CHAPTER 2

ATOMIC STRUCTURE

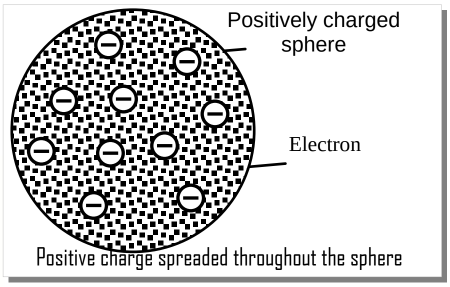
1. ATOMIC MODEL

(I) Dalton's model of atom :-

Dalton, in 1808 proposed Dalton’s atomic theory and according to theory matter was made up of extremely small, indivisible particles called atoms.

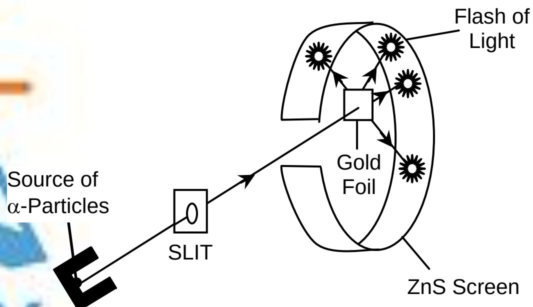
(II) Thomson's model of atom :-

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement Many different names are given to this model, for example, **plum pudding,raisin pudding or watermelon.**



(III) Rutherford’s Atomic Model The Nuclear Atom:

They directed a stream of very highly energetic α-particles from a radioactive source against a thin gold foil provided with a circular fluorescent zinc sulphide screen around it. Whenever α-particle struck the screen. A tiny flash of light was produced at the point.



Rutherford and Marsden’s α-particle scattering

Observation

(i) Most of the α-particles (99.9%) passed through the foil without undergoing any deflection.

(ii) Few α-particles underwent deflection through small angles.

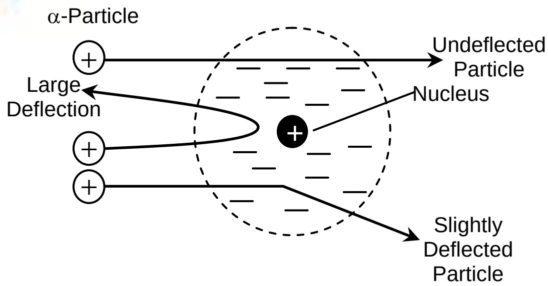
(iii) Very few (only one in 20,000) were deflected back i.e. through an angle greater than 90°.

Conclusion

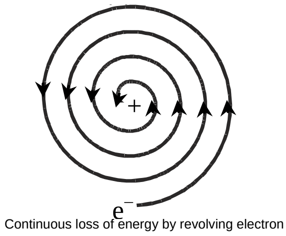
(1) Atom has a tiny dense central or the nucleus which contains practically the entire mass of the atom of the nucleus is about 10^{-13} cm. as compared to that of the atom 10^{-8} cm. It was this empty space around the nucleus which allowed the α-particles to pass through undeflected.

(2) The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around it. It was due to the presence of the positive charge on the nucleus that α- particles (He^{2+}) were repelled by it and scattered in all directions.

(3) The electrons were moving in orbit or closed circular paths around the nucleus like planets around the sun.



How nuclear atom causes scattering of α-



Continuous loss of energy by revolving electron

Drawbacks of Rutherford’s model Instability of Atomic Structure :

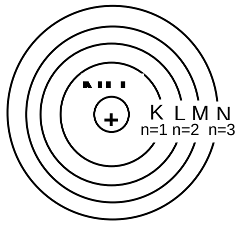
According to Rutherford’s model, electrons are removing around the nucleus in circular orbits. The centrifugal force (which arises due to the circular motion of electrons) acting outwards balances the electrostatics force of attraction (between the positively charged nucleus and the negatively charged electrons) acting inwards. This prevents the electrons to fall the nucleus. However, it had been shown by Clark Maxwell that a charge and accelerated particle loses energy constantly,due to electrostatic force of attraction; the electrons will fall is to nucleus. fig. since such a collapse of the atom does not take place , therefore, Rutherford’s model of the atom is faulty.

Failure to Explain Atomic Spectra :

Rutherford's model could not explain the formation of line spectrum. According to electromagnetic theory, frequency of radiation of a charged body is equal to its frequency of revolution. Since the electron orbit is continuously changing the frequency of revolution also changes continuously. As a result, atomic spectra of hydrogen should have been continuous rather than line spectra. This is not in agreement with the observed facts.

(IV) Bohr's Atomic Model

Neil's Bohr (1913) developed a new theory of the atomic structure on the basis of quantum theory of radiation. The main point of his theory are –



Circular orbits (energy levels / stationary states) around the

Bohr's Assumptions

(i) An atom consist of a dense nucleus situated at the centre around which the electrons in circular orbit.

(ii) Of the very large number of possible circular orbits around the nucleus, the electron can move only in certain fixed orbits known as stationary state.

(iii) Each fixed or stationary state associated with a definite amount of energy.

These different energy levels are numbered as 1, 2, 3, 4 etc. (from nucleus outward) or alternatively they are designated as K, L, M, N shell etc.

(iv) The electron in an atom can have certain definite or discrete value of energy which are characteristics of that atom. In other words: The electronic energy of an atom is quantized.

(v) The electron in an atom can revolve only in those energy levels for which the angular momentum of an electron is a whole number multiple $\frac{h}{2\pi}$ i.e.

For circular motion, the magnitude of the angular momentum of the electron is mvr

Bohr's quantization of the angular momentum is $L = mvr = \frac{nh}{2\pi}$ (where n = 1, 2, 3, ….)

Hence the integer n is called principal quantum number.

where m → mass of an electron.
v → velocity
r → radius of orbit in which the electron moving
n → orbit of the electron

(VI) The emission or absorption of electromagnetic radiation occurs only when there is a transition of electrons between two stationary states. When an electron changes from a higher energy orbit to a lower energy orbit. The excess energy is emitted as a photon. $\Delta E = En_2 - En_1 = h\nu$

Limitations of Bohr's Theory

(i) It is unable to explain the line spectra of multi electronic atoms.

