on black body are absorbed completely. At equilibrium, this black body radiates the same radiations in all directions and this radiation is called as **Black body radiation**. Or in other words, It is an ideal body which emits and absorbs radiations of all frequencies is called a black body and radiation emitted is called black body radiation.



Rayleigh-Jeans Law: The electromagnetic field is a collection of oscillators of all possible frequencies. This was based on equipartition theorem.

$dE = \rho d\lambda$ And $\rho = \frac{8\pi K T}{\lambda^4}$ this implies $dE = \left\{ \frac{8\pi K T}{\lambda^4} \right\} d\lambda$, dE is energy density in a range of wavelength $d\lambda$, ρ is proportionality constant, or for particular wavelength $E = \frac{2\pi C K T}{\lambda^4}$ C is velocity of light $3 \times 10^8 \text{ m s}^{-1}$, K is Boltzmann's constant $1.381 \times 10^{-23} \text{ J K}^{-1}$, T is Absolute temperature in Kelvin and λ is wavelength m.

Conclusion: Applicable at longer wavelength regions only

Drawback: It predicts an infinity energy density at shorted wavelength which is called as ultraviolet catastrophe, while the experimental results always remain finite and go to zero as wavelength (λ) goes to zero.

Stefan-Boltzmann law: The intensity of total radiation from a blackbody is proportional to fourth power of its absolute temperature.

$E = \sigma T^4$ $\sigma = \text{Stefan's constant} = 56.7 \text{ W m}^{-2} \text{ K}^{-4}$, $E = \text{Intensity of total radiation from black body orenergy density i.e., total electromagnetic energy in a region derived by the volume of the region. } T = \text{Absolute temperature.}$

Wein displacement law: The wavelength of maximum intensity is inversely proportional to the absolute temperature of black body

$$\lambda_{\max} T = \text{constant} = 2.9 \times 10^{-3} \text{ mK} \quad \lambda_{\max} \text{ is wavelength associated with maximum intensity.}$$

$$E_{\lambda} = \frac{a}{\lambda^5} \left\{ \frac{1}{e^{\frac{b}{\lambda T}}} \right\} \quad \text{where a,b are constants,}$$

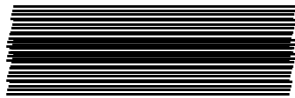
Conclusion: This holds good for short wavelengths satisfactorily

Plancks law or Quantum mechanics or Plancks radiation theory:

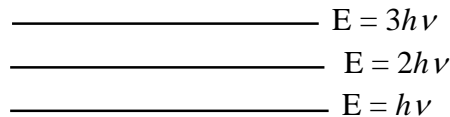
1. The energy of each oscillator (a group of atoms oscillating with same frequency) is limited to discrete values and cannot be varied continuously (This is against the classical theory which allows all possible energies). This postulate led to the concepts of quantization of energy and quanta.

$$E = n h\nu \quad n \text{ is possible integer} = 1,2,3,\dots \text{ And } n \neq 0, \text{ fractional values } h = \text{plancks constant} = 6.623 \times 10^{-34} \text{ JS, } \nu = \text{frequency radiation.}$$

2. Oscillators can be excited only if they acquire energy of at least $h\nu$



An oscillator obeying classical mechanics has continuous values of energy and can gain or loss energy in arbitrary amounts



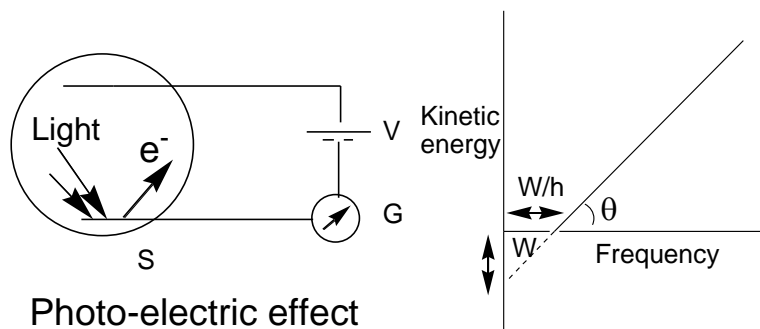
An oscillator obeying quantum mechanics has discontinuous values of energy and can gain or loss energy only in amounts that correspond to difference between two energy levels

$$E_{\lambda} = \frac{2\pi hc^2}{\lambda^5} \left[\frac{1}{e^{\left\{ \frac{hc}{\lambda T} \right\}} - 1} \right]$$

This Plancks law agrees with Rayleigh-Jeans Law, Stefans-Boltzmann`s law and also accounts for Weins displacement law.

PHOTOELECTRIC EFFECT:

When light of certain frequency (visible or ultra violet radiation) strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is called as photoelectric effect.



1. For each metal, a certain minimum frequency of incident light is needed to eject electrons. This is known as threshold frequency, ν_0 . A light of smaller frequency than this cannot eject electrons no matter how long it falls on the metal surface or how high is its intensity. The threshold frequency is different for different metals.
2. The kinetic energy of ejected electrons is independent of the intensity of the incident light but varies linearly with its frequency.
3. The number of ejected electrons from the metal surface depends upon the intensity of the incident radiation. The greater the intensity, the larger is the number of ejected electrons.
4. The kinetic energy of the emitted electrons increases linearly with increases in frequency of incident light.

According to classical mechanics, energy of light depends on its intensity. If this is true, then light of any frequency, if made sufficiently intense, can cause ejection of electrons. But this does not happen.

According to quantum mechanics, light consists of bundles of energy called photons, the energy of each photon being equal to $h\nu$ where ν is frequency of light. When a photon of light ν_0 (threshold frequency) strikes an electron in a metal, it imparts its entire energy ($= h\nu$) to the electron. This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of the light is less than ν_0 , there will be no ejection of electron. When frequency of light falling on a metal surface is higher than the threshold frequency, then some of its energy (which is equal to the energy binding the electron with the nucleus) is consumed to separate the electron from the metal and the remaining energy will be imparted to the ejected electron to give it a certain velocity u (i.e., kinetic energy $= \frac{1}{2} m_e u^2$)

$$h\nu = \phi + \frac{1}{2} m_e u^2 \quad (a) \quad \text{this is called as Einstein photoelectric equation}$$

Where ϕ is the threshold energy (or the work function W) of the metal and $\frac{1}{2} m_e u^2$ is the kinetic energy imparted to the ejected electron. Evidently, $\phi = h\nu_0$ (b)

Using (a) and (b) $\frac{1}{2} m_e u^2 = h(\nu - \nu_0)$ (c)

The energies of photoelectrons can be measured by applying a negative voltage so that the speed can be restored. The maximum negative potential required to stop completely the photoelectric current is called the stopping potential.

$$eVs = \frac{1}{2} m_e u^2 = h\nu - W$$

Atomic and molecular spectra: the appearance of discrete lines at distinct frequencies in atomic and molecular species was one of the prominent failures of classical mechanics. This can be only be explained if the energy of atoms or molecules is confined to discrete values. Only then the change in energy during absorption and emission will have discrete values.

If ΔE is the change in energy during absorption and emission, then $\nu = \frac{\Delta E}{h}$, a line will appear at a discrete frequency in the spectra.

The failure of classical mechanics led to the development of wave mechanics

Wave particle duality of electron: Einstein has suggested, in 1905, that light has a dual character: as wave and also as particle. De Broglie proposed that matter also has a dual character: as a wave and as particle

De-Broglie's Hypothesis:

1. All matter has wave particle duality. i.e., they have particle as well as wave characteristics.
2. The wave length associated with the matter is inversely proportional to momentum (mv) of the particle.
3. Heavier the particle, smaller will be the wavelength associated with it.

However, de Broglie's equation is mostly applicable to smaller objects

$$E = mc^2 \text{ and } E = h\nu = \frac{hc}{\lambda} \text{ this implies } \frac{hc}{\lambda} = mc^2 \text{ this implies } \lambda = \frac{h}{mc} = \frac{h}{P}$$

Where λ is wavelength, $P = mc$ = momentum, $h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ JS}$

Let us consider an electron, accelerated through a potential of 1V. If e is the charge of the electron then the kinetic energy of the electron in the potential field = 1eV

K.E = $\frac{1}{2} mu^2$, where "u" is the velocity of the electron in 1V potential field. Thus, $\frac{1}{2} mu^2 = 1 \text{ eV}$

$$u = \sqrt{\frac{2 \times 1 \text{ eV}}{m}} \quad \text{momentum} = mu = P = m \times \sqrt{\frac{2eV}{m}} = \sqrt{2meV} \quad \text{De-Broglie's wavelength} = \lambda = \frac{h}{P} = \frac{h}{\sqrt{2meV}}$$

Hence, the wave length associated with an electron moving through a potential field can be calculated by using the above equation.

Heisenberg Uncertainty principle (conformation of the wave particle duality):

‘It is impossible to measure both the position and momentum of a microscopic particle simultaneously with accuracy’

$$\Delta x. \Delta P \geq \frac{h}{4\pi} \text{ and } \Delta P = m\Delta V$$

Where Δx is the uncertainty in position or error in determining the position and ΔP is the uncertainty in momentum.

Significance of the principle: Let us consider take the case of an electron. To determine its position we need a microscopic and pass a beam of light through it. We consider light as photons. Visible light cannot be used, as its wavelength is much larger than the diameter of the electron. In order to observe a microscopic particle, the wavelength of the incident light should be smaller than the diameter of the particle. The diameter should be within $\frac{\lambda}{2}$ range. So we require light of shorter wavelength to locate the position of an electron.

But shorter the wavelength, greater will be its energy ($E = \frac{hc}{\lambda}$). The photons must collide with the electron to know its position. More energetic particle will transfer more energy to the electron in momentum. Thus if we adjust the wavelength of light to locate the position accurately there will be inaccuracy in measuring the momentum. If we want to determine the momentum accurately by using lower energetic photon, then it will be difficult to locate the particle accurately.

The important significance of this principle is

1. It has no significance for larger or macroscopic objects as such objects scatter as well as reflect incident light. The reflected light falls in the visible region of light. The velocity also does not change appreciably after colliding with incident photon.
2. It is quite significant for microscopic particle, more so in case of moving particle. The particle cannot be observed without disturbing it due to collision with incident photon. This produces Compton Effect.
3. This introduces the concept of probability of locating a microscopic particle with a probable velocity.

Laplacian operator: This is a very common operator used in quantum mechanics. It is represented by ∇^2 , and is defined as $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

The Schrodinger wave equation: Erwin Schrodinger gave a wave equation to describe the behavior of electron waves in atoms and molecules. In **Schrodinger**'s wave model of an atom, the discrete energy

levels or orbits proposed by Bohr are replaced by mathematical functions, (ψ), which are related to the probability of finding electrons at various places around the nucleus.

The Schrodinger wave equation is written as $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8m\Pi^2}{h} \{E - V\}\psi = 0$

In terms of Laplacian operator it may be written as

$$\nabla^2 \psi + \frac{8m\Pi^2}{h} \{E - V\}\psi = 0$$

Hamiltonian operator: Schrodinger wave equation may be written in the form of

$$\nabla^2 \psi = - \frac{8m\Pi^2}{h} \{E - V\}\psi \quad \text{or} \quad \nabla^2 \psi = - \frac{8m\Pi^2}{h} \{E\psi - V\psi\}$$

$$- \frac{h^2}{8m\Pi^2} \nabla^2 \psi + V \psi = E\psi \quad \text{or} \quad \left\{ - \frac{h^2}{8m\Pi^2} \nabla^2 + V \right\} \psi = E\psi$$

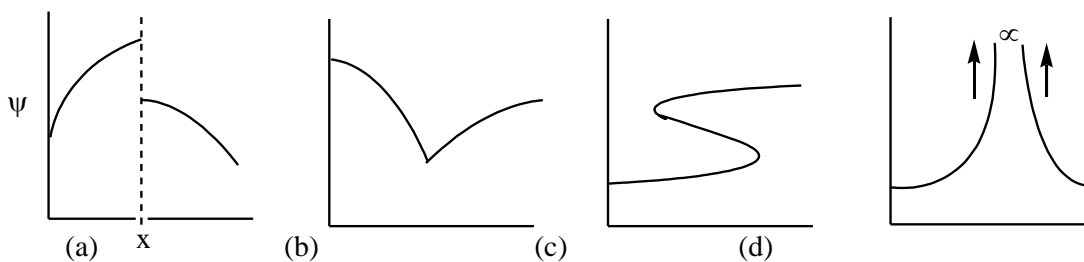
The operator $\left\{ - \frac{h^2}{8m\Pi^2} \nabla^2 + V \right\}$ carried on the function ψ w equal to the total energy multiplied with the function ψ . The operator $\left\{ - \frac{h^2}{8m\Pi^2} \nabla^2 + V \right\}$ is called Hamiltonian operarot and is represented by \hat{H} .

Therefore $\hat{H} = - \frac{h^2}{8m\Pi^2} \nabla^2 \psi + V \Rightarrow \hat{H}\psi = E\psi$

The time dependent wave function can be written as $\hat{H}\psi = i\hbar \left(\frac{\partial\psi}{\partial t} \right)$

The exact solutions of this equation is dirctectly applicable in the following conditions

1. Particle in a One-dimentional box and three dimenstional box.
2. One dimentional simple harmonic oscillator (SHO).
3. The rigid rotor.
4. The hydrogen atom.



The wave function must satisfy important conditions for it to be acceptable. (a) Unacceptable because it is not continuous, (b) Unacceptable because its slope is discontinuous, (c) Unacceptable because it is not single valued, (d) Unacceptable because it is infinite over a finite range. The properties of wave function ψ :

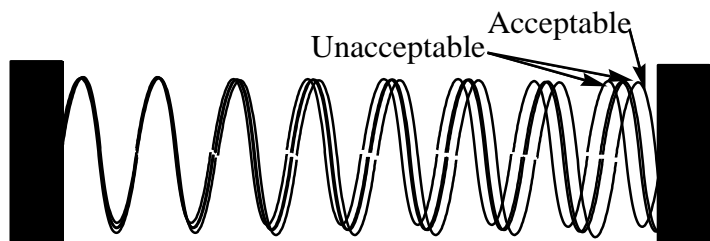
The Schrödinger's equation is a 2nd order differential equation which has several solutions. All of them are not necessarily correspond to any physical or chemical reality. Such wave functions are therefore considered unacceptable. Acceptable wave functions are those which satisfy the following conditions.

1. ψ must be finite. An infinite value of ψ at any point would mean infinite probability of finding the particle at that point, which would be absurd.
2. ψ must be single valued at all points, i.e., it must have one and only one value at a particular point. This restriction arises because the probability at any point must be unambiguous.
3. ψ must be continuous.

Third, the function ψ and its first derivative must be continuous at all points in the space specified for the system, i.e., they must not change abruptly at any point for a slight change in coordinates.

3. The first derivatives, i.e., $\frac{\partial \psi}{\partial x}$ etc. must be continuous. This is necessary which shows that $\frac{\partial^2 \psi}{\partial x^2}$ must be finite everywhere. This is only possible if $\frac{\partial \psi}{\partial x}$ has no discontinuity at any boundary where the potential changes.

4. $\int \psi^2 dx$ must be finite



The physical significance of ψ and ψ^2 :

In Schrödinger's wave equation the wave function ψ represents the amplitude of the wave. For this equation the value of ψ for 1S electron situated at a distance of r from the proton in the ground state of hydrogen atom is

$$\Psi_{1S} = C_1 e^{-C_2 r} \text{ where } C_1 \text{ and } C_2 \text{ both are constants}$$

The wave function ψ by itself has no physical meaning we can extract from the wave mechanical approach to the internal structure of the atom is through ψ^2 which measures the probability of finding an electron of given energy in an extremely small volume around the nucleus.

The probability or chance of finding an electron in the space around the nucleus is called probability function D

$$\text{The electron probability function } D = \text{vol. of the spherical shell} \times \psi^2 \quad D = 4\pi r^2 dr \psi^2$$

The interpretation of ψ :

The only dependable variable in the equation is ψ , the amplitude function and it depends on the coordinates of the particle. ψ and ψ^* do not have any physical significance.

The interpretation of ψ^2 :

In classical theory, the square of the amplitude at any point interpreted as the intensity of the radiation at that point. Maxborn interpreted electron as particle and extended the classical concept to the electron. According to this, ψ^2 at any point is the probability of finding the electron at that point at the given time. If the wave function of particle has a value ψ at some point x then probability of finding the particle between x and $x+dx$ is proportional to $|\psi|^2 dx$. The wave function may be real or imaginary but probability has to be real. Thus, ψ and ψ^* do not have any physical significance but $\psi \psi^*$ or $|\psi|^2$ has. It represents the measure of electronic charge density around the nucleus for an electron.

Eigen functions:

ψ must be finite because if it is infinite, to $|\psi|^2 d\tau$ would be infinite and consequently N would be infinite. Then the normalized wave function would be zero everywhere except where is infinite. This cannot be accepted. This rules out many possible ψ values. The second derivative of ψ must be well defined, if the equation is to be applicable all over the space. The second derivative must be finite over whole space and the acceptable solutions of the schrodingers equations are called as eigen functions.

This is normalized condition:

If ψ is a solution to schrodingers wquation the $N\psi$ is also a solution to it, where N is any constant. In order to know the exact wave function, the following condition will be followed *i.e.*,

$$\int_{-\infty}^{+\infty} N\psi \cdot N\psi^* d\tau = 1 \quad \text{or} \quad \int_{-\infty}^{+\infty} \psi \cdot \psi^* d\tau = 1$$

This is normalized condition. From the normalized wave function, $\psi\psi^* d\tau$ gives direct measure of probability density. Greater the amplitude, greater is the probability of finding the particle or electron at that point at that time or taking the case of time interval, longer the time interval, greater the time the electron or particle spends at that point.

Normalized wave function:

The solutions of Schrödinger wave equation must be normalized if they must satisfy the relation

$$\int_{-\infty}^{+\infty} \psi^2 dr = 1 \text{ where } dr \text{ is a small volume element.}$$

Eigen values:

Max born interpretation puts severe restriction on the acceptability of wave function. Schrödinger wave equation is a second order differential equation. It gives rise to many solutions and hence there will be more than one value for sign. However, all of them are not acceptable. For a function to be an acceptable function, it must be consistent with certain conditions. Only those energy values corresponding to those ψ values as per $\hat{H}\psi = E\psi$ are called **Eigen values**.

An acceptable wave function cannot be zero everywhere. So, acceptable solutions of Schrödinger wave equation exist only for discrete values of energy *i.e.*, **Eigen value**. This implies that particles may possess only certain energies. This is quantization of energy.

Eigenvalues and Eigen functions:

The Schrödinger's wave equation is a second order degree differential equation. It has several solutions. Some of these are imaginary and are not valid. The valid wave functions ψ are called as **Eigen functions**. As a consequence of the restriction on its wave function, the energy of a particle is quantized and corresponding to these energy values (E) called as **Eigen values**.

Wave mechanical model of atom:

The atomic model that takes into account the wave and particle nature of the electron is referred to as the wave mechanical model of the atom. In this model Erwin Schrödinger visualized the atom as a positively charged nucleus surrounded by a standing stationary electron wave extending around the nucleus in Bohr's circular orbit.

As the Eigen values correspond very nearly to the energy values associated with different Bohr-orbitals, the Bohr's model may be considered as a direct consequence of the wave mechanical approach.

LIMITATIONS OF VALENCE BOND THEORY (VBT):

1. No explanation for coordinate bond.

2. Magnetic properties were not explained satisfactorily
3. Does not consider odd electron bond such as H_2^+ .

MOLECULAR ORBITAL THEORY (MOT):

1. The molecules are considered for the molecules as a whole i.e., for all the nuclei separated by fixed equilibrium distances. The molecular orbitals are polycentric while atomic are monocentric.
2. The electrons occupy the molecular orbitals as per Pauli's exclusion principle and Aufbau's principle.
3. The wave function for a molecular orbital is obtained by Linear Combination of atomic Orbitals (LCAO) method.

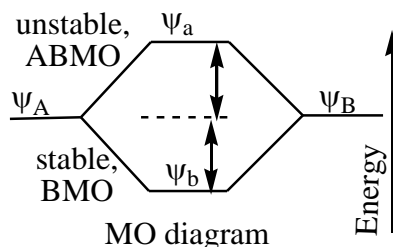
Differences between Atomic and Molecular orbital

Atomic orbital	Molecular orbital
1. It belongs to a single atom	It belongs to a molecule as a whole, and is formed by the combination of two or more atomic orbitals, belonging to the combining atoms.
2. It is monocentric, i.e., the electrons in an atomic orbital are under the influence of one nucleus only	It is polycentric, i.e., the electrons are under the influence of two or more nuclei.
3. Each atomic orbital has its own shape and size	Shape and size of the molecular orbitals depend upon the shape, size, number and orientation of the combining atomic orbitals.
4. No bonding and antibonding orbitals are present in it.	Bonding and antibonding orbitals are known to exist.
5. Atoms remain their characteristics.	Bonded atoms do not retain their characteristics.
6. Atomic orbitals are less stable and possess the usual tendency to acquire stability by forming bond with some other atoms.	Molecular orbitals, generally, are comparatively more stable than atomic orbitals and they do not. Usually, form bonds with other atoms or molecules.
7. Atomic orbitals give the probability of distribution of electron-cloud around a nucleus of an atom.	Molecular orbital gives the probability of distribution of electron clouds, around a group of nuclei.

RULES FOR LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO):

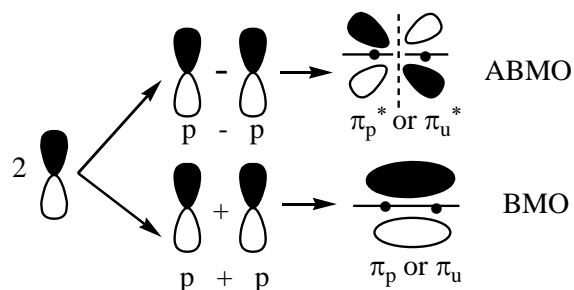
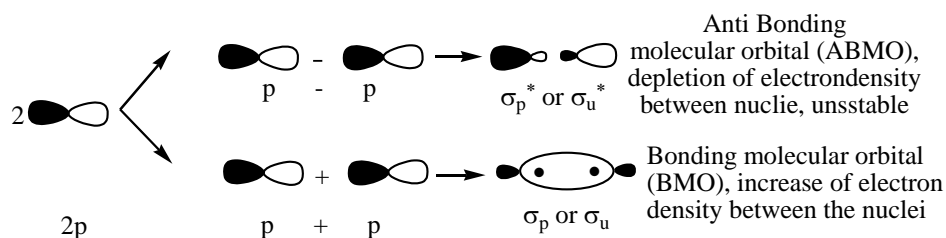
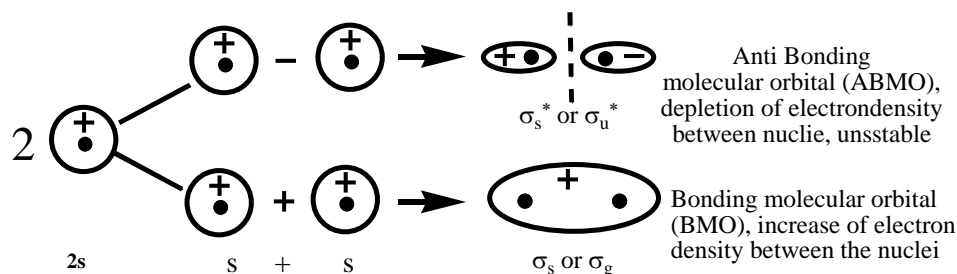
- (1) The atomic orbitals forming the molecules must have similar energies.
- (2) The atomic orbitals must overlap as much as possible to form the molecular orbitals. This is called the principle of maximum overlap.
- (3) The number of molecular orbitals (MO) formed is equal to the number of AO's participated.

Let ψ_A and ψ_B are wave functions of two atoms A and B respectively, then according to MO theory it will give two molecular orbitals i.e. bonding molecular orbital (BMO), $\psi_b = \psi_a + \psi_b$ and anti bonding molecular orbital (ABMO) $\psi_a = \psi_A - \psi_B$

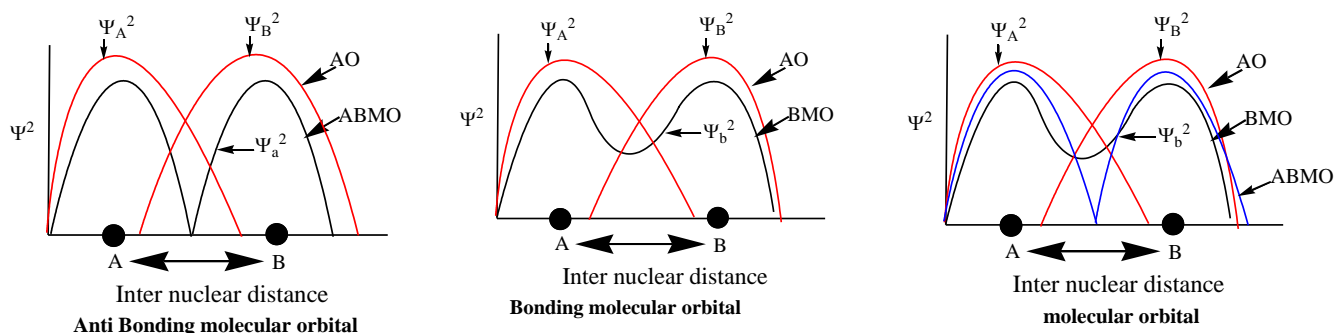


When a point on an orbital is inverted an equal distance through the centre of molecule, the orbital is said to be *gerade* (g) if it has the same sign at the two ends; otherwise it is said to be *ungerade* (u).

Example: s orbital is 'g', a p orbital is 'u', d orbital is 'g' and f orbital is 'u'.

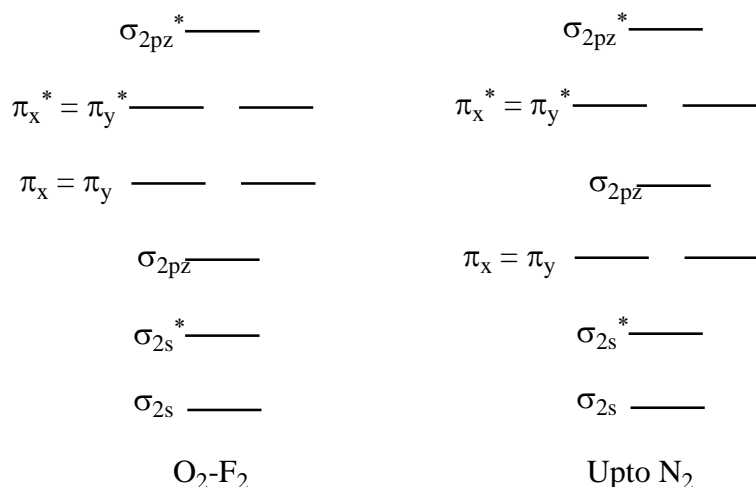


Combination of s, s, and p, p atomic orbitals to form molecular orbitals of different symmetries. The figures display the counters of the atomic and molecular orbitals. The traditional shapes of s and p orbitals arise from the projection of the contours on the respective axes.



Rules in filling up of Molecular orbitals:

1. The molecular orbitals are filled in order of increasing energy (aufbau principle).
2. No two electrons can have all the four quantum numbers alike i.e., Each molecular orbital can not have more than two electrons having opposite spin (Pauli's exclusion principle).
3. Pairing of electrons in a degenerate molecular orbital takes place after each MO one electron each (Hund's rule).



Energy level diagram of homo nuclear diatomic molecules

It is important to note that difference of sequence of MOs between upto N₂ and above N₂. This is due to the fact that the sequence of O₂ and F₂ is the generalized one and based on the assumption that no interaction takes place between σ_s and σ_p orbitals. But actually it takes place for atom having similar s and p orbital energy. There will be repulsion between pairs of orbitals of the same type i.e., between two σ and two σ^* orbitals. There will be destabilization of σ_{2pz} and σ_{2pz}^* and stabilization of σ_{2s} σ_{2s}^* . This shift depends on energy difference of s and p orbitals. It increases from Li(2eV) upto Ne. But it continues upto N₂ after that the energy difference is large enough to treat s-p interaction negligible.

Bond order:

Bond order is defined as the number of covalent bonds between two combining atoms and it is equal to one half the difference between the number of electrons on bonding and antibonding MOs

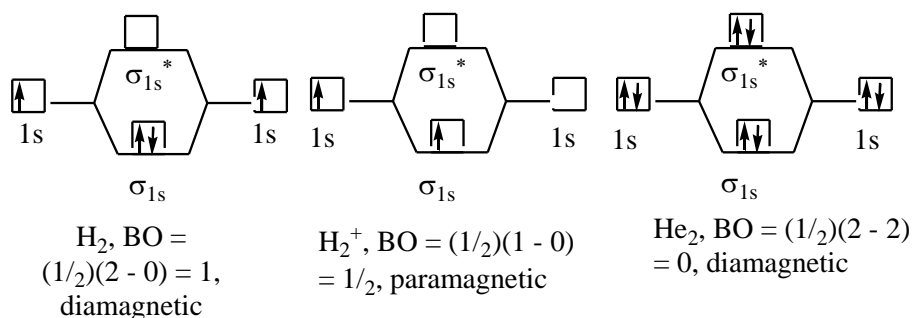
Bond order = $\frac{1}{2}(n_b - n_a)$ n_b = Number of electrons in the bonding MO. n_a = Number of electrons in the antibonding MO.

Significance of calculations of Bond order:

1. Bond order gives the number of bonds existing between the two atoms.
2. More the bond order more is the number of bonds and greater is the stability of the molecule i.e., stability increases with bond order.
3. Bond order is inversely proportional to bond length i.e., more the bond order, shorter is the bond length.
4. A **positive** or net value of bond order implies that the molecule exists and is **stable**. A **-ve** or **zero** value implies the molecule is **unstable** and cannot exist. One of the limitations of VBT is its failure to explain the **magnetic property**. MOT explains this also. Presence of one or more unpaired electrons in the molecular orbitals makes the molecule **para magnetic nature**. In absence of unpaired electrons, the molecule will be **diamagnetic in nature**. The magnetic properties of different molecules are compared by calculating the number of **unpaired electrons** present in molecular orbitals.

Differences between bonding and antibonding molecular orbitals

Bonding molecular orbital	Antibonding molecular orbital
1. It is result of the linear overlapping of two atomic orbitals, when their wave functions ψ_1 and ψ_2 and added Thus: $\psi_b = \psi_1 + \psi_2$	It is result of the linear overlapping of two atomic orbitals, when their wave functions ψ_1 and ψ_2 and subtracted Thus: $\psi_a = \psi_1 - \psi_2$
2. It is formed when two atomic orbitals with same signs of their lobes combine.	It is formed when two atomic orbitals with opposite signs of their lobes combine.
3. Its energy is less than the total of combining atomic orbitals.	Its energy is more than the total of combining atomic orbitals.
4. It increases the electron density between the nuclei.	It decreases the electron density between the nuclei.
5. It stabilizes the molecule.	It destabilizes the molecule.
6. The difference in energy between the combining atomic orbitals and the bonding molecular orbital so formed, is called stabilization energy.	The difference in the energy between antibonding molecular orbitals so formed and the combining atomic orbitals, is called destabilization energy.



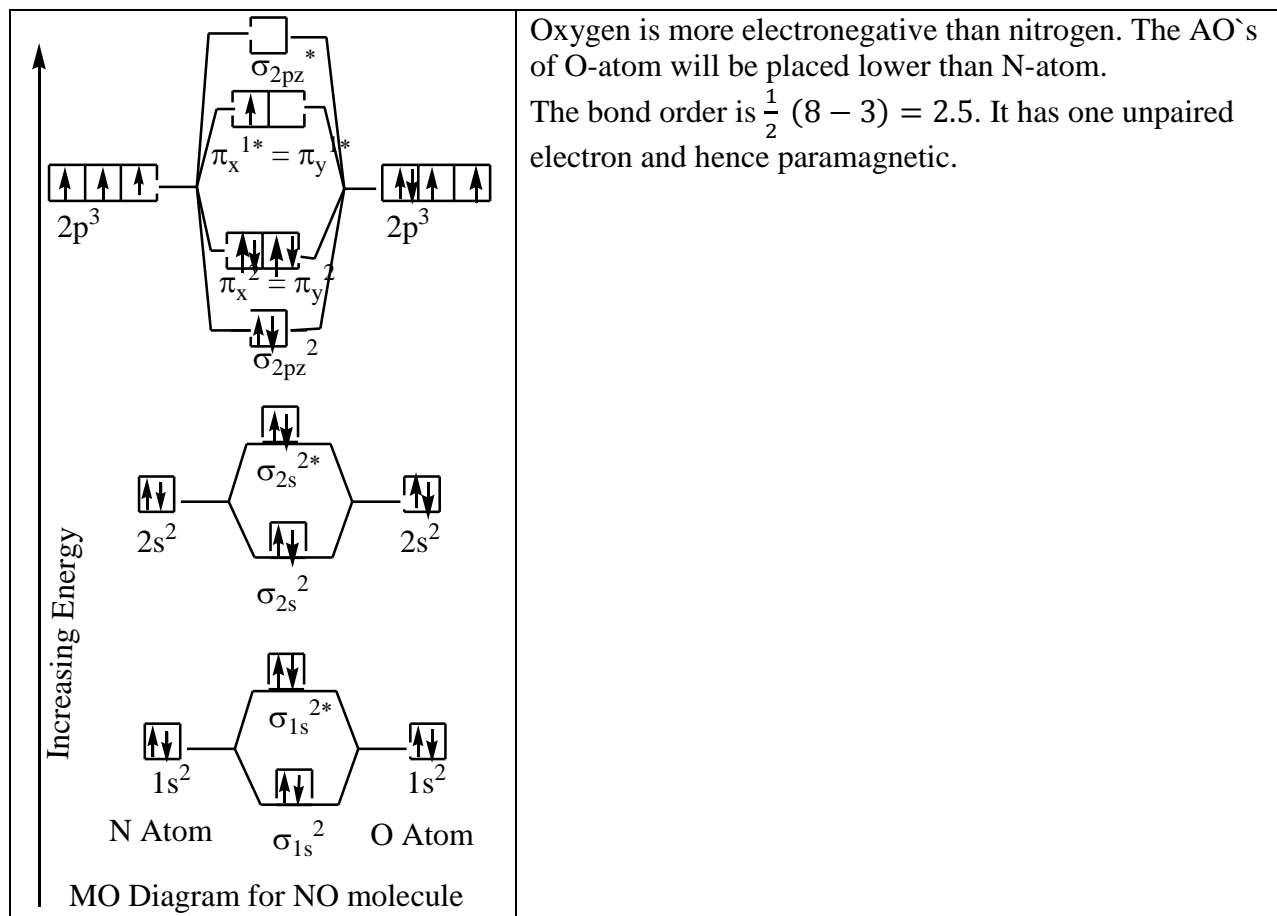
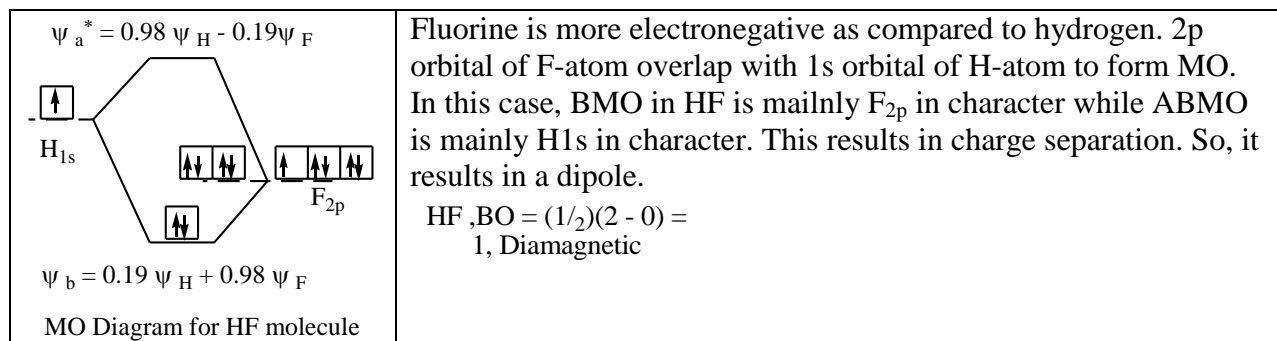
<p>Boron molecule B_2:</p> <ol style="list-style-type: none"> The electronic configuration of B atom is $1s^2 2s^2 2p^1$ (at.no.5). The total number of electrons for B_2 molecule is 10. The total number of atomic orbitals are $(5 + 5)$ is 10. 	<p>Nitrogen molecule N_2:</p> <ol style="list-style-type: none"> The electronic configuration of N atom is $1s^2 2s^2 2p^3$ (at.no.7). The total number of electrons for N_2 molecule is 14. The total number of atomic orbitals are $(5 + 5)$ is 10. 	<p>Nitrogen molecule N_2^+:</p> <ol style="list-style-type: none"> The total number of electrons for N_2 molecule is 13. The total number of atomic orbitals are $(5 + 5)$ is 10.
<p>B_2, $BO = (1/2)(6 - 4) = 1$, paramagnetic</p>	<p>N_2, $BO = (1/2)(8 - 2) = 3$, diamagnetic</p>	<p>N_2^+, $BO = (1/2)(7 - 2) = 2.5$, paramagnetic</p>

<p>Oxygen molecule O_2:</p> <ol style="list-style-type: none"> The electronic configuration of O atom is $1s^2 2s^2 2p^4$ (at.no.8). 	<p>Oxygen molecule O_2^+:</p> <ol style="list-style-type: none"> The total number of electrons for O_2^+ molecule is 15. 	<p>Oxygen molecule O_2^-:</p> <ol style="list-style-type: none"> The total number of electrons for O_2^- molecule is 19.
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<p>2. The total number of electrons for O₂ molecule is 16. 3. The total number of atomic orbitals are (5 + 5) is 10.</p>	<p>2. The total number of atomic orbitals are (5 + 5) is 10.</p>	<p>17. 2. The total number of atomic orbitals are (5 + 5) is 10.</p>
<p>O₂, BO = (1/2)(8 - 4) = 2, paramagnetic</p>	<p>O₂⁺, BO = (1/2)(8 - 3) = 2.5, paramagnetic</p>	<p>O₂⁻, BO = (1/2)(8 - 5) = 1.5, paramagnetic</p>

Molecular Orbital treatment for Heteronuclear Diatomic Molecule:

- (1) Atomic orbitals with similar or comparative energies overlap to form molecular orbital. It is not necessary that 1s of atom A will combine with 1s of atom B only as in the case of homonuclear diatomic molecule.
- (2) Atomic orbitals combining must have same symmetrical properties
- (3) The atomic orbitals must overlap sufficiently.
- (4) The bonding molecular orbitals lie closer to more electronegative atom while antibonding molecular orbital lies closer to less electronegative atom. This is because of difference of energies of two atomic orbitals.



METALLIC BONDING:

Metallic properties:

1. They have High conductivity for heat and electricity.

2. They have characteristics metallic luster i.e., brilliant shine.
3. They are malleable and ductile. (sheets, wires), highly elastic.
4. They form alloys.
5. High coordination no 8 and 12.

The metals have low ionization potential and low electro negativity and a large number of vacant orbitals in their valence shell. Metals atoms are neither held by ionic bonds nor covalent bonds. The various theories are developed to explain these things.

Ionic bond	Metallic bond	Covalent bond
This bond is formed by the transfer of electrons between two dissimilar atoms.	This bond is formed by the simultaneous attractive interaction between the kernels and mobile electrons in a metal crystal	This bond is formed by sharing of electrons between two similar atoms
Ionic compounds are brittle	Metals are malleable. It is a weak bond because mobile electrons are simultaneously attracted by a large number of nuclei.	It is strong bond because bonded electron pair is strongly attracted by nuclei.
It is stronger bond due to strong electrostatic force of attraction	It is weak bond	Covalent compounds are usually liquids and gases.
Inoci compounds are bad conductors of electricity	Metals are good conductors	Covalent compounds are bad conductors of electricity

<p>The variation of the electrical conductivity of a substance with temperature of a substance with temperature is the basis of its classification as a metallic conductor, semiconductor, or a super conductor.</p>	<p style="text-align: center;">Metallic conductor</p> <p style="text-align: center;">Superconductor</p> <p style="text-align: center;">Semiconductor</p> <p style="text-align: center;">Conductivity ($S\text{ cm}^{-1}$)</p> <p style="text-align: center;">Temperature, T</p>	<p>A metallic conductor is a substance with a conductivity that decreases as the temperature is raised.</p> <p>A semiconductor is a substance with a conductivity that increases as the temperature is raised.</p> <p>A super conductor is a solid that conducts electricity without resistance.</p>
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Classical free electron theory:

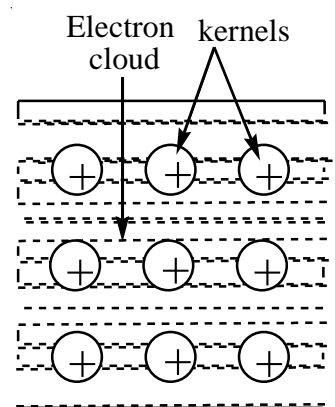
Electron gas model (Lorentz`s theory):

1) All metals have low ionization energy. Their valence electrons are loosely held by the nucleus. Thus, a metal atom is made of two parts.

a) Valence Electrons: These electrons are loosely held by the nucleus.

b) Kernel: It is the 'portion of atom' that is left behind after the loss of valence electrons. It is positively charged e.g., Li-atom ($1s^2, 2s^1$) has one valence electron ($2s^1$) and Kernel (Li^+ ie., $1s^2$).

2) Kernels occupy closely packed fixed positions while valence electrons occupy positions in between the kernels Fig.



3) The valence electrons are loosely held by the nucleus. These can, thus leave one kernel and enter into the influence of another kernel through valence orbitals. These electrons are, thus, not stationary and are called mobile or delocalized electrons.

4) Strength of the metallic bond is directly proportional to the number of valence electrons and nuclear charge of the metal atom.

The simultaneous force of attraction between the kernels and mobile electrons which hold the metal atoms together is called metallic bond.

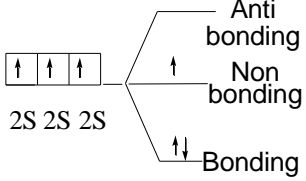
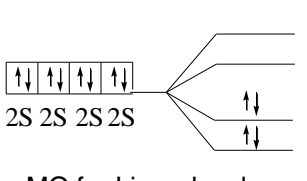
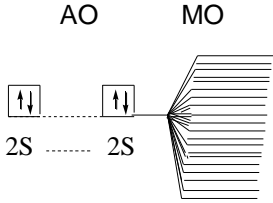
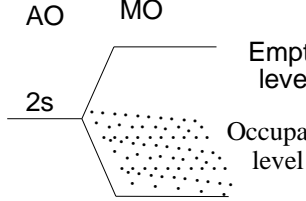
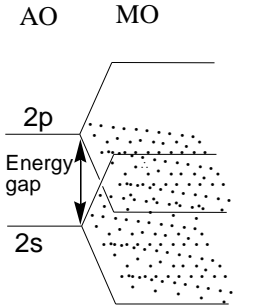
Drawbacks: Electrical properties of conductors, insulators and semiconductors. Metallic Bonding was not satisfactorily explained.

Valence bond theory:

<p>The structure is a mixture of all the possible forms <i>i.e.</i>, all the possible structures contribute towards the true structure. The more the possible structures lower is the energy. This implies that cohesive force is large. The cohesive energy of lithium metal is three times that of Li_2 molecule. This theory fails to explain the condition and listre properties of metals.</p>	$\begin{array}{c} \text{Li} & \text{Li} - \text{Li} & \text{Li} \\ & & \\ \text{Li} & \text{Li} - \text{Li} & \text{Li} \end{array}$ <p>(a)</p>	$\begin{array}{c} \text{Li} - \text{Li} & \text{Li} - \text{Li} \\ \text{Li} - \text{Li} & \text{Li} - \text{Li} \end{array}$ <p>(b)</p>
	$\begin{array}{c} \text{Li} & \text{Li} - \overset{\oplus}{\text{Li}} - \text{Li} \\ & & \\ \text{Li} & \text{Li} - \text{Li} & \ominus \text{Li} \end{array}$ <p>(c)</p>	$\begin{array}{c} \text{Li} - \text{Li} & \text{Li} - \overset{\ominus}{\text{Li}} \\ \overset{\oplus}{\text{Li}} & \text{Li} - \text{Li} & \\ & & \text{Li} \end{array}$ <p>(d)</p>
	<p>More structures can be formed by taking the ionic form</p>	

Drawbacks: Electrical properties of conductors, insulators and semiconductors. Metallic Bonding was not satisfactorily explained.

Molecular orbital theory:

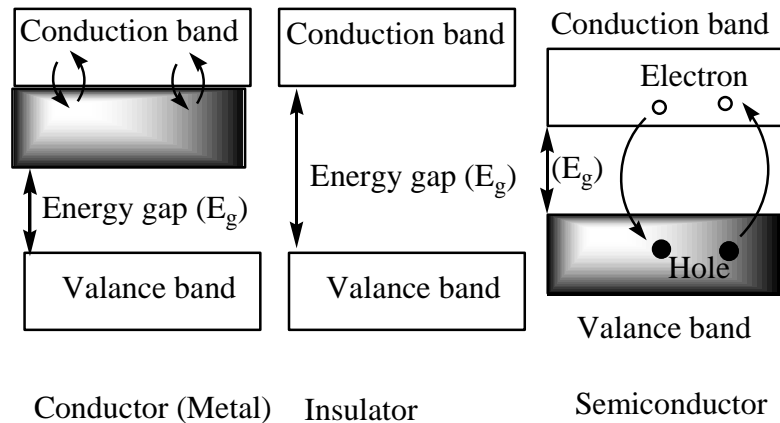
 <p>MO for Li₃ molecule</p>	<p>In Li₂ molecule, the atomic orbitals overlap to give molecular orbitals. The molecular orbital configuration is $\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2$.</p>	 <p>MO for Li₄ molecule</p>
<p>AO MO</p>  <p>MO for Li_n molecule</p>	<p>Extending it to there will be N-number of molecular orbitals with decrease in the energy gaps between the MO`s. they are so close that, it seems they are a continuum. Each MO can accommodate two electrons, so half of the energy levels are filled for Li_n, molecule. Electron can be easily excited to vacant MO, with expenditure of little amount of energy. The transfer of electrons from filled MO to vacant MO without expenditure of large amount of energy successfully explains the high conductivity of metal. These MO`s extent over the whole the whole crystal. All the observed properties can now be explained easily. The vacant orbitals are called conduction bands and the 2 MO`s are called valence band.</p>	
<p>AO MO</p>  <p>MO for Li_n molecule</p>		
<p>AO MO</p>  <p>MO for Beryllium molecule</p>	<p>The energies 2s and 2p AO of Be atom differ by 160KJ/mol. Then 2p molecular orbitals overlap with upper part of 2s MO due to this energy difference and part of 2p band is occupied leaving 2s partly vacant. This explains why the conductivity takes place very much. The width of the band does not depend on the number of atoms but on the extent of overlapping. Larger band width results for the high energy orbitals because of greater overlap.</p> <p>The band formed from overlap of s orbitals is called the s band. If the atoms have p orbitals available, the same procedure leads to a p band and there may be a band gap, a range of energies to which no orbital corresponds.</p>	

The bonding orbitals forms a band which is known as valence band and others are known as conduction band. The valence band and others are known as conduction band.

The valence band contains only outer valence electrons when the electrons jumps to the conduction band it is able to conduct electricity.

The basic difference between conductors, Semiconductors and Insulator lies in the number of free electrons present in the material.

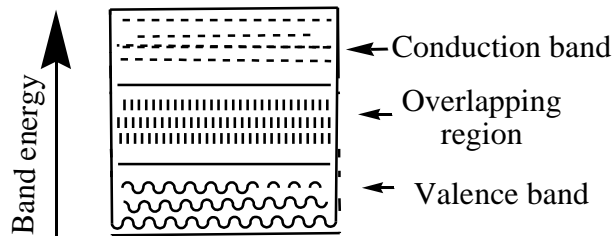
Energy band diagrams



Explanation of conductors, insulators and semiconductors:

1. Conductor: Conductors are those solid in which plenty of free electrons are available for electrical conduction.

Example: Ag, Cu, Al etc.



2. These materials have very low electrical resistance. In terms of energy bands these materials have overlapping of valence bands and conduction bands.

3. Availability of large no. of conduction electrons help in conductivity in the solids. In the case of metals the top most band is not completely filled but partially filled with electrons and is known as conduction band.

electronic conduction takes place easily with the expenditure of little energy. Here either the valence band is partly filled or overlapping of valence and conduction and takes place.

Insulator:

1. In this type of materials the valence electrons are bound very tightly to their parent atoms. It requires large electric field to remove the electrons from the attraction forces of the nuclei.

Examples: wood, plastic and rubber etc.

2. In terms of energy band the insulators have full valence band and empty conduction band and large energy gap in between them.

3. In insulating solids the valence electrons are held very tightly with the nuclei of the parent atoms and requires a large amount of electronic field to remove these from the attractive forces of the nuclei.

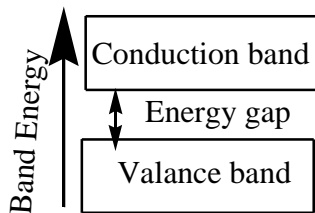
Electronic conduction will not take place. The energy gap or band gap between vacant band and conduction band is large and it is not possible to excite the electron to the next higher band.

Semiconductors:

1. Semiconductors are solid materials either non-metallic elements or compounds which allow the electrons to pass through them so that they conduct electricity in much the same way as the metal but the electrical conductivity is less than that of the metal.

Example: Si, Ge, As, Sb, Cu_2O , Al_2O_3 , TiO_2 , ZnS .

2. There is a little energy gap in between valence band and conduction band.



3. Valence band is completely filled and conduction band is empty but with increase of temperature electrical conductivity increases since an electron jumps from the V.B. to the CB., it leaves behind a hole in the VB. The hole is positively charged and since an electron can jump into the hole from another part of VB it is as if the hole was moving. Conduction can occur either by the negative electrons moving within the CB or by the positive holes moving within the VB.

The electric conduction property is in between conductor and Insulator

1. They are insulator at Room temperature

2. At higher temperature, thermal energy is sufficient to excite the electron to next higher band.

3. Then electron in the conduction band and the valency in the valency band now help in the conduction.

Semiconductors are of two types

a) Intrinsic SMC: The conductivity increases with increase in temperature.

b) Extrinsic SMC: External impurities are added to conduct electricity. The impurity band acts as medium for electronic conduction.

Electronic conductors are classified as metallic conductors or semi conductors according to the temperature dependence of their conductivities. An Insulator is a semiconductor with a very low electrical conductivity.

a) According to the band theory, electrons occupy molecular orbitals formed from the overlap of atomic orbitals. Full bands are called valence bands and empty bands are called conduction bands. b) Semiconductors are classified as p-type or n-type according to whether conduction is due to holes in the valence band or electrons in the conduction band.

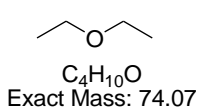
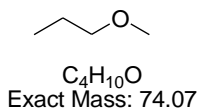
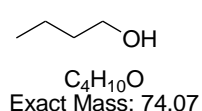
2. Spectroscopy and photochemistry: Interaction and radiation with matter, microwave, IR and UV-VIS spectroscopy: Basic Concepts of selection rules and application to molecular structure determination. (No of lectures-5)

SPECTROSCOPY

Introduction:

Significance of spectroscopy:

The determination of molecular structure has been a central problem in chemistry. Many methods using electromagnetic radiations have been developed to understand and to elucidate the molecular structure. These are spectroscopic methods and provide molecular spectra.



The study of molecular spectra provides valuable information regarding the structure of molecules, arrangement and presence of various groups, internuclear distance (bond lengths, bond angles), geometry of molecules, etc.

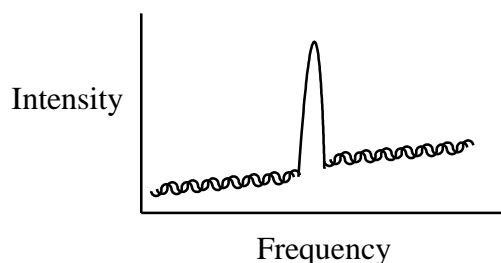
In order to obtain molecular spectra the matter is exposed to electromagnetic radiations and the resulting change in e.m radiation results spectrum.

DEFINITION:

SPECTROSCOPY: Spectroscopy is both detection and analysis of the interacted electromagnetic radiation with the matter.
OR

Spectroscopic data is often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency or wave number.

SPECTRUM:



The record of spectral intensity as a function of frequency (ν) or Wavelength (λ) of the radiation emitted or absorbed by an atom or a molecule is called its spectrum.

The equivalent word of Spectrum in Greek is appearance. It consists of a series of lines or sharply defined emission or absorption peaks.

APPLICATION:

It gives the proof in determining the structure of molecule considered.

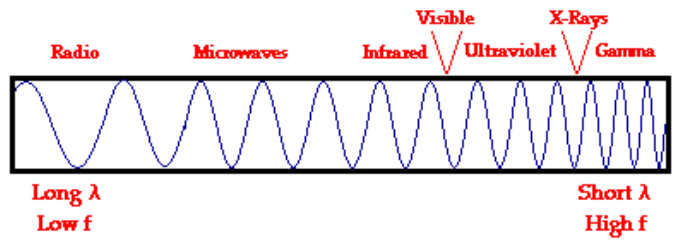
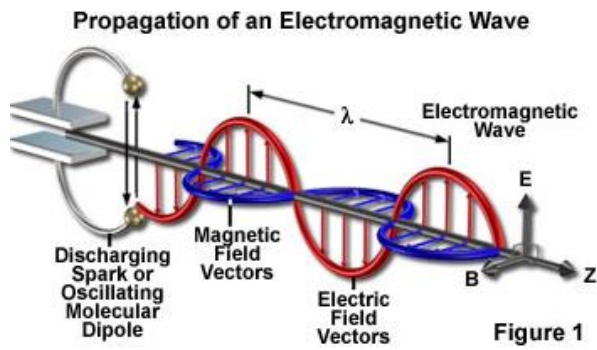
Advantages of spectroscopy:

1. Spectroscopic methods are much more rapid and much less time consuming.
2. They give information which is recorded in the form of a permanent chart generally in an automatic or semi-automatic manner.
3. They require very small amount (at mg and μg levels) of the compound even this amount can be recovered at the end of examination in many cases.
4. The structural information gained by spectroscopic methods is much more precise and reliable; they are highly reliable in establishing the identity of two compounds.
5. They are much selective and sensitive and are extremely valuable in the analysis of highly complex mixtures and in the detection of even trace amounts of impurities.
6. In general the sample can be recycled.
7. With these methods, continuous operation is often possible and this facilitates automatic control of process variables in industry.

GENERATION OF ELECTROMAGNETIC RADIATION (EMR):

When an electric charge is rotated within a magnetic field or a magnet is rotated within an electric field, electromagnetic radiation is produced which has an electric component and a magnetic component perpendicular to each other and both these components are perpendicular to the direction of propagation of the radiation.

Electromagnetic waves exist with an enormous range of frequencies. This continuous range of frequencies is known as the **electromagnetic spectrum**. The entire range of the spectrum is often broken into specific regions. The subdividing of the entire spectrum into smaller spectra is done mostly on the basis of how each region of electromagnetic waves interacts with matter.



CHARACTERISTICS OF ELECTROMAGNETIC RADIATION:

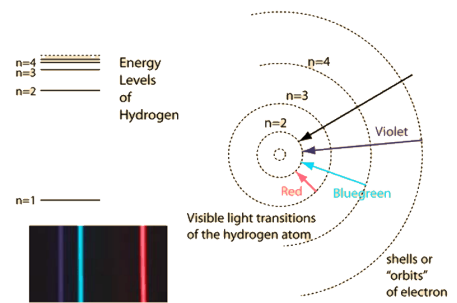
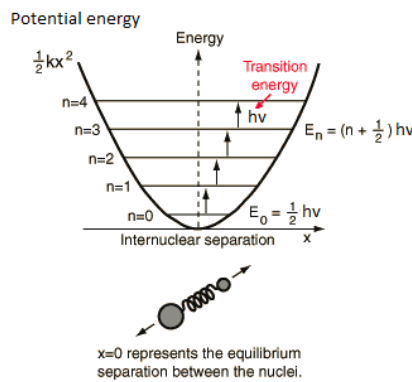
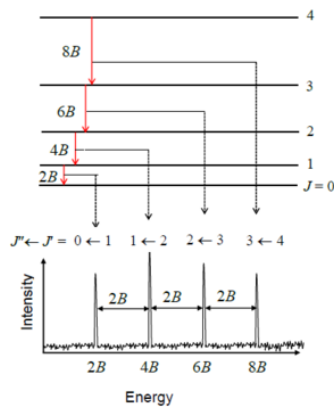
1. EMR has electric and magnetic component perpendicular to each other.
2. It is not deflected by either electric field or by magnetic field.
3. It doesn't require any medium for its propagation.
4. All types Electromagnetic radiations have same velocity *i.e.*, velocity of light $3 \times 10^8 \text{ms}^{-1}$, however their energies and frequencies may be different.

Properties of matter:

Quantization of Energy:

Max Planck theory:

A Molecule in space can have many sorts of energy e.g., it may possess rotational energy by virtue of bodily rotation about its center of gravity; it will have vibrational energy due to periodic displacement of its atom from their equilibrium positions; it will have electronic energy since the electrons associated with each atom or bond are in unceasing motion, etc.



The rotational, vibrational and other energies of a molecule are also quantized- a particular molecule can either exist in a variety of rotational, vibrational, etc., energy levels and can move from one level to another only by a sudden jump involving a finite amount of energy.

$$\begin{array}{c}
 E_2 \text{-----} \\
 \uparrow \Delta E = E_2 - E_1 \\
 E_1 \text{-----} \\
 \downarrow = N h \nu \\
 N = 6.02 \times 10^{23} \\
 \text{Avagadro number} \\
 h = 6.63 \times 10^{-34} \text{ JSmolecule}^{-1} \\
 \text{Plancks constant}
 \end{array}$$

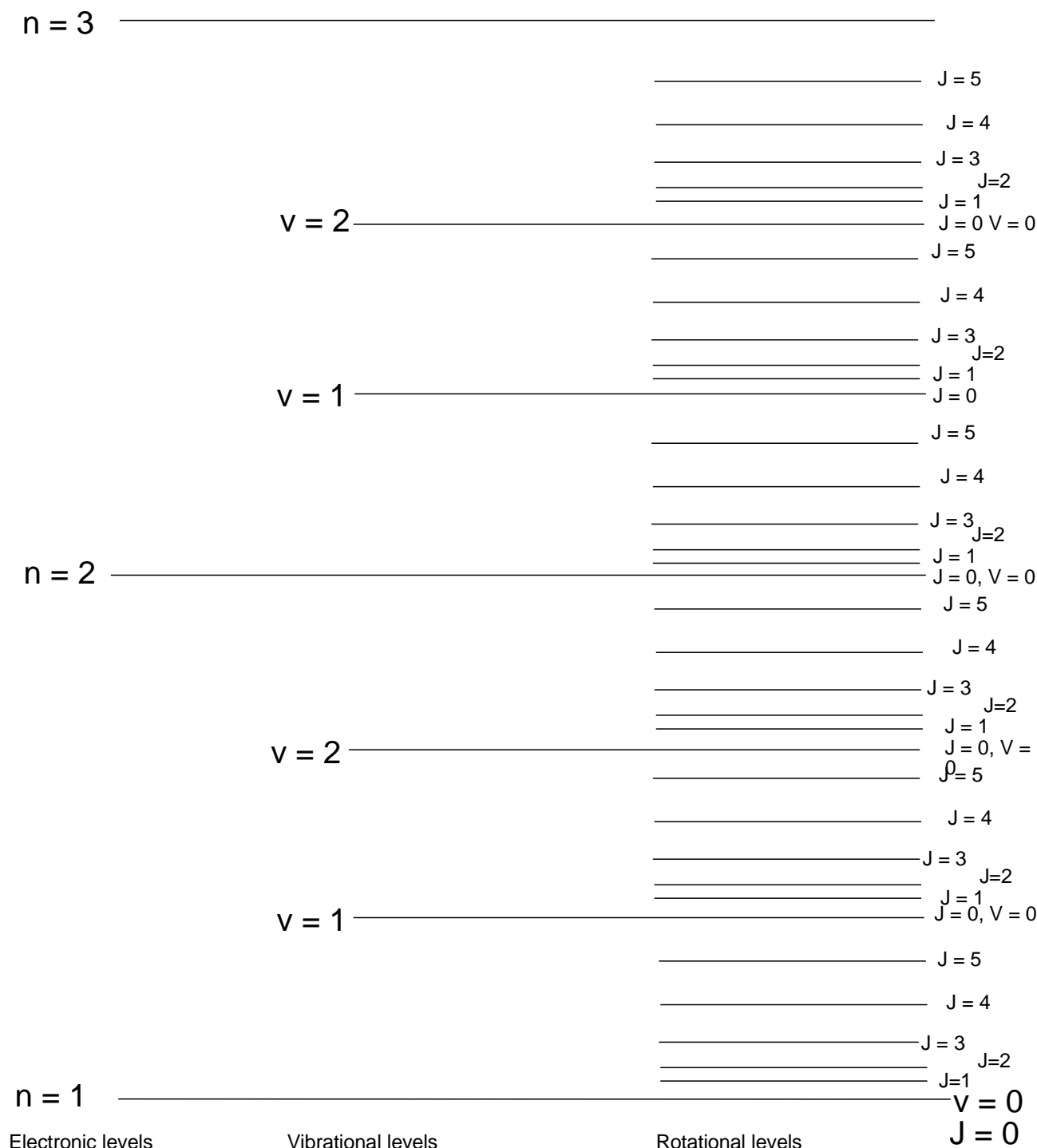
Transitions can take place between the levels E_1 and E_2 provided the appropriate amount of energy (ΔE) can be either absorbed or emitted by the system.

The spectroscopist measures the various characteristics of the absorbed or emitted radiation during transitions between energy states interms of wavenumber (cm^{-1}) rather than Hz.

Mechanism of energy absorption

In all branches of chemistry three things are important. First the absorbing body and the second is the electromagnetic radiation that is incident on the absorber, absorbed and then results in an absorption spectrum which is detected by an instrument called spectrometer. The spectrometer constitutes the third important thing. The absorbing body consists of molecules, atoms, electrons and nuclei. Each of these individual things have different energy levels. All these energy levels are quantized. If the molecule is in a lower energy level E_1 , it can be promoted to E_2 providing the frequency of radiation is such that $\Delta E = h\nu$.

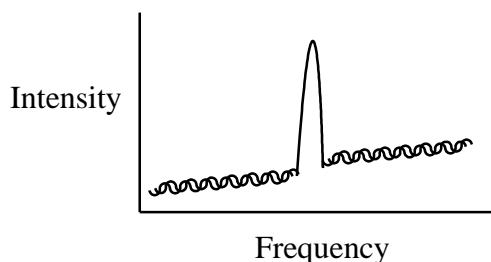
In such a case, energy energy and amount of radiation absorbed is recorded by the spectrometer and is presented in the form of a spectrum. Most often a spectrum results by plotting intensity (I) or function of it against energy (E) of incident radiation.



Electronic vibrational and rotational energy levels in a diatomic molecule

Intensity is defined as the number of photons of the incident radiation absorbed per unit area of the absorber in unit time. The energy of radiation is usually replaced by wave length (λ , \AA^0), wave number ($\bar{\nu}$, cm^{-1}), frequency (ν , Hz) or any other function related to it.

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$



A typical spectrum for absorption spectroscopy

The mechanism of energy absorption is varied depending on the nature of transition involved.

REGIONS OF THE SPECTRUM:

Radiofrequency region (NMR + ESR spectroscopy) $3 \times 10^6 - 3 \times 10^{10}$ Hz: 10m- 1cm wavelength.

Energy associated with reversal spin of nucleus (nmr) or electron (esr) belongs to this region and is of the order 0.001-10J/mole. The

Microwave region (Rotational spectroscopy or Microwave spectroscopy) $3 \times 10^{10} - 3 \times 10^{12}$ Hz: 1cm – 100 μ m wavelength.

Energy associated with the transition of molecules between various rotational energy levels belong to this region. The separation between the rotational levels of molecules is of the order of 100J/mol.

Infrared region (Vibrational Spectroscopy) $3 \times 10^{12} - 3 \times 10^{14}$ Hz: 100 μ m- 1 μ m wavelength.

Energy associated with the transition of molecules between various vibrational energy levels belong to this region. The separation between the vibrational levels of molecules is of the order of 10,000J/mol.

Visible of Ultra violet region (Electronic spectroscopy) $3 \times 10^{14} - 3 \times 10^{16}$ Hz: 1 μ m- 10nm wavelength.

Energy associated with the transition of molecules between various electronic energy levels belong to this region. The separation between the electronic levels of molecules is of the order of 1lakhJ/mol.

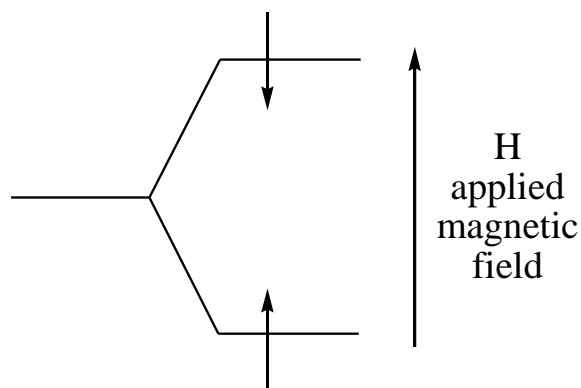
X-Ray $3 \times 10^{16} - 3 \times 10^{18}$ Hz: 10nm - 100pm wavelength.

Transitions involving the inner electrons of an atom or a molecule will takes place in this region and it is of the order of 1 crore J/mole = 10^7 J/Mole.

γ -Ray $3 \times 10^{16} - 3 \times 10^{18}$ Hz: 100pm – 1 pm wavelength.

The rearrangement of nuclear particles of an atom or molecule will take place in this region and it is of the order of 100 – 10,000 crore J/mole ($10^9 - 10^{11}$ J/Mol).

1. The radio frequency region: we may consider the nucleus and electron to be tiny charged particles, and it follows their spin is associated with a tiny magnetic dipole. The reversal of this dipole consequent upon the spin reversal which can interact with the magnetic field of electromagnetic field of electromagnetic radiation at the appropriate frequency. Consequently all such spin reversals produce an absorption or emission spectrum.

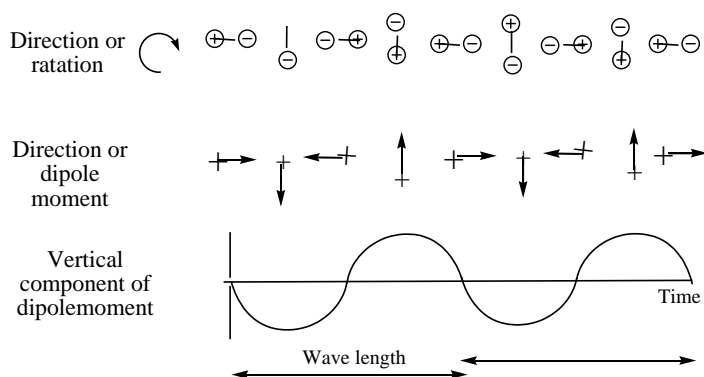


The amount of energy exactly needed to flip the proton depends on the external field strength. The stronger the field more becomes the frequency of radiation needed to do the flipping.

$$\nu = \frac{\gamma H}{2\pi}$$

ν = Frequency in Hz, H = strength of magnetic field in gauss, γ = the gyromagnetic ratio, a nuclear constant and has a value of 26750 for a proton

2. The microwave region:



Rotation of a polar diatomic molecule showing the fluctuation in the dipole moment measured in a particular direction

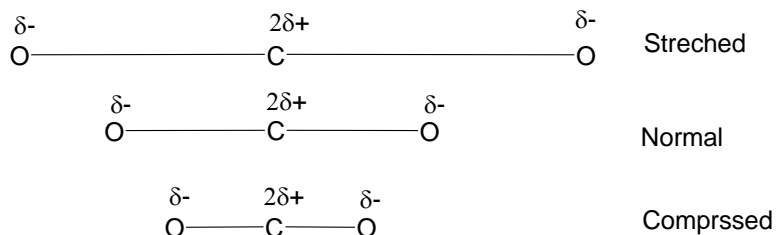
A molecule such as hydrogen chloride, HCl, in which one atom (the hydrogen atom) carries a permanent net positive charge and the other a net negative charge, is said to have a permanent electric dipole moment. H_2 and Cl_2 , on the other hand in which there is no such charge separation, have a zero dipole moment.

If we consider the rotation of HCl (notice that if only a pure rotation takes place, the centre of gravity of the molecule must not move), the plus and minus charges change places periodically, and the component dipole moment in a given direction (say upwards in the plane of the paper) fluctuates regularly. This fluctuation is plotted in the lower half of the figure and it is seen to be exactly similar in form to the fluctuating electric field of radiation. Thus interaction can occur, energy can be absorbed or emitted, and the rotation gives rise to a spectrum.

All molecules having a permanent dipole moment are said to be microwave active. If there is no dipole, as in case of H_2 or Cl_2 no interaction can take place and the molecule is microwave inactive. This imposes a limitation on the applicability of microwave spectroscopy.

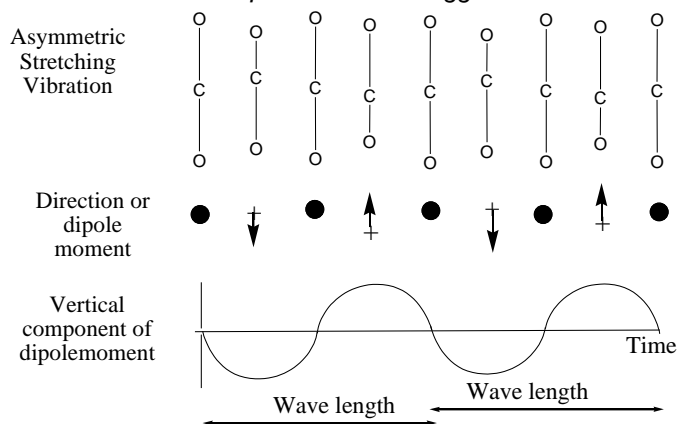
3. The infra-red region:

Here it is a vibration, rather than a rotation; which must give rise to a dipole change. Consider the carbon dioxide molecule as an example, in which the three atoms are arranged linearly with a small net positive charge on the carbon and small negative charges on the oxygen.



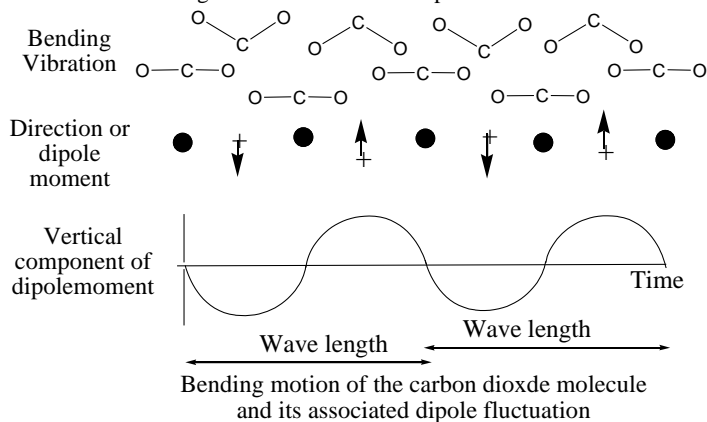
During the mode of vibration known as 'symmetric stretch', the molecule is alternatively stretched and compressed, both C-O bonds changing simultaneously. Plainly the dipole moment remains zero throughout the whole of this motion, and this particular vibration is thus infrared inactive.

Symmetric stretching vibration of the carbon dioxide molecule with amplitude much exaggerated



In anti-symmetric stretch (or asymmetric stretch), one bond stretches while the other bond is compressed, and vice versa. There is a periodic alternation in the dipole moment, and the vibration is thus infrared active.

Asymmetric stretching vibration of the carbon dioxide molecule showing the fluctuation in the dipole moment



Bending vibration is infrared active. In neither of these motions does the centre of gravity move. Note particularly that the relative motions of the atoms are very much exaggerated, but in real molecules, the displacement of atoms during vibration is seldom more than about 10% of the bond length.

Although dipole change requirements do impose some limitation of the application of infra-red spectroscopy, the appearance or non-appearance of certain vibration frequencies can give valuable information about the structure of a particular molecule.

4. The visible and ultraviolet region: The excitation of a valence electron involves the moving of electronic charges in the molecule. The consequent change in the electric dipole gives rise to a spectrum by its interaction with the electric field of radiation.

5. Photoelectron spectra (PES): PES offers one of the most accurate methods for determining the **ionization energies of molecules**. Photoelectron spectra can be studied either using the **X-ray** photons or **UV** photons. In the former case, they are called **XPES** spectra and in the latter case, **UVPES** (or **UPES**) spectra. If the energy of the incident photon is greater than the ionization energy, the ejected electron will possess excess kinetic energy. In **PES**, a beam of photons of known energy is allowed to fall on the sample and the kinetic energy of the ejected electrons is measured. The difference between the photon energy and the excess kinetic energy gives the **binding energy of the electron**.

6. Mössbauer spectra (also called Nuclear Gamma resonance (NRF) spectra): Mössbauer spectra constitute a type of nuclear resonance spectra like nuclear magnetic resonance spectra. Mössbauer However, while NMR spectra result absorption of low energy photons of frequency around 60MHz, Mössbauer spectra result from absorption of high energy γ -photons of frequency around 10^{13} MHz by the nuclei. γ ray spectra have been used specifically for the study of compounds of iron and tin. In this case, γ radiations from ^{57}Co source are allowed to fall on a sample in which the iron nuclei are in an environment identical with that of the source atoms. This results resonant absorption of γ rays. The splitting in **Mössbauer lines** are found to be of the same order as in NMR spectroscopy.

MICROWAVE SPECTROSCOPY OR ROTATIONAL SPECTROSCOPY

Moments of inertia

The moment of inertia of a molecule is defined as the mass of each atom multiplied by the square of its distance from the rotational axis through the centre of mass of the where r_i is the perpendicular distance of the atom i from the axis of rotation. The moment of inertia depends on the masses of the atoms present and the molecular geometry, so we can suspect (and later shall see explicitly) that rotational spectroscopy will give information about bond lengths and bond angles.

$$I = \sum m_i r_i^2$$

The spectroscopy in the microwave region is concerned with the study of rotating molecules. The rotation of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity- the principle axes of rotation. Thus a body has three principle moments of inertia, one about each axis, usually designed as I_A , I_B and I_C .

Molecules can be classified into groups according to the relative values of their principle moments of inertia.

1. Linear molecules: All the atoms are arranged in a straight line, HCl or OCS, C₂H₂ etc.

$$I_A = 0, I_B = I_C$$

The three directions of rotation may be taken as (a) about the bond axis, (b) end-over-end rotation in the plane of the paper, and (c) end-over-end rotation at right angles to the plane.

2. Symmetric tops: CH₃F, BCl₃ etc, $I_B = I_C \neq I_A, I_A \neq 0$

There are two subdivisions of this class.

$I_B = I_C > I_A$, then the molecule is called a prolate symmetric top: if $I_B = I_C < I_A$, it is referred to as oblate symmetric top BCl₃ and in this case $I_A = 2I_B = 2I_C$.

3. Spherical tops: If a molecule has all three moments of inertia are identical, CH₄, $I_A = I_B = I_C$.

Due to their symmetry, rotation alone can't produce dipole moment and hence no rotational spectrum is observable.

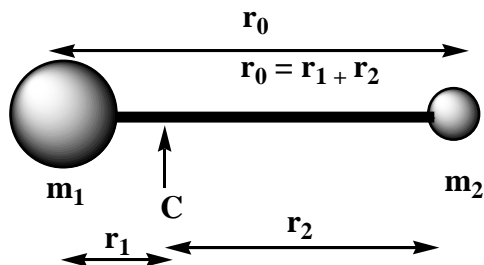
4. Asymmetric tops: These molecules, to which the majority of substances belong, have all three moments of inertia different $I_A \neq I_B \neq I_C$: H₂O, CH₂=CHCl.

The rotational energies are quantized, this means that a molecule cannot have any arbitrary amount of rotational energy (i.e., any arbitrary value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned.

The permitted energy values or also called as rotational energy levels may in principle be calculated for any molecule by solving Schrodinger equation for the system represented by that molecule.

Diatomic molecules:

1. Rigid diatomic molecule: Assume that there is no any vibration during the rotation of a molecule i.e., the bond length is constant.



A rigid diatomic molecule treated as two masses, m_1 and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$

Masses m_1 and m_2 are joined by a rigid bar (the bond) whose length is $r_0 = r_1 + r_2$, the molecule rotates end-over-end about a point C, the center of gravity: this is defined by the moment, or balancing, equation:

$m_1 r_1 = m_2 r_2$, The moment of inertia about C is defined by

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \\ &= r_1 r_2 (m_1 + m_2) \end{aligned}$$

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

$$\therefore r_1 = \frac{m_2 r_0}{m_1 + m_2} \text{ and } r_2 = \frac{m_1 r_0}{m_1 + m_2} \Rightarrow I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

It defines the moment of inertia conveniently in terms of the atomic masses and the bond length, where μ is called the *reduced mass* of the system.

By the use of Schrodinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{h^2}{8I\pi^2} J(J + 1), \text{ Joules, where } J = 0, 1, 2, \dots$$

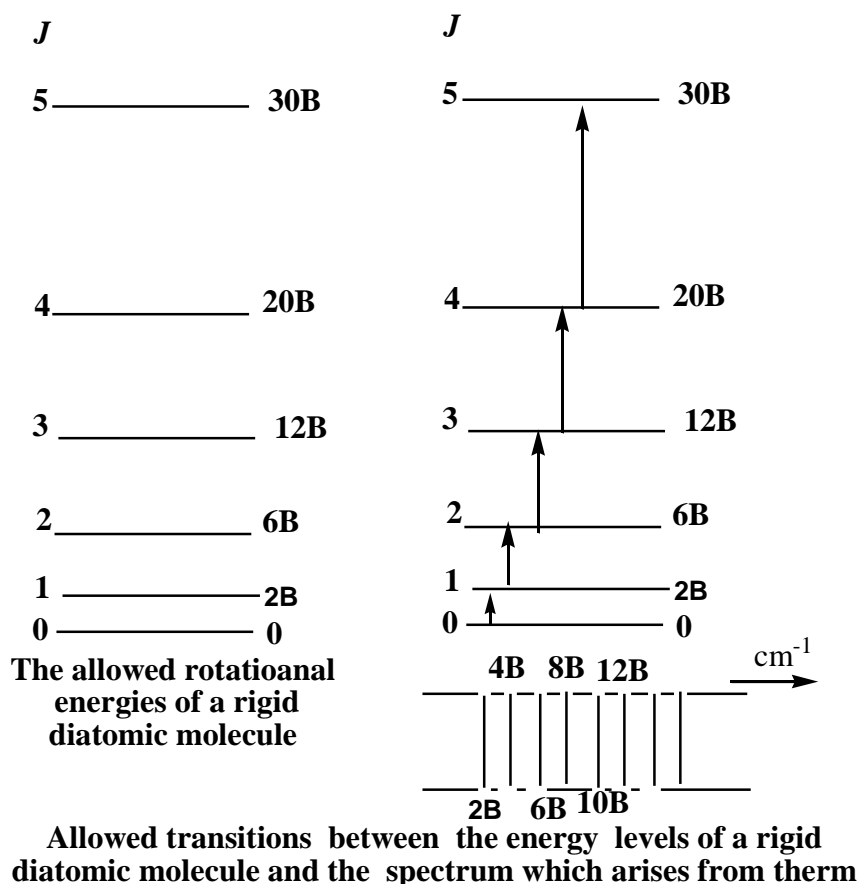
In this expression, h is Planck's constant, and I is the moment of inertia, either I_B or I_C since both are equal. The quantity J , which can take integral values from zero upwards, is called the rotational quantum numbers: its restriction to integral values arises directly out of the solution to the schrodinger equation and is by no means arbitrary, and it is this restriction which effectively allows only certain discrete rotational energy levels to the molecule.

Equation expressed the allowed energies in joule: and difference between these energies, or more particularly, in the corresponding frequency, $\nu = \Delta E / h$ Hz, or wave number, $\bar{\nu} = \Delta E / hc$ cm^{-1} , of the radiation emitted or absorbed as a consequence of changes between energy levels.

In the rotational region spectra are usually discussed in terms of wavenumber. So it is useful to consider energies expressed in these units,

$$\epsilon_J = \frac{E_J}{hc} = \frac{h^2}{8I\pi^2} J(J + 1), \text{ cm}^{-1}, \text{ where } J = 0, 1, 2, \dots$$

Where c , the velocity of light, is here expressed in cm s^{-1} , since the unit of wave number is reciprocal centimeters.



$$\epsilon_J = \frac{E_J}{hc} = B J (J + 1), \text{ cm}^{-1}, \text{ where } J = 0, 1, 2, \dots$$

Where B, the rotational constant, is given by $B = \frac{h^2}{8I\pi^2} \text{ cm}^{-1}$

For $J = 0$, $\epsilon_J = 0$, and the molecule is not rotating at all.

For $J = 1$, $\epsilon_J = 2B$ and a rotating molecule has its lowest angular momentum and it may continue to calculate ϵ_J with increasing J values and, in practice, there is no limit to the rotational energy the molecule may have. But there comes a point at which the centrifugal force of a rapidly rotating diatomic molecule is disrupted, but this point is not reached at normal temperatures.

In order to consider spectrum, the difference between the successive levels is important since the **selection rule is $\Delta J = \pm 1$** ,

Allowed transitions are $J = 0 \leftrightarrow J = 1$, $J = 1 \leftrightarrow J = 2$, $J = 2 \leftrightarrow J = 3$ etc

Forbidden transitions are $J = 0 \leftrightarrow J = 2$, $J = 1 \leftrightarrow J = 2$, $J = 2 \leftrightarrow J = 3$ etc

The difference between the first two energy levels is

$$\varepsilon_1 - \varepsilon_0 = \bar{\nu}_{J=0 \rightarrow J=1} = 2B - 0 = 2B \text{ cm}^{-1},$$

If the molecule raised from the $J = 1$ to $J = 2$ level by the absorption of more energy then

$$\varepsilon_2 - \varepsilon_1 = \bar{\nu}_{J=1 \rightarrow J=2} = 6B - 2B = 4B \text{ cm}^{-1},$$

In general, to raise the molecule from the state J to state $J + 1$,

$$\begin{aligned} \varepsilon_{J+1} - \varepsilon_J &= \bar{\nu}_{J \rightarrow J+1} = B(J+1)(J+2) - BJ(J+1) \\ &= B \{(J^2 + 3J + 2) - (J^2 + 1)\} \end{aligned}$$

$$\bar{\nu}_{J \rightarrow J+1} = 2B (J+1) \text{ cm}^{-1}$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \dots \text{cm}^{-1}$, while a similar lowering would result in an identical emission spectrum.

Application of rotational spectroscopy is to find the bond lengths of a molecule.

Rotational constant B can be deduced from the spectrum thereby I can be calculated provided the reduced mass of the molecule is known, and then there will be a possibility to calculate the bond length.

2 Spherical top molecules:

There are two directions of rotations, one through the axis **a**, other through **b** and **c**. Hence two quantum numbers J and K are needed for rotation around top axis C-F and J is used for end-over-end rotation around axis **b** and **c**. (I_B and I_C)

K may take the values $0, \pm 1, \pm 2, \pm 3, \dots, \pm J$ where + values represents rotation in a clockwise and anticlockwise direction about top axis.

$$\bar{\nu}_{J,K} = B J (J+1) + (A-B) K^2$$

$$\Delta\bar{\nu} = 2B (J+1)$$

Thus spectrum is just the same as for linear molecule and that the end-over-end rotation can only be measured in symmetric top molecules.

3. Spherical top molecules:

Such molecules don't have dipole moment and hence microwave inactive ($\text{CH}_4, \text{CCl}_4, \text{SF}_6$).

4. Asymmetric top molecules:

Those molecules possess three different moments of inertia and complex rotational levels. A simple general expression can't be derived for them because tedious computation is necessary (H_2O).

Vibrational spectroscopy or Infrared spectroscopy :

When IR radiation is incident on a molecule (having permanent or temporary dipole moment) its vibrational energy increases. Hence from the absorption of radiation in IR region of electromagnetic spectrum, information about the vibrational level of a molecule can be obtained.

When IR radiation is incident on a molecule present in gaseous phase, both vibrational, rotational energy changes occur, which makes this spectrum highly complex.

Such complexity may be however be avoided by taking the molecule in pure liquid state or in a solution medium where closely neighboring molecules prevent its rotation and only vibrational changes occur.

A particle undergoes harmonic motion if it experiences a restoring force proportional to its displacement: Hooke's law: the restoring force is proportional to the displacement.

$$F = -kx,$$

Where k is the force constant: the stiffer the 'spring', the greater the value of k . Because force is related to potential energy by $F = -dV/dx$, the force in corresponds to a potential energy.

This expression, which is the equation of a parabola, is the origin of the term 'parabolic potential energy' for the potential energy characteristic of a harmonic oscillator. The Schrodinger equation for the particle is therefore

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \varphi}{\partial x^2} + \frac{1}{2} Kx^2 \varphi = E\varphi$$

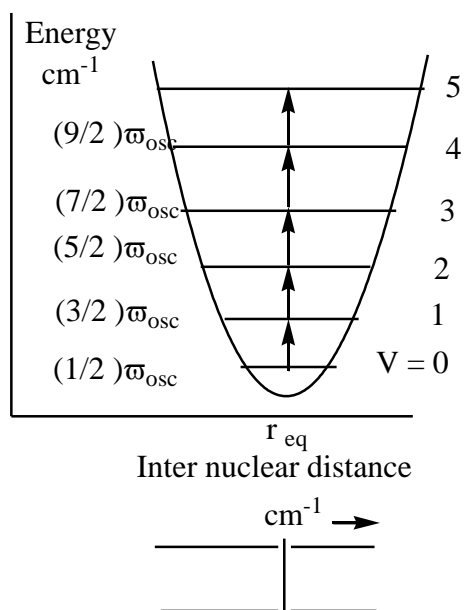
The energy levels

Quantization of energy levels arises from the boundary conditions: the oscillator will not be found with infinitely large compressions or extensions, so the only allowed solutions are those for which $\Psi = 0$ at $x = \pm\infty$

The permitted energy levels are

$$E_V = \left(V + \frac{1}{2}\right) h\omega \quad \text{Joules} \quad V = \text{vibrational quantum number, } 0, 1, 2, \dots$$

where $\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ Hz $\tilde{\omega}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$ cm⁻¹ and Where μ is the reduced mass of the system.



The vibrational energy levels and allowed transitions between them for a diatomic molecule under going simple harmonic motion

It follows that the separation between adjacent levels is

$$\epsilon_{V+1} - \epsilon_V = \tilde{\omega}_{osc}$$

Which is the same for all v . Therefore, the energy levels form a uniform ladder of spacing $\tilde{\omega}_{osc}$.

Selection rule:

The specific selection rule, which is obtained from an analysis of the expression for the transition moment and the properties of integrals over harmonic oscillator wavefunctions $\Delta V = \pm 1$ Transitions for which $\Delta V = + 1$ correspond to absorption and those with $\Delta V = - 1$ correspond to emission.

The wave mechanical treatment of molecular vibrations has a fundamental difference from the classical treatment in the fact that when the molecule is present at zero vibrational level, it still vibrates i.e., the vibrational energy at the ground vibrational level is not zero. The energy at this level is known as zero point energy (ZPE) is $\left(\frac{1}{2}\right)\tilde{\nu}$.

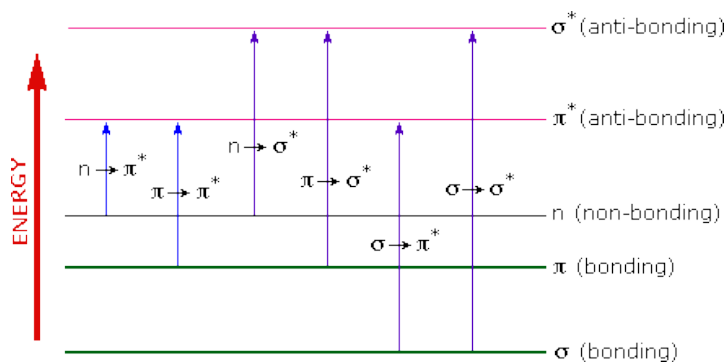
The gross selection rule for a change in vibrational state brought about by absorption or emission of radiation is that *the electric dipole moment of the molecule must change when the atoms are displaced relative to one another*. Such vibrations are said to be infrared active. The classical basis of this rule is that the molecule can shake the electromagnetic field into oscillation if its dipole changes as it vibrates, and vice versa.

Electronic spectroscopy

All molecules show electronic spectra since changes in the electronic distribution must always result in a change in dipolemoment.

$$\Delta E_{\text{electronic}} = 10^3 \times \Delta E_{\text{vibrational}} = 10^6 \times \Delta E_{\text{rotational}}$$

1. Electrons in majority of molecules may be classified into three types, such as σ , Π , and η (non bonding electrons).
2. A single bond contains only σ electrons and multiple bond contains both σ and Π electrons.
3. Atoms present in group VA, VI, VIIA possess nonbonding electrons (η).
4. σ electrons most firmly bound to nuclei and hence require high energy to undergo transitions.
5. Π and η electrons require less energy than electrons and electrons require still lesser energy than Π .



$\sigma \rightarrow \sigma^*$, $\Pi \rightarrow \sigma^*$, and $\eta \rightarrow \sigma^*$ transitions falls into far UV, $\Pi \rightarrow \Pi^*$ transitions falls into near UV region, and $\eta \rightarrow \Pi^*$ transitions falls into visible region

6. Saturated hydrocarbons having $\sigma \rightarrow \sigma^*$ transitions only and no $\eta \rightarrow \Pi^*$ or $\Pi \rightarrow \Pi^*$
7. However insertion of group containing η electrons such as $-\text{NH}_2$ allows possibility of $\eta \rightarrow \sigma^*$ transitions and at the same time it tends to increase the wave length of $\sigma \rightarrow \sigma^*$ transition (tends to decrease the energy). As a consequence, spectrum can be analyzed easily.
8. For isolated multiple bonds present in a molecule, $\sigma \rightarrow \sigma^*$ and $\Pi \rightarrow \Pi^*$ transitions are observed examples $-\text{C}\equiv\text{C}-$, $>\text{C}=\text{C}<$.
9. Compounds containing $-\text{C}\equiv\text{N}$, $>\text{C}=\text{O}$ groups may have additional $\eta \rightarrow \sigma^*$ and $\eta \rightarrow \Pi^*$

Beer-Lambert law:

Concentration and path length of the sample: If the concentration of the sample or its path length is increased, intensity of absorption increases. More the concentration of the sample, more intense is the spectral line.

The relationship between intensity (I_0) before absorption, intensity (I) after absorption, concentration of the sample (C) and path length (L) is given by Beer- Lambert's law.

$$I / I_0 = e^{-kCL} \quad \text{Where } k \text{ is a constant for a particular transition. } I / I_0 = e^{-\epsilon CL} = T$$

The above equation can be written as:

T is the Transmittance and ϵ is called the molar absorption coefficient. ϵ is called the molar absorption coefficient. ϵ depends on the wavelength and nature of absorbing material. Its unit is $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$. $\log(I/I_0) = \epsilon CL = \text{Absorbance (A) or optical density}$.

The Beer-Lambert law implies that the intensity of electromagnetic radiation transmitted through a sample at a given wave number decreases exponentially with the sample thickness and the molar concentration. If the transmittance is 0.1 for a path length of 1 cm (corresponding to a 90 per cent reduction in intensity), then it would be $(0.1)^2 = 0.01$ for a path of double the length (corresponding to a 99 percent reduction in intensity overall).

SOLID STATE

INTRODUCTION:

Solid is defined as that form of matter which possesses rigidity and hence a definite shape and definite volume. The rigidity is due to the absence of translational motion of the structural units.

Classification of solids:

Solids are of two types, Crystalline and Amorphous.

Crystalline solid: In which the constituent units (atoms, ions, molecules etc) are arranged with perfect order which repeats itself over very long distances. Examples: NaCl, Diamond... Etc.

Amorphous solid: In which the constituent units are arranged with irregular order. Examples: Rubber etc.

	CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS	
1.	Crystalline solids have definite geometrical configuration i.e., atoms; molecules are arranged in a regular 3-D pattern.	Amorphous solids do not have definite shape.	
2.	They have sharp melting point i.e., they change to liquid state abruptly.		They do not have sharp melting point. On heating they melt over a wide range of temperature.
3.	These are anisotropic i.e., the magnitude of the physical properties like electrical conductivity, thermal conductivity, refractive index are different along different directions.	These are isotropic i.e., they exhibit the same value of any property in all directions.	
4.	They have crystal symmetry i.e., when rotated about an axis, the appearance does not change	They don't possess symmetry.	

Structure determination of solids by X-ray diffraction: (Bragg's equation)

The structure of solids is determined by diffraction of X-rays

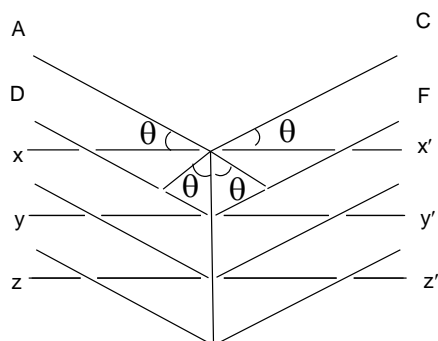
Braggs equation is

$$n \lambda = 2 d \sin \theta$$

n = serial order of diffracted beams = 1,2,3,....

d = distance between two planes

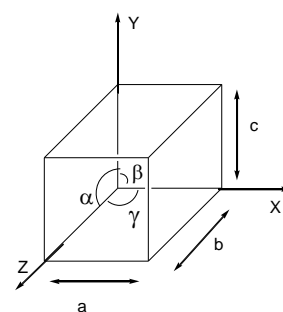
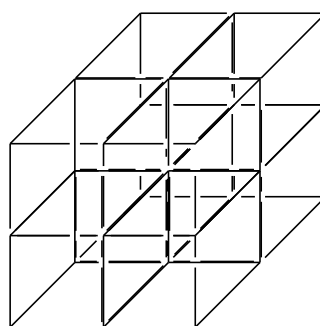
θ = angle of incident



CRYSTAL LATTICE: A regular arrangement of the constituent particles (atoms, molecules or ions) of a crystalline solid in 3-dimensional plane is called crystal lattice or space lattice. The positions which are occupied by the atoms, molecules or ions in the crystal lattice are called lattice points or sites.

UNIT CELL: The smallest 3-dimensional portion of a complete space lattice which when repeated over and over again in different directions, produces complete space lattice is called unit cell.

These are known as building blocks of crystal lattice. The size and shape of a unit cell is determined by the length of the edges a, b and c and by three angles α, β and γ .



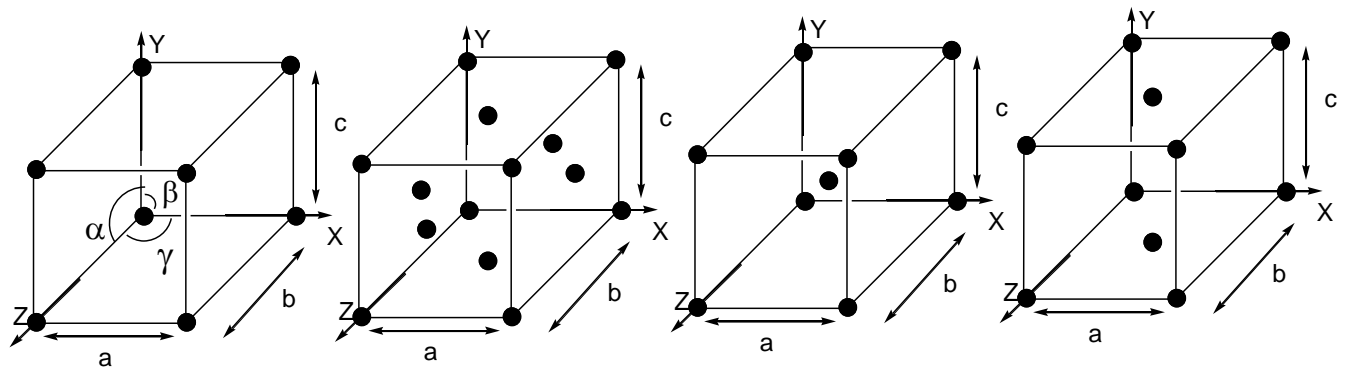
Based on the dimension of the unit cell, the unit cells are divided into seven types of units, called crystal system. Any crystal solid must belong to one of these crystal systems.

1. Simple or primitive unit cell (SU): A unit cell having lattice points only at the corners.

2. Face centered cubic cell (FCC): A unit cell having lattice points at the centre of each face in addition to the lattice points at the corners.

3. Body centered cubic cell (BCC): A unit cell having lattice points at the center of the body in addition to the lattice points at the corners.

4. End face centered cubic cell (EFCC): A unit cell having lattice points in the face center of only one set of faces in addition to the lattice points at the corners.



1. Simple or primitive (SU) 2. Face centered (FCC) 3. Body centered (BCC) 4. End face centered (EFCC)

Rank of a crystal: The rank of the crystal is defined as the number of atoms per unit cell. The rank of different unit cells is given in the following table.

1. Each particle at the corner of a unit cell is shared by 8 unit cells in the lattice and hence contributes only $1/8^{\text{th}}$ to a particular unit cell.
2. Each particle at the centre of a face of a unit cell is shared by two unit cells in the lattice and hence contributes only $1/2$ part to a particular unit cell.
3. A particle at the body center of a unit cell belongs only to the particular cell and hence it contributes wholly to a particular unit cell.

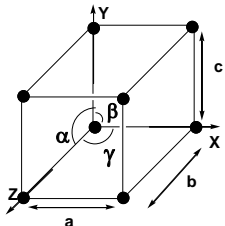
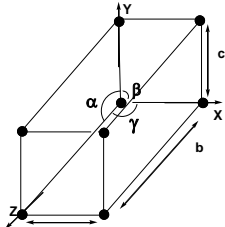
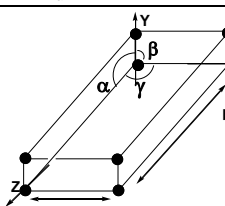
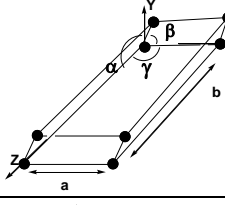
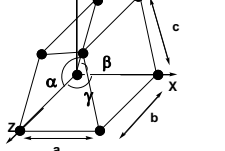
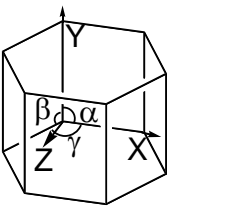
$$\text{Number of atoms per unit cell cubic structure} = \text{Rank of a crystal} = n = (n_c / 8) + (n_f / 2) + (n_i / 1)$$

n_c is total number of particles at corners in a unit cell, n_f is the total number of particles at face in a unit cell and n_i is body center.

	Unit cell	No. of atoms at corners	No. of atoms at faces	No. of atoms in center	Total no. of atoms or Rank
1.	Simple cubic (SU)	$8 (1/8) = 1$	0	0	1
2.	Body centered (BCC)	$8 (1/8) = 1$	0	1	2
3.	Face centered cubic (FCC)	$8 (1/8) = 1$	$6 (1/2) = 3$	0	4
4.	End face centered cubic (EFCC)	$8 (1/8) = 1$	$2 (1/2) = 1$	0	2
5.	HCP	$12 (1/6) = 2$	$2 (1/2) = 1$	3	6

Based on the dimension of the unit cell, the unit cells are divided into seven types of units, called crystal system. Any crystalline solid must belong to one of these crystal systems.

Crystal system and example	Shape	Parameters	No. of space lattice
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1.	Cubic system (NaCl, KCl, Diamond)		$a = b = c,$ $\alpha = \beta = \gamma = 90^\circ$	3 (SU, FCC and BCC)
2.	Tetragonal (Sn and SnO ₂)		$a = b \neq c,$ $\alpha = \beta = \gamma = 90^\circ$	2 (SU and BCC)
3.	Orthorhobic or Rhobic (Rhombic Sulphur, BaSO ₄)		$a \neq b \neq c,$ $\alpha = \beta = \gamma = 90^\circ$	4 (SU, FCC, Bcc and EFCC)
4.	Monoclic (Monoclinic Sulphur) 1-D tilted nature		$a \neq b \neq c,$ $\alpha \neq 90^\circ$ $\beta = \gamma = 90^\circ$	2 (SU and EFCC)
5.	Triclinic (CuSO ₄ 5H ₂ O)		$a \neq b \neq c,$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	1 (SU)
6.	Trigonal (As, Sb and Bi)		$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	1 (SU)
7.	Hexagonal (Zn and Cd)		$a = b \neq c,$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	1 (HCP)
				Total = 14 (Bravais lattices)

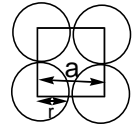
Bravais lattices:

1. There are only 14 different types of space lattices in several crystal systems which are known as Bravais lattice.

2. A combination of Bravais lattices with elements of symmetry produces 230 different arrangements which are known as Space groups

Relationship between r (radius) and a (lattice parameter)

1. Atomic radius of a simple cubic structure:



If a = lattice parameter i.e., length of cube edge, r = atomic radius, $a = 2r$, or $r = a / 2$.

2. Atomic radius of an FCC structure:



If a = lattice parameter and r = atomic radius

$$r = \{a (2)^{1/2}\} / 4 \quad \text{and, } AC^2 = AD^2 + CD^2$$

$$(r + 2r + r)^2 = a^2 + a^2 = 2 a^2, \quad 16 r^2 = 2 a^2$$

3. Atomic radius of B.C.C structure: $r = \{a (3)^{1/2}\} / 4$

4. Atomic Packing Factor (APF): The ratio of the volume occupied by the constituent particles to the volume of the unit cell is termed as the atomic packing factor (APF).

APF = Volume of the atoms per unit cell / Volume of the unit cell

$$= \{ \text{no. of atoms per unit cell} \times \text{volume of atom} \} / \text{Volume of the unit cell}$$

$$= \{ \text{Rank} \times \text{volume of atom} \} / \text{Volume of the unit cell}$$

1. for simple cubic structure:

$$\text{APF} = \{1 \times (4\pi r^3/3)\} / a^3 \quad \text{where } r = a/2 \quad \text{APF} = \{4 \pi a^3/3\} / \{8 \times a^3\} = \pi / 6 = 0.52$$

2. for FCC structure:

$$r = \{a (2)^{1/2}\} / 4 \quad \text{and} \quad \text{APF} = \{4 \times (4\pi r^3/3)\} / a^3$$

$$= \pi / 3(2)^{1/2} = 0.74$$

3. For BCC structure:

$$\text{APF} = 2 \times (4\pi r^3/3) / a^3 = \pi (3)^{1/2} / 8 = 0.68$$

Determination of Density of the solid:

n = no. atoms per unit cell in a cubic crystal., a = lattice parameter or edge length of the unit cell

M = Atomic weight of the solid material, N = Avagadro number

Density (D) = Mass / Volume = Mass of the unit cell / Volume of the unit cell

$$= \{ \text{rank of the system} \times \text{Molecular weight} \} / \{ \text{Avogadro number} \times (\text{lattice parameter})^3 \}$$

$$D = \{ n \times M \} / \{ N \times (a^3) \}$$

COORDINATION NUMBER:

Definition:

The number of oppositely charged ions surrounded an ion is the coordination number of that ion. The coordination number depends upon the relative size of the cations and anions.

In ionic crystals the positions are occupied by positive and negative ions in equivalent amounts. In such crystals the positive ions surrounded by negative ions and vice-versa.

1. FCC or CCP:

The crystal having the FCC or CCP arrangement has coordination number of the atom is 12.

It follows that each atom is in contact with 6 atoms in the same layer, 3 atoms above and 3 atoms below layer ($6 + 3 + 3$) = 12 atoms. (74 % available space). This type of arrangement gives ABC, ABC,.....

Example: Metals such as Cu, Ag, Au, Al, Ni, Fe,.....

2. BCC structure: In this type of arrangement the coordination number is 8, one atom is surrounded by four atoms in the same layer 2 atoms above and 2 atoms below the layer.

Example: Mn, Cr, Fe,..... (68 % of available space occupied by atoms)

3. HCP structure: In this type of arrangement one atom is surrounded by 12 atoms and hence the coordination number is 12. It has only two layers and the arrangement is of the type AB AB AB,.....

Example: Zn, Mg, Cd.... 74% of the available space is occupied by atoms.

In ionic compounds the coordination of the ions and the structure of the ionic compounds depends upon the radius ratio

Assumption: All the constituent particles are assumed to be spherical.

The ratio of the radii of the cation and the anion is called the radius ratio

	Limiting radius ration (r_+ / r_-)	Coordination number	Structure	Examples
1.	0 to 0.155	2	Linear	BeF ₂

2.	0.155 to 0.225	3	Planar triangle	
3.	0.225 to 0.414	4	Tetrahedral	ZnS, Cd, HgS
4.	0.414 to 0.732	4	Square Planar	$[\text{PtCl}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$
5.	0.414 to 0.732	6	Octahedral	NaCl, CaO, AgCl etc
6.	0.732 to 0.999	8	BCC	CsCl, CsBr, CsI

Tetrahedral hole: Vacant site is surrounded by the four spheres (Zinc blend).

Octahedral hole: Vacant site is surrounded by six spheres.

Coordination number of some simple ionic compound:

1. Ionic compounds of AX category:

Sodium Chloride (NaCl), Rock salt:

1. The (r_+ / r_-) of NaCl is 0.52 which is in the range of 0.414 to 0.732. It further indicates that NaCl has coordination number 6.
2. The structure may be regarded as CCP. An FCC array of bulky anions in which the cations occupy all octahedral holes.

Cesium Chloride structure (CsCl):

1. The (r_+ / r_-) of CsCl is 0.93 which is in the range of 0.732 to 0.999
2. Hence it is BCC arrangement having coordination number is 8.

Zinc blend structure:

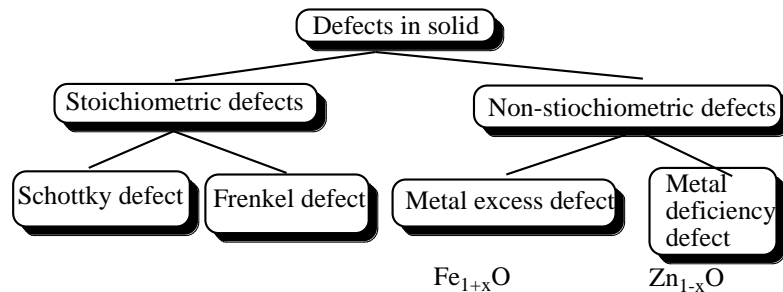
The radius ration is 0.40 which suggest a tetrahedral arrangement. Hence an extended FCC anionic lattice where cations occupy tetrahedral holes (4:4). Examples are ZnS, CdS HgS.....

Ionic compounds of AX₂ (CaF₂):

1. Radius ratio = 0.73,
2. Coordination number = 8:4
3. IN this type of structure the Ca²⁺ ions forms a FCC arrangement and F⁻ ions occupy all the tetrahedral holes.
4. Each Ca²⁺ ions are surrounded by 8 F⁻ ions and each F⁻ ions are surrounded by 4 Ca²⁺ ions.
5. This type of structure the coordination number is 8:4

Rutile Structure:

1. The radius ratio of this type of structure was found to be 0.41 to 0.73.
2. The structure was distorted BCC structure
3. The coordination number is 6:3
4. Each Ti^{4+} is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion has three Ti^{4+} around it in a plane triangular arrangement.



STIOCHIOMETRIC DEFECT:

In the ionic compounds (stoichiometric compound) irregularity in the arrangement of the ions in a lattice can occur due to the vacancy at a cation or anion site or by the migration of an ion to some other interstitial site. Two common types of such defects are Schottky defect and Frenkel defect.

Schottky defect:

1. This defect is caused if some of the lattice points are unoccupied i.e., atoms or ions are missing from their normal lattice sites. The lattice sites which are unoccupied are lattice vacancies or holes. In such case the number of positive ion and negative ions missed are same and thus the crystal remains neutral.

	<p>Conditions causing Schottky defects: It usually observed in highly ionic compounds having</p> <ol style="list-style-type: none"> 1. High coordination number. 2. Ions $\{(+)\text{ or }(-)\}$ of almost similar sizes e.g., NaCl, KCl, KBr, CsCl. <p>The number of Schottky defects per cc is given by</p> $n_s = e^{\left\{-\frac{w_s}{2KT}\right\}}$ <p>Where N is the number of sites /cc that could be left vacant. w_s is the work needed to form a Schottky defect, K = Boltzmann constant and T is the temperature.</p>
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Consequences:

1. Electrical conductivity increases.
2. Due to presence of holes in the crystal its density decreases.
3. Due to presence of holes, the stability (Lattice energy) of the crystal decreases.

Frenkel Defects:

It arises when an ion is missing from its normal position and occupies an interstitial site between lattice points. In this case also, the number of (+) and (-) ion remains same, so the crystal remains electrically neutral.

	<p>Conditions for causing frenkel defects: It occurs in compounds in which</p> <ol style="list-style-type: none"> 1. Coordination number is low. 2. Anion size > Cation size (AgCl, AgI, ZnS). This is because of small of size of Ag(+) that can go into interstitial sites. The number of frenkel defects per cc is given by $n_f = \sqrt{[NN']} e^{\{-\frac{W_f}{2KT}\}}$ <p>Where N is the number of sites / cc that could be left vacant N' is the number of interstitial position, W_f is the work necessary.</p>
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Consequences:

1. Electrical conductivity of the crystal increases.
2. It does not affect the density of the crystal.
3. Presence of holes decreases the stability of crystal (*i.e.*, lattice energy).

Both Schottky defect and Frenkel defects are called thermodynamic defects.