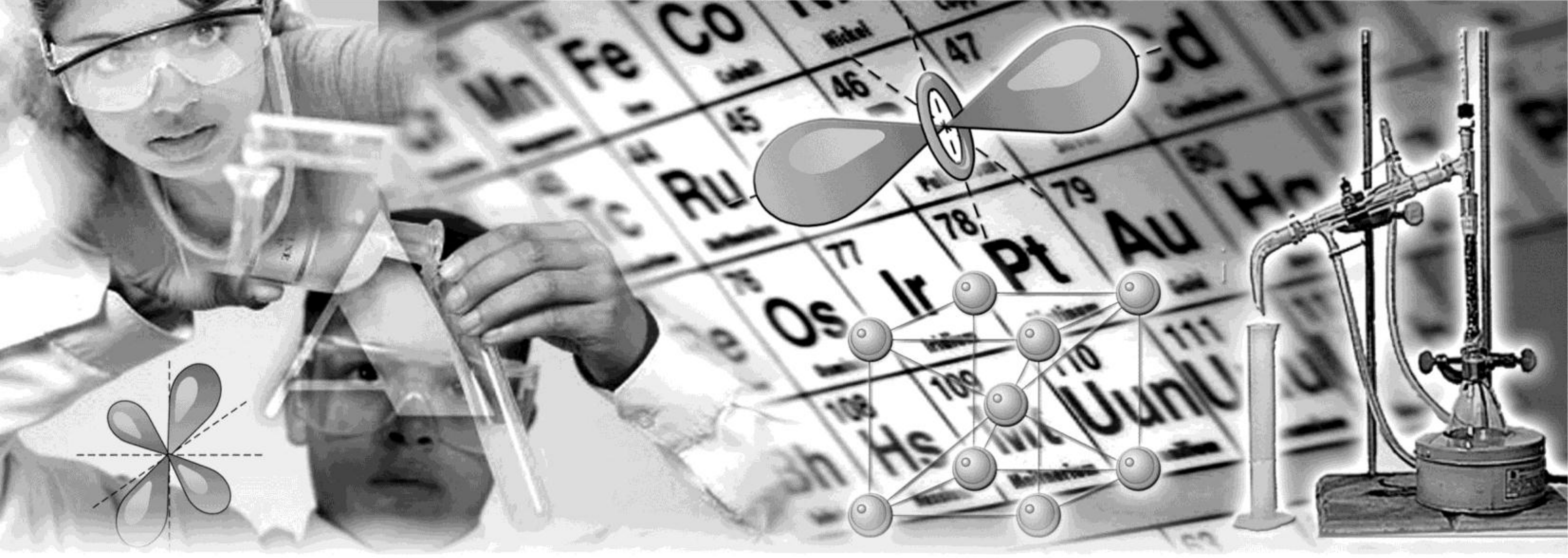


Chapter
2
Structure of atom

John Dalton 1808, believed that matter is made up of extremely minute indivisible particles, called *atom* which can takes part in chemical reactions. These can neither be created nor be destroyed. However, modern researches have conclusively proved that atom is no longer an indivisible particle. Modern structure of atom is based on Rutherford's scattering experiment on atoms and on the concepts of quantization of energy.

Composition of atom

The works of J.J. Thomson and Ernst Rutherford actually laid the foundation of the modern picture of the atom. It is now believed that the atom consists of several *sub-atomic particles* like electron, proton, neutron, positron, neutrino, meson etc. Out of these particles, the electron, proton and the neutron are called *fundamental subatomic particles* and others are *non-fundamental particles*.

Electron ($_{-1}e^{0}$)

(1) It was discovered by ***J.J. Thomson*** (1897) and is *negatively charged particle*. Electron is a component particle of cathode rays.

(2) Cathode rays were discovered by ***William Crooke's & J.J. Thomson*** (1880) using a cylindrical hard glass tube fitted with two metallic electrodes. The tube has a side tube with a stop cock. This tube was known as ***discharge tube***. They passed electricity (10,000 *V*) through a discharge tube at very low pressure $(10^{-2}$ to $10^{-3} mm\ Hg)$. Blue rays were emerged from the cathode. These rays were termed as ***Cathode rays***.

(3) **Properties of Cathode rays**

(i) Cathode rays travel in straight line.

(ii) Cathode rays produce mechanical effect, as they can rotate the wheel placed in their path.

(iii) Cathode rays consist of negatively charged particles known as *electron*.

(iv) Cathode rays travel with high speed approaching that of light (ranging between 10^{-9} to 10^{-11} *cm/sec*)

(v) Cathode rays can cause fluorescence.

(vi) Cathode rays heat the object on which they fall due to transfer of kinetic energy to the object.

(vii) When cathode rays fall on solids such as $Cu, X-$rays are produced.

(viii) Cathode rays possess ionizing power *i.e.*, they ionize the gas through which they pass.

(ix) The cathode rays produce scintillation on the photographic plates.

(x) They can penetrate through thin metallic sheets.

(xi) The nature of these rays does not depend upon the nature of gas or the cathode material used in discharge tube.

(xii) The e/m (charge to mass ratio) for cathode rays was found to be the same as that for an e^{-} $(-1.76 \times 10^{8}$ coloumb per *gm*). Thus, *the cathode rays are a stream of electrons.*

(xiii) According to *Einstein's theory of relativity, mass* of electron in motion is, $m' = \dfrac{\text{Rest mass of electron(m)}}{\sqrt{[1-(u/c)^2]}}$

Where u = velocity of electron, c= velocity of light.

When $u=c$ than mass of moving electron $=\infty$.

Proton (H, H, P)

(1) Proton was discovered by ***Goldstein*** and is positively charged particle. It is a component particle of anode rays.

(2) **Goldstein (1886)** used perforated cathode in the discharge tube and repeated Thomson's experiment and observed the formation of anode rays. These rays also termed as *positive* or *canal rays*.

(3) **Properties of anode rays**

(i) Anode rays travel in straight line.

(ii) Anode rays are material particles.

(iii) Anode rays are positively charged.

Table : 2.1 Comparison of mass, charge and specific charge of electron, proton and neutron

Name of constant	*Unit*	**Electron(e^-)**	**Proton(p^+)**	**Neutron(n)**
Mass (*m*)	Amu *Kg* Relative	0.000546 9.109×10^{-31} 1/1837	1.00728 1.673×10^{-27} 1	1.00899 1.675×10^{-27} 1
Charge(*e*)	Coulomb (*C*) Esu Relative	-1.602×10^{-19} -4.8×10^{-10} – 1	$+1.602 \times 10^{-19}$ $+4.8 \times 10^{-10}$ +1	Zero Zero Zero
Specific charge (*e/m*)	C/g	1.76×10^{8}	9.58×10^{4}	Zero
Density	Gram / cc	2.17×10^{-17}	1.114×10^{14}	1.5×10^{-14}

- The atomic mass unit (amu) is 1/12 of the mass of an individual atom of ${}_6C^{12}$, *i.e.* $1.660 \times 10^{-27}\,kg$.

Table : 2.2 Other non fundamental particles

Particle	Symbol	Nature	Charge esu $\times 10^{-10}$	Mass (amu)	Discovered by
Positron	$e^+, 1e^0, \beta^+$	+	+ 4.8029	0.0005486	Anderson (1932)
Neutrino	ν	0	0	< 0.00002	Pauli (1933) and Fermi (1934)
Anti-proton	p^-	–	– 4.8029	1.00787	Chamberlain Sugri (1956) and Weighland (1955)
Positive mu meson	μ^+	+	+ 4.8029	0.1152	Yukawa (1935)
Negative mu meson	μ^-	–	– 4.8029	0.1152	Anderson (1937)
Positive pi meson	π^+	+	+ 4.8029	0.1514	Powell (1947)
Negative pi meson	π^-	–	– 4.8029	0.1514	
Neutral pi meson	π^0	0	0	0.1454	

(iv) Anode rays may get deflected by external magnetic field.

(v) Anode rays also affect the photographic plate.

(vi) The *e*/*m* ratio of these rays is smaller than that of electrons.

(vii) Unlike cathode rays, their e/m value is dependent upon the nature of the gas taken in the tube. It is maximum when gas present in the tube is hydrogen.

(viii) These rays produce flashes of light on *ZnS* screen.

Neutron (n, N)

(1) Neutron was discovered by ***James Chadwick*** (1932) according to the following nuclear reaction,

$${}_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1$$

$$\text{or } {}_5B^{11} + {}_2He^4 \rightarrow {}_7N^{14} + {}_0n^1$$

(2) Neutron is an unstable particle. It decays as follows,

$$\underset{\text{neutron}}{{}_0n^1} \longrightarrow \underset{\text{Proton}}{{}_1H^1} + \underset{\text{electon}}{{}_{-1}e^0} + \underset{\text{antinutrino}}{{}_0\nu^0}$$

Atomic number, Mass number and Atomic species

(1) **Atomic number or Nuclear charge**

(i) The number of protons present in the nucleus of the atom is called *atomic number* (*Z*).

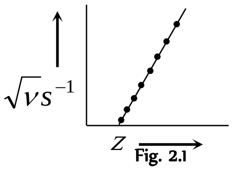


Fig. 2.1

(ii) It was determined by **Moseley** as,

$\sqrt{\nu} = a(Z - b)$ or $aZ - ab$

Where, $\nu = X$ – ray's frequency

Z= atomic number of the metal a & b are constant.

(iii) Atomic number = Number of positive charge on nucleus = Number of protons in nucleus = Number of electrons in nutral atom.

(iv) *Two different elements can never have identical atomic number.*

(2) **Mass number**

Mass number (A) = Number of protons or Atomic number (*Z*) + Number of neutrons or Number of neutrons = *A* – *Z* .

(i) Since mass of a proton or a neutron is not a whole number (on atomic weight scale), weight is not necessarily a whole number.

(ii) The atom of an element X having mass number (*A*) and atomic number (Z) may be represented by a symbol, ${}_ZX