(ii) It also fails to account for the multiple of fine structure of the spectral lines. Each spectral line has been found to consist of a number of component line was observed closely in a spectroscope of high revolving power. This suggested the presence of sub energy level in a main energy level, which was not suggested by Bohr.

(iii) The further splitting up of spectral lines under the influence of strong magnetic field (Zeeman's effect) is not explained by Bohr.

(iv) Bohr gave a flat model of the atom in which electrons are revolving in circular orbits around the nucleus. But at present it is believed that atom has a three dimensional model. The new model leads the concept of orbitals in place of Bohr's definite orbits.

(v) This theory cannot explain the directional bonding between atoms in some molecules and thus the shape of such molecules. de-Broglie concept of dual character of matter. According to this concept, an electron behaves not only as a particle but also as a wave. Bohr, however, considered electrons only as discrete particles.

$$E = \frac{N\,hc}{\lambda}$$

Study of Emission and Absorption Spectra

A radiation which consists of one wavelength only is called **Monochromatic.** Light such as sunlight which consists of radiation of different wavelength is known as polychromatic. When a polychromatic light is passed through a prism, it splits in to radiations of different wavelengths. This splitting of a polychromatic light in to its constituent radiation is called dispersion. It is due to bending of radiations (of different wavelength) through different angles. The pattern of radiations obtained due to dispersion, is called **Spectrum.**

The spectra are broadly classified into

1. Emission spectra 2. Absorption spectra

These are briefly explained below :

1. Emission spectra. When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc. is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called 'Emission spectrum'. Depending upon the source of radiation, the emission spectra are mainly of two types :

(i) **Continuous spectra** When white light from any source such as sun, a bulb or any hot glowing body is analyzed by passing through a prism, it is observed that it splits up into seven different wide bands of colours from violet to red, (like rainbow), as shown in fig. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum. It may be noted that on passing through the prism, red colour with the longest wavelength is deviated least while violet colour with shortest wavelength is deviated the most.

(ii) **Line spectra** When some volatile salt (e.g., sodium chloride) is placed in the bunsen flame or electric discharge is passed through a gas at low pressure as given in fig. , light is emitted. If this light is resolved in a spectroscope, it is found that no continuous spectrum is obtained but some isolated coloured lines are obtained on the photographic plate separated from each other by dark spaces.

2. Absorption spectra When white light from any source is first passed through the solution or vapours of a chemical substance and then analyzed by the spectroscope, it is observed that some dark lines are obtained in the otherwise continuous spectrum.

This shows that the wavelengths absorbed were same as were emitted in the emission spectra. The spectrum thus obtained is, therefore, called 'absorption spectrum.'

Emission spectrum of Hydrogen When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen . It is found to consist of a large number of lines which are grouped into different series, named after the discoverers.* The names of these series and the region in which they are found to lie are given in fig. The wavelength of different lines I.

Rydberg formula. Although a large number of lines are present in the hydrogen spectrum, rydberg in 1890 gave a very simple theoretical equation for calculation of the wavelengths of these lines. The equation gives the calculation of the wave numbers.

$\bar{v}$ of the lines by the formula $\bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$. where R is a constant , called **Rydberg constant**** and has a value equal to 109,677 cm^{-1}, n_1 and n_2 are whole numbers and for a particular series n_1 is constant and n_2 varies.For example,

When an electron jumps from an outer orbit in which its quantum number is 'n_2' to an inner orbit in which it is 'n_1'; the energy emitted as radiation is given by

$$E_{n_2} - E_{n_1} = \frac{2\pi^2 Z^2 e^4 m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{(b)}$$

and the frequency expressed in wave number will be

$$\bar{\upsilon} = \frac{2\pi^2 Z^2 e^4 m}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where R is the Rydberg constant. For hydrogen R is 109677.8 cm^{-1}.

Bohr's model explains sucessfully the spectrum of hydrogen atom and species having one electron. It explains the appearance of five series of lines in hydrogen spectrum.

Comparative study of important spectral series of Hydrogen atom

S.No.	Spectral series	Lies in the region	Transition
1. 2.	Lymen series	Ultraviolet region	$n_1 = 1 \quad n_2 = 2,3,4....\infty$
2.	Balmer series	Visible region	$n_1 = 2 \quad n_2 = 3,4,5....\infty$
3.	Paschen series	Infra red region	$n_1 = 3 \quad n_2 = 4,5,6....\infty$
4.	Brackett series	Infra red region	$n_1 = 4 \quad n_2 = 5,6,7....\infty$
5.	Pfund series	Infra red region	$n_1 = 5 \quad n_2 = 6,7,8....\infty$

S.No.	Spectral series	Lies in the region	Transition	$\lambda_{max} = \frac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R}$	$\lambda_{min} = \frac{n_1^2}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{n_2^2}{n_2^2 - n_1^2}$
1.	Lymen series	Ultraviolet region	$n_1 = 1$ $n_2 = 2,3,4....\infty$	$n_1 = 1$ and $n_2 = 2$ $\lambda_{max} = \frac{4}{3R}$	$n_1 = 1$ and $n_2 = \infty$ $\lambda_{min} = \frac{1}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{4}{3}$
2.	Balmer series	Visible region	$n_1 = 2$ $n_2 = 3,4,5....\infty$	$n_1 = 2$ and $n_2 = 3$ $\lambda_{max} = \frac{36}{5R}$	$n_1 = 2$ and $n_2 = \infty$ $\lambda_{min} = \frac{4}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{9}{5}$
3.	Paschen series	Infra red region	$n_1 = 3$ $n_2 = 4,5,6....\infty$	$n_1 = 3$ and $n_2 = 4$ $\lambda_{max} = \frac{144}{7R}$	$n_1 = 3$ and $n_2 = \infty$ $\lambda_{min} = \frac{9}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{16}{7}$
4.	Brackett series	Infra red region	$n_1 = 4$ $n_2 = 5,6,7....\infty$	$n_1 = 4$ and $n_2 = 5$ $\lambda_{max} = \frac{16 \times 25}{9R}$	$n_1 = 4$ and $n_2 = \infty$ $\lambda_{min} = \frac{16}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{25}{9}$
5.	Pfund series	Infra red region	$n_1 = 5$ $n_2 = 6,7,8....\infty$	$n_1 = 5$ and $n_2 = 6$ $\lambda_{max} = \frac{25 \times 36}{11R}$	$n_1 = 5$ and $n_2 = \infty$ $\lambda_{min} = \frac{25}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{36}{11}$

The above expression is called Rydberg formula.

Sommerfeld theory (1915) : It states that :

(i) The orbits in which the electrons move are in most cases elliptical.

(ii) The orbits are capable of interpenetrating and electrons in these orbits are spinning like a top.

(iii) The orbits are further divided into sub-orbits or sub-states which are denoted as '*s*' '*p*' '*d*' '*f*' orbitals.

A result of sommerfeld model suggests that $\frac{n}{k}=\frac{\text{length of major axis}}{\text{length of minor axis}}$

e.g., if principal quantum no. $n=4$.

The values of k can be 1, 2, 3, 4 only, since k is an integer

$\therefore$ 4th shell have 4 subshells.

Schrodinger wave equation : Bohr treated electron as a particle. However, de Broglie suggested that e^- has a dual nature, *i.e.,* it behaves both as a particle as well as wave. The wavelength λ of moving particle is

$$\lambda=\frac{h}{m\,v} \quad ....(1)$$

Where v and m are the velocity and mass of moving particle respectively. If *r* is radius of the wave, $2\pi r$ its circumference, then

$$\lambda n=2\pi r \quad ....(2)$$

Thus according to wave theory, an electron is a stationary wave moving around the nucleus in a circular path. The wave character was later on confirmed by Davison, Germer (1927) and Thomson (1928).

From eq. (1) and (2), we have

$$2\pi r=\frac{nh}{mv} \text{ or } mvr=\frac{nh}{2\pi}$$

According to Schrodinger, the electron does not move round the nucleus in fixed orbits, but may, infact, be any where with different probabilities. The probability of its presence near the nucleus is greatest and as the distance from nucleus increases the probability decreases. Schrodinger from mathematical treatment of wave motion gave a general wave equation describing the behaviour of a small particle. Consider a system such as a stretched string. For its vibration,

$\Psi=A\sin\frac{2\pi x}{\lambda}$. Where $x=$ displacement , $\Psi=$ wave function , $A=$ amplitude of the wave, $\lambda=$ wavelength

$$\frac{d^2\Psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-P.E.)\Psi=0$$

Ψ^2 for an electron at a given point indicates the probability of occurrence of the electron at that point.

(8) Electromagnetic spectrum : When sunlight is passed through a prism, it absorbs wavelength range of black colour radiation and other splits into a series of colour bands known as emission spectrum and black colour band which is known as absorption spectrum.

The splitting of light into seven colours is called emission Spectrum.The characteristic range of wavelength of electromagnetic radiation situated in an increasing or decreasing order called

electromagnetic spectrum.

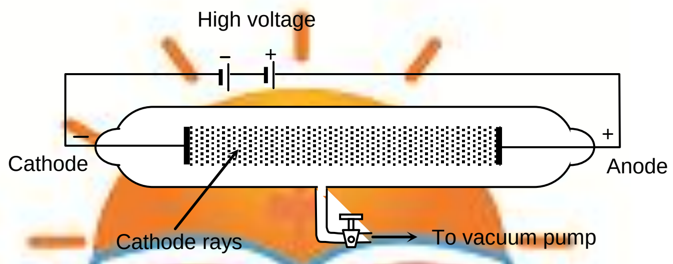
Wavelengths and frequencies of electromagnetic radiation's

Electromagnetic radiation	Wavelength(Å)	Frequency (Hz or sec-1)
Radiowaves	3×10^{13} to 3×10^{9}	1×10^{5} to 1×10^{9}
Microwaves	3×10^{9} to 6×10^{6}	1×10^{9} to 5×10^{11}
Infra red (IR)	6×10^{6} to 7600	5×10^{11} to 3.95×10^{14}
Visible (Decreasing λ, Increasing ν, E ↓)	**7600 to 3800**	**3.95×10^{14} to 7.9×10^{14}**
Ultraviolet (UV)	3800 to 150	7.9×10^{14} to 2×10^{16}
X–Rays	150 to 0.1	2×10^{16} to 3×10^{19}
Gamma rays	0.1 to 0.01	3×10^{19} to 3×10^{20}
Cosmic rays	0.01 to zero	3×10^{20} to infinity

Discovery of Electron Discharge Tube Experiment

We know that under normal condition of pressure, a gas is a poor conductor of electricity. However, if pressure is reduced, the gas be comes conducting, i.e. electricity starts flowing through the gas.

William Crooks, in 1879, studied the conduction of electricity through gases at low pressure. He performed the experiment in a discharge tube which is cylindrical hard glass tube about 60 cm in length. It is sealed at both the ends and fitted with two metal electrodes as shown in figure.



Emission of light under reduced pressure of 10^{-2} atm.

Emission of light under reduced pressure 10^{-2} atm.

The electrodes are connected to a source of high voltage while the tube is connected to a vacuum pump in order to reduce the pressure inside it and the following observation are made.

1. Under normal pressure (1 atmosphere). Nothing is observed even by applying high voltage of 10000 volts. This means that gas does not conduct the electric current.
2. The pressure inside the tube is slowly reduced by working the vacuum pump. When pressure is reduced to 10^{-2} atmosphere, the gas is found to emit light and colour of light depend upon of the nature of gas.
3. The emission of light cease when the pressure is reduced to 10^{-4} atmosphere, but the walls of the discharge tube opposite to cathode starts glowing with a faint greenish light called fluorescence.

Origin of Cathode Rays

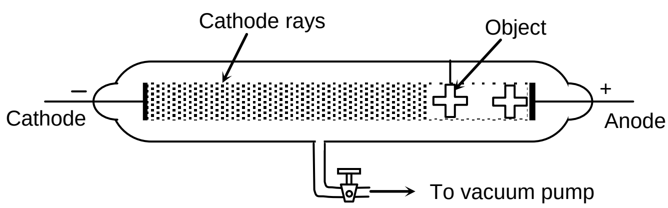
Cathode rays initially originate form the metal which constitutes the cathode. These are also formed due to bombardment of the molecules of the gas inside the discharge tube by the high speed of particles. (electrons) which are emitted from the cathode.

Properties of Cathode rays

The properties of cathode rays were studied by J.J. Thomson and co-workers based upon certain experiments.

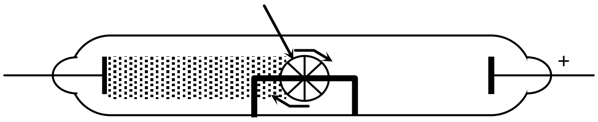
These are described as follows :

(i) **Cathode rays travel in straight line :** When a solid object is placed in the path of the cathode rays, its shadow is noticed immediately behind it. This shows that the cathode rays travel in straight line.



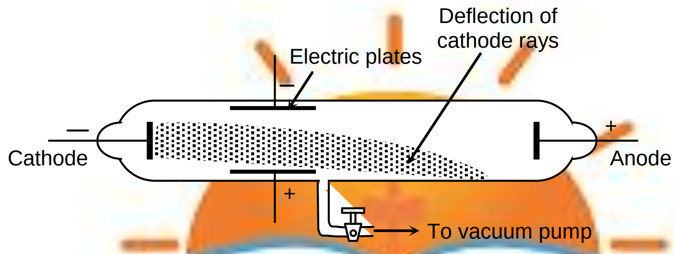
Cathode rays cast shadow of the object

(ii) **Cathode rays are made up of material particles :** If a light paddle wheel made from mica are mounted on an axis is placed in the path of the cathode rays, it starts rotating. This shows the cathode rays consists of material particle.



Cathode rays rotate light paddle wheel

(iii) **Cathode rays consist of negatively charged particle :** When electrical field is applied on the cathode rays with the help of a pair of metal plates as shown in figure, Cathode rays are found to be deflected towards the positive plate indicating the pressure of negative charge.



Deflection of cathode rays in electric field

similarly, when a magnetic field is applied, these are deflected in a direction which shows that they carry negative charge. R.A. Millikan (1917) by its oil drop experiment established that electron has charge = **e = 1.60 × 10^{-19} C** or **4.8 × 10^{-10} e.s.u.**

(iv) J.J. Thomson (1897) found that $\frac{e}{m} = \frac{\text{charge}}{\text{mass}}$ = Specific charge = 1.76 × 10^8 C / gm.

(v) Cathode rays produce heating effect. When these rays are made to strike on a metal foil, the latter gets heated.

(vi) Cathode rays produce X-rays when they strike on surface of hard metals such as tungsten copper molybdenum etc.

(vii) Cathode rays can pass through thin foils of metals like aluminium. However, they are stopped if the foil in quite thick.

(viii) Cathode rays ionize the gas through which they pass.

(ix) Cathode rays affect the photographic plate. This is called fogging.

(x) When cathode rays strike against a glass surface or a screen coated with zinc sulphide, they produce. fluorescence (glow).

Mass of Electrons :

By using the Thomson's value of e/m and the Milikan's value of e , the absolute mass of an electron can be termed

e/m = –1.76 × 10^8 coulomb/g. (THOMSON)

e = –1.60 × 10^{-19} coulomb. (MILIKAN)

$\therefore \quad e \Big/ {}^{e}\!/_{m} = \dfrac{1.6\times10^{-19}}{1.76\times10^{8}} q$

m = 9.1×10^{-28} gm.

= 9.1×10^{-31} kg.

Mass of Electron Relative to Hydrogen :

Avogadro number , the number of atoms in one gram atom of any element is 6.023×10^{23}

From this we can find the absolute mass of hydrogen atom 6.023×10^{23} atoms of Hydrogen

$$= 1.008 \text{ a.m.u.} = \frac{1.008}{6.023\times10^{23}} \text{gm}$$

$$= 1.67\times10^{-24} \text{g}$$

But the mass of electron = 9.1×10^{-28} g.

$$\therefore \quad \frac{\text{mass of H atoms}}{\text{mass of electron}} = \frac{1.67\times10^{-24}}{9.1\times10^{-28}} = 1{,}835 \times 10^{3} = 1835$$

Thus a H atom is 1835 times as heavy as an electron.

In other words, The mass of an electron is $\frac{1}{1835}$th of the mass of hydrogen.

An electron is a negatively charged subatomic particle which bears charge 1.6×10^{-19} coulombs and has mass 9.1×10^{-28} gm or 9.1×10^{-31} Kg.

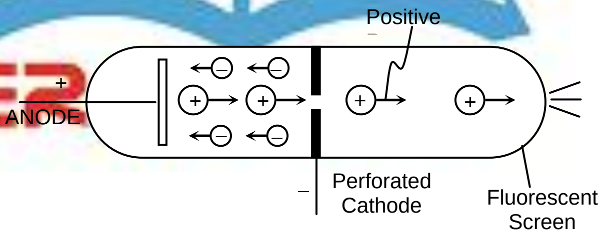
Alternatively, an electron may be defined as, A particle which bears one unit negative charge and mass 1/1835th of a hydrogen atom.

Anode Rays :

How are Anode rays produced ?

When high speed of electrons (cathode rays) strike molecules of a gas placed in the discharge tube, they knock out one or more electrons from it and results positive ions.

$$m \rightarrow m^{+} + e^{-}$$



Production of Positive rays

These positive ions pass through the perforated cathode and appears as positive rays. When electric discharge is passed through the gas under high electric pressure, its molecules are dissociated in to atoms and the positive atoms (ions) constitute the positive rays.

Properties of Anode Rays :

(i) They travel in a straight line in a direction opposite to cathode.

(ii) They are deflected by electric as well as magnetic field in a way indicating that they positively charged.

(iii) The charge to mass ratio (e/m) of positive particles varies with the nature of the gas placed in the discharge tube.

(iv) They possess mass many times the mass of an electron.

(v) They cause fluorescence in zinc sulphide.

Proton (Goldstein-1886) :

E-Goldstein discovered protons in the discharge. Tube containing hydrogen.

$$H \longrightarrow \underset{\text{Proton}}{H^{+}} + e^{-}$$

It was J.J. Thomson who studied their nature. He showed that

(1) The actual mass of the proton is 1.672×10^{-24} gram. On the relative scale, proton has mass 1 atomic mass unit. (a.m.u.)

(2) The electrical charge of protons is equal in magnitude but opposite to that of the electron.

Thus proton carries a charge $+1.6\times10^{-19}$ coulombs or +1 elementary charge unit .

Since proton was the lightest positive particle found in atomic beams in the discharge tube. It was taught to be a unit present in all other atoms. protons were also obtained in a Variety of nuclear reaction indicating further that all atoms contains protons.

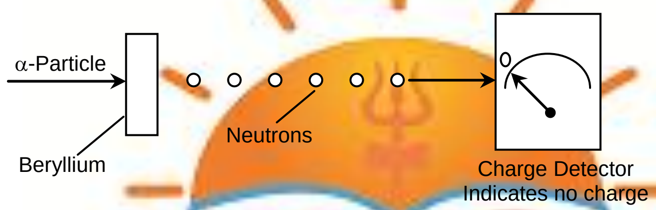
Thus a proton is defined as a subatomic particle which has a mass of 1.a.m.u. and charge +1 elementary charge unit or simplifying.

A proton is a subatomic particle which has one unit mass and one unit positive charge.

Neutrons (James Chadwick-1932):

James chadwick discovered the third subatomic particle – He directed a stream of alpha particle ${}_{2}^{4}He$ at a beryllium target. He found that a new particle was ejected. It has almost the same mass (1.674×10^{-24} gm) as a proton and has no change.

$${}_{2}^{4}He + {}_{4}^{9}Be \longrightarrow {}_{6}^{12}c + {}_{0}^{1}n$$



(α-particles directed at beryllium sheet eject neutrons whereby the electric charge detector remains unaffected)

(α-particle directed at beryllium sheet eject neutrons where by the electric charge detector remains unaffected.)

The assigned relative mass of a neutron is approximately one atomic mass unit. (a.m.u.) Thus, A neutron is a subatomic particle, which has mass equal to that of proton and has no charge.

SUBATOMIC PARTICLE

Particle	Symbol	Nature	Charge	Mass(a.m.u)	in kg	Discover
Electron	$-1e^{o}$ or e	Negatively charged particle	-1.6×10^{-19} Coulombs or one unit negative charge or 4.8×10^{-10} e.s.u	0.000549	9.1×10^{-31}	J.J. Thomson
Proton	P or ${}_{1}H^{1}$	Hydrogen nucleus	$+1.602 \times10^{-19}$ c or one unit positive charge	1.00758	1.672×10^{-27}	Goldstein
Neutron	${}_{0}n^{1}$	Neutral particle	Zero Charge	1.00893	1.674×10^{-27}	Chadwick
Positron	$+{}_{1}e^{O}$		one unit positive charge i.e. +1	0.000549	9.1×10^{-31}	Anderson
Neutrino Antineutri–No	${}_{O}e^{O}$		Zero charge	less than the mass of electron 0.00002		Fermi
Antiproton	${}_{-1}p$		Negative charge	1.00758		Chamber Lain

Meson	π	Positive (π^+) Neutral (π^0) Negative (π^-)	+ve charge No charge –ve charge	273 times heavier than the mass of electron.		Yukawa

(3) **Other fundamental particles and Antiparticles**

Bryons : These are heavy particles and include protons, neutrons etc.

Mesons : These are particles of intermediate mass.

Leptons : These are lighter particles viz. electron, μ particles and neutrions.

Positron : C.D. Anderson (1932) discovered it. It has same negligible mass and same amount of charge as of the electron. But charge is+ve and of short life 10^{-8} *sec*.

Meson : Yukawa (1935) discovered it. It has mass in between that of proton and electron in cosmic rays. The charge may be +*ve*, –*ve* or zero.

Neutrino (υ): Pauli (1927) suggested the existence of a particle called neutrino. It has a variable mass less than that of an electron. The charge on this particle is zero. Allen and Rodebeek (1952), showed their free existence.

Antiproton (p^- **) :** Segre (1956) discovered it. It has mass equal to that of a proton but with a negative charge.

Allotropy : When the element exists in 2 or more forms in the same state that differ in physical properties, it is said to exhibit allotropy, while these forms are called allotropes of that element.

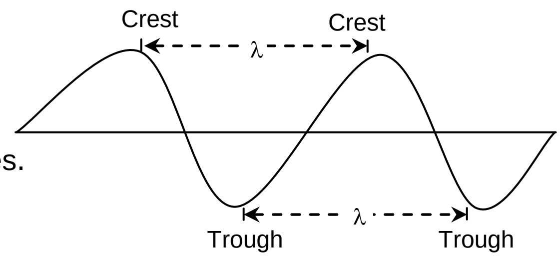
Note : ❑ The mass (*m*) of a particle (electron) at high speed is given by:

$$m = \frac{m_{rest}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$, Where , v = velocity of particle, c = velocity of light

If $v = c$, then $m = \infty$.

Nature of Light and Electromagnetic Spectrum:

According to Newton, light was regarded as a stream of particles also known as the corpuscles of light. The particle nature could explain certain phenomena such as refraction and reflection associated with light. But at the same time, it failed to explain two other important phenomena called interference diffraction. The corpuscular theory of light was, therefore , replaced by wave theory given by **Huygens**. In 1856, James Clark Maxwell stated that light, X-rays, γ-rays and heat etc. emit energy continuously in the form of radiations or waves and the energy is called **radiant energy.** These waves are associated with electric and magnetic fields and are, therefore, known as electromagnetic waves (or radiations).



Propagation of waves

Electromagnetic Wave Theory

A few important characteristics of these waves are listed :

(i) They emit energy continuously in the form of radiations or waves.

(ii) The radiations consists of electric and magnetic fields which oscillate perpendicular to each other and also perpendicular to the direction in which the radiations propagate.

(iii) All the electromagnetic waves travel with the velocity of light (3.0×10^8 ms^{-1}).

(iv) These rays do not require any medium for propagation.

Some important Characteristics of a Wave

(a) **Wavelength** (λ or lamda). The electromagnetic waves propagate as crests and Troughs. Wavelength may be defined as the distance between any two consecutive crests or troughs.

Wavelength may expressed in different units such as Angstron , micron, millimicron, nanometre, picometre etc. All of them are related to S.I . unit i.e. metre as follows :

1A = 10^{-10} m; 1 micron(μ) = 10^{-6} m, 1 milli micron (mμ) = 10^{-9} m

1 nm = 10^{-9} m; 1 pm = 10^{-12} m.

(b) **Amplitude** (a) is the height of the crest or depth of the trough and is also expressed in the units of length.

(c) **Frequency (ν or nu)** is the number of the wavelengths which passes through a point in one second. The units of the frequency are cycles per second (or sec^{-1}) or Hertz (Hz)

1 Hz = 1 cycle per second

It may be noted that a cycle is complete when a wave consisting of one crest and one trough passes through a point. The electromagnetic waves differ in their frequency and wavelength.

(d) **Velocity (c)** of a wave is the linear distance travelled by the wave in one second. It is measured in ms^{-1}.

(e) **Wave number** ($\bar{\nu}$) may be defined as the number of wavelengths which can be accommodated one cm length along the direction of propagation. The SI unit of $\bar{\nu}$ is m^{-1}. But the units cm^{-1} is also commonly used.

Wave number $(\bar{\nu}) = \dfrac{1}{\text{Wavelength}\,(\lambda)}$

Electromagnetic spectrum :

Different types of electromagnetic waves (or radiation) differ with respect to wavelength and frequency. The wavelength of electromagnetic waves increase in the order: wavelengths increase in the following order :

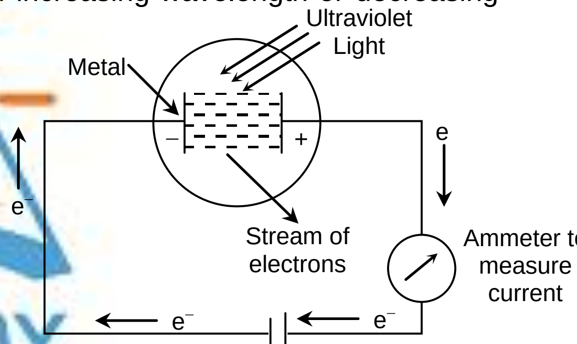
Cosmic rays < γ-rays < X-rays < Ultra violet rays < Visible < Infrared < Microwaves < Radiowaves.

The complete range of the electromagnetic waves is known as **electromagnetic spectrum.** It may be defined as : The arrangement of different electromagnetic radiations in order of increasing wavelength or decreasing frequency . It may be shown as follows.

Limitations of Electromagnetic Wave Theory

PHOTOELECTRIC EFFECT

When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface. This phenomenon is known as Photoelectric effect.



Apparatus for measuring the photoelectric effect

For higher frequencies $\nu > \nu_o$ a part of energy goes to loosen the electron and remaining for imparting kinetic energy to the photoelectron, thus –

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

Black Body Radiation

An ideal black body is that which is a perfect absorber and a perfect emitter of radiations. When radiant energy is allowed to fall on a carbon black or a blackened metallic surface the energy is almost completely absorbed. When such a body is heated, it becomes first of all red, then orange, then yellow and last of all white at a very high temperature.

It emits radiations more than any other body on heating and hence it is also a perfect radiator.

What is mass number ?

The total number of protons and neutrons in the nucleus of an atom is called the mass number; it is represented by A.

Composition of Nucleus :

Knowing the atomic number (Z) and mass number (A) of an atom, we can tell the number of protons and neutrons contained in the nucleus; By-definition.

Atomic Number, Z = Number of protons = No. of electons.

Mass Number , A = Number of protons + Number Of Neutrons

$\therefore$ The number of neutrons is given by the express ion N = A – Z

Isotopes : These are the atoms of the same element which have the same atomic number but different mass number

e.g $\;{}^{1}_{1}H$ (Protium), ${}^{2}_{1}H$ (Deuterium), ${}^{3}_{1}H$ (Tritium)

O-atom is also having three isotopes

$${}^{16}_{8}O \quad {}^{17}_{8}O \quad {}^{18}_{8}O$$

Isotopes arises because of different number of neutrons and same number of protons.

Cl-atom is having two Isotopes

$${}^{35}_{17}Cl \quad \& \quad {}^{37}_{17}Cl$$

Isobars : The atoms which have the same mass number but different atomic number are called Isobars. The word isobar meaning 'Equally heavy'

iso = equal and barys = heavy For e.g. ${}^{40}_{18}Ar, {}^{40}_{19}K,$ and ${}^{40}_{20}Ca$ are isobaric atoms . Similarly ${}^{235}_{92}U, {}^{235}_{93}Np$ and ${}^{235}_{94}Pu$ are isobars.

Isotones :

Atoms which have different atomic numbers and different atomic masses but the same numbers of neutrons are called Isotones. For e.g. ${}^{14}_{6}C$, ${}^{15}_{7}N$ and ${}^{16}_{8}O$ are isotones since each contains eight neutrons.

Isoelectronic : The species which have the same number of electrons are called Isoelectronic.

e.g. O^{2-}, Ne, Na^{+}, F^{-}

Size of Isoelectronic species is inversely proportional to its nuclear charge.

i.e. Order of their size is $O^{2-} > F^{-} > Ne > Na^{+} > Mg^{2+}$

Isodiaphers : Species with same isotopic number *i.e.* (A-2*Z*) or (*n–Z)*

Planck's Quantum theory of Radiations:

Max Planck in 1900 , put forward a theory known as **Planck's Quantum Theory.** This was further extended by Einstein in 1905. The main points of the theory are :

(1) The radiant energy is emitted or absorbed discontinuously in the form of small energy packets called Quanta. In case of light, these energy packets are known as photons.

(2) The energy of each quantum is directly proportional to the frequency of the radiation

$$E \propto \nu \qquad \text{or} \qquad E = h\nu = h\frac{c}{\lambda}$$

Here h is a constant known as Planck's constant. Its value is 6.62×10^{-34} J sec or 3.99×10^{-13} kJ sec mol^{-1}.

(3) The total amount of energy emitted or observed by a body is some whole number or integral multiple of quantum i.e.

$$E = nh\nu$$

(Here n is an integer)

The energy associated with Avogadro's number of quanta is called Einstein energy (E). Its value may be given as

Dual Nature of Matter(de-Broglie Equation)

In 1924, Louis de-Broglie suggested that just as light exhibits wave and particle properties all microscopic material particles in motion such as electrons, protons, atoms, ions, molecules etc. have also dual character.

IN OTHER WORDS

All material particles in motion possess wave characteristics.

According to de-Broglie, " the wavelength associated with a particle of mass m, moving with velocity v is given by the relation".

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad (p = m \cdot v)$$

where h is the Planck's constant and mv is the momentum of the particle. The wave associated with material particles are called ***Matter waves***.

Derivation Of de-Broglie Equation

He derived a relationship between the magnitude of the wavelength associated with mass 'm' of a moving body and its velocity.

According to Planck, photon of light having energy E is associated with a wave of frequency ν as –

$$E = h\nu \qquad \ldots(i)$$

where h is the Planck's constant and ν the frequency of radiation.

By applying Einstein's mass energy relationship the energy associated with photon of mass m.

$$E = m \cdot c^2 \qquad \ldots(ii)$$

where c is the velocity of light.

Combining the above two relation in equation (i) and (ii), we get :-

$$h\nu = mc^2$$

Now, since $\nu\lambda = c$ or $\nu = \frac{c}{\lambda}$

$\therefore$ $\frac{hc}{\lambda} = mc^2$

$\frac{h}{\lambda} = mc$ or $\lambda = \frac{h}{mc}$

The equation is valid for a photon. de-Broglie suggested that on substituting the mass of the particle m and its velocity v in place of velocity of light c the equation can also be applied to a material.

Thus, the wavelength of material particles, λ is

$$\boxed{\lambda = \frac{h}{mv}}$$

This equation is known as de-Broglie's equation.

or $\lambda = \frac{h}{p}$

where p stands for the momentum (mv) of the particle since h is constant

Heisenberg's uncertainty principle

According to uncertainty principle "It is impossible to specify at any given moment both the position and momentum of an electron".

Mathematically it is represented as , $\boxed{\Delta x . \Delta p \geq \frac{h}{4\pi}}$

Where $\Delta x =$ uncertainty is position of the particle, $\Delta p =$ uncertainty in the momentum of the particle

Now since $\Delta p = m\,\Delta v$

So equation becomes, $\Delta x . m\Delta v \geq \frac{h}{4\pi}$ or $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

QUANTUM NUMBERS

Quantum numbers are the index numbers which are used to specify the position and energy of an electron in an atom. The word quantum is used to signify that all the energy levels which are available to an electron are governed by the laws of quantum mechanics.

There are four quantum numbers. The significant aspects of the four quantum numbers are described below :

1. Principle quantum number (*n*)

It was proposed by *Bohr's* and denoted by '*n*'. It determines the average distance between electron and nucleus, means it is denoted the size of atom.

$$r = \frac{n^2}{Z} \times 0.529\,\mathring{A}$$

It determine the energy of the electron in an orbit where electron is present.

$$E = -\frac{Z^2}{n^2} \times 313.3\, Kcal\, per\, mole$$

The maximum number of an electron in an orbit represented by this quantum number as $2n^2$. No energy shell in atoms of known elements possess more than 32 electrons. It gives the information of orbit *K, L, M, N*------------.

The value of energy increases with the increasing value of *n.* It represents the major energy shell or orbit to which the electron belongs. Angular momentum can also be calculated using principle quantum number

$$mvr = \frac{nh}{2\pi}$$

2. Azimuthal quantum number (*l*)

Azimuthal quantum number is also known as angular quantum number. Proposed by *Sommerfield* and denoted by '*l*'. It determines the number of sub shells or sublevels to which the electron belongs. It tells about the shape of subshells. It also expresses the energies of subshells $s < p < d < f$ (increasing energy).The value of $l = (n-1)$ always where '*n*' is the number of principle shel

Value of *l*	=	0	1	2	3……….(n-1)
Name of subshell	=	s	p	d	f
Shape of subshell	=	Spherical	Dumbbell	Double dumbbell	Complex

It represent the orbital angular momentum. Which is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$. The maximum number of electrons in subshell $= 2(2l+1)$.

Let	*l* =1	$m = -1$	0	+1
		p_x or p_y	p_z	p_y or p_x
Let	$l = 2$	$m = -2$	-1 0	+1 +2
		d_{xy} or	d_{xz} or d_{z^2},	d_{yz} or $d_{x^2-y^2}$,
		$d_{x^2-y^2}$	d_{yz}	d_{xz} or d_{xy}

3. Magnetic quantum number (*m*)

It was proposed by *Zeeman* and denoted by '*m*'. It gives the number of permitted orientation of subshells. The value of *m* varies from –*l* to +*l* through zero. It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proved the Zeeman effect.

Sub orbit or Sub shell	Value of l	Value of m
s	0	0
p	1	-1, 0, +1
d	2	-2, -1, -0, +1, +2
f	3	-3, -2, -1, -0, +1, +2, +3

4. Spin quantum numbers (*s*)

It was proposed by *Goldshmidt & Ulen Back* and denoted by the symbol of 's'. The value of $'s'$ is $+1/2$ and $-1/2$, which is signifies the spin or rotation or direction of electron on it's axis during movement.The spin may be clockwise or anticlockwise.

It represents the value of spin angular momentum is equal to $\frac{h}{2\pi}\sqrt{s(s+1)}$.

Maximum spin of an atom $= 1/2 \times$ number of unpaired electron.

Electronic configuration of elements is governed by the following rules :-

Aufbau Principle (German : Aufbau means building up)

According to this principle, the electrons are filled in various orbitals in order of their increasing energies. Thus an orbital with lowest energy will be filled first. The energy content of the two sub-shell can be compared by means of (n + l) rule as explained below.

(i) The subshell with lower (n + l) value will possess lower energy and will be filled first for e.g. 4s subshell is filled first than 3d

(a) for 4s – subshell : n + l = 4 + 0 = 4

(b) for 3d – subshell : n + l = 3 + 2 = 5

Since (n + l) value of 4s subshell is less than 3d, the 4s subshell has lower energy and is filled first.

(ii) The subshell with lower value of n possesses lower energy if (n + l) values for both subshell are equal for e.g. 3p subshell is filled than 4s

(a) for 3p subshell : n + l = 3 + 1 = 4

(b) for 4s – subshell n + l = 4 to 4

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d.

The order is diagrammatically illustrated in figure.

***(n + l)* rule :** The subshell with lower values of $(n+l)$ possesses lower energy level and should be filled first.

e.g., $_{19}K$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$ is correct

$n+l$ of $4s = 4+0 = 4$

$n+l$ of $3d = 3+2 = 5$

Thus, 4*s* should be filled first.

If $(n+l)$ is same for two subshells, the one with lower values of *n* possess lower energy and should be filled first. e.g. $_{21}Sc$: $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 4p^1$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1, 4s^2$ is correct

$n+l$ of $4p = 4+1=5$

$n+l$ of $3d = 3+2=5$

Thus, $3d$ should be filled first.

Θ n of $3d < n$ of $4s$

(iv) A subshell having nearly full filled or nearly half filled configuration tends to acquire exactly full filled or exactly half filled nature in order to attain stability i.e. lower energy level.

e.g. $_{24}Cr$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4, 4s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$ is correct

$_{29}Cu$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$ is correct

$_{46}Pd$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^8, 5s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}$ is correct

Number of nodes : Total number of nodes in a shell $=(n-1)$

Angular nodes $= l$

Spherical nodes $= n-l-1$

Nodes and Nodal planes

As we have learnt nodes are the positions where radial wave function passes through zero. These are also called radial nodes.

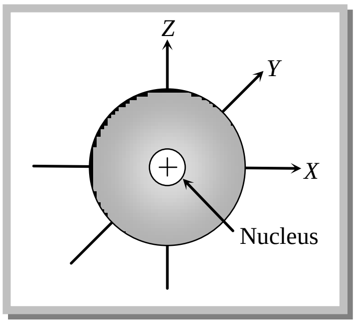
Beside radial nodes, the probability density functions for np and nd orbitals are zero at the planes passing through the nucleus. For example as shown in figure, in case of $2p^3$ orbital, xy plane is a nodal plane. This is called Angular Node or Nodal Plane. Similarly, for of the 3d orbitals ($3d_{xy}$, $3d_{yz}$, $3d_{3x}$ and $3d_{x^2-y^2}$) have two perpendicular nodal planes that intersect in a line passing through the nucleus. For example, $3d_{xy}$ orbital have two nodal planes, passing through the origin and bisecting the xy plane containing z-axis. The number of angular nodes or given by 'l' i.e, one angular node for p orbitals, two angular nodes for d-orbitals and so on.

In general, in an orbital : Total number of nodes = n – 1, Angular nodes = l, Radial nodes = n – l – 1.

Hund's Rule of Maximum Multiplication

According to this rule "Electron filling will not take place in orbitals of same energy until all the available orbitals of a given subshell contain one electron each with parallel spin".

	1s	2s	2p
N Z = 7	↑↓	↑↓	↑ ↑ ↑
O Z = 8	↑↓	↑↓	↑↓ ↑ ↑
Ne Z = 10	↑↓	↑↓	↑↓ ↑↓ ↑↓



Pauli's exclusion principle

According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers *n*, *l*, *m* and *s* . In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different.

Shape of orbitals

(1) Shape of 's' orbital

(i) For 's' orbital *l*=0 & *m*=0 so 's' orbital have only one unidirectional orientation i.e. the probability of finding the electrons is same in all directions.

(ii) The size and energy of 's' orbital with increasing '*n*' will be $1s < 2s < 3s < 4s$.

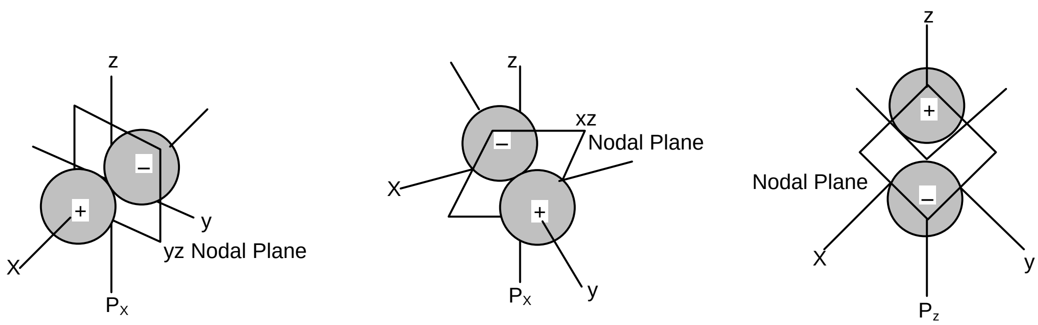
(iii) It does not possess any directional property. *s* orbital has spherical shape.

(2) **Shape of '*p*' orbitals**

(i) For '*p*' orbital *l*=1, & *m*=+1,0,–1 means there are three '*p*' orbitals, which is symbolised as p_x, p_y, p_z.

(ii) Shape of '*p*' orbital is dumb bell in which the two lobes on opposite side separated by the nodal plane.

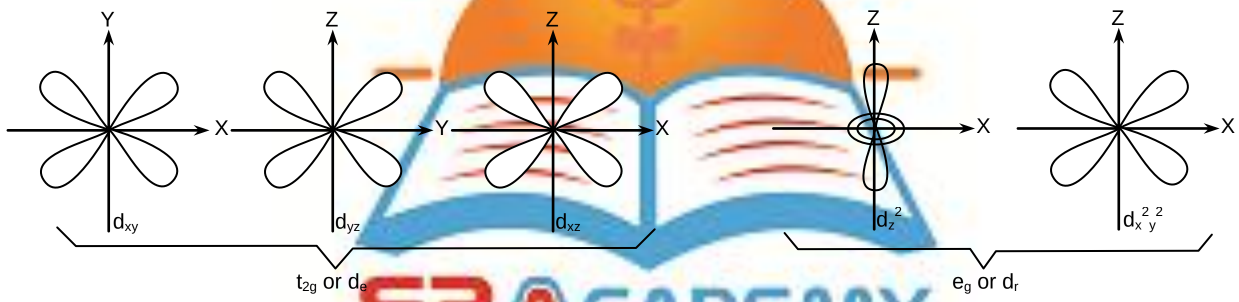
(iv) *p*-orbital has directional properties.



(3) **Shape of '*d*' orbital**

(i) For the 'd' orbital *l* =2 then the values of '*m*' are –2,–1,0,+1,+2. It shows that the '*d*' orbitals has five orbitals as $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$.

(ii) Each '*d*' orbital identical in shape, size and energy. (iii) The shape of *d* orbital is double dumb bell .(iv) It has directional properties.



(4) **Shape of '*f*' orbital**

(i) For the '*f*' orbital *l*=3 then the values of '*m*' are –3, –2, –1,0,+1,+2,+3. It shows that the '*f*' orbitals have seven orientation as $f_{x(x^2-y^2)}, f_{y(x^2-y^2)}, f_{z(x^2-y^2)}, f_{xyz}, f_{z^3}, f_{yz^3}$ and f_{xz^2}.

(ii) The '*f*' orbital is complicated in shape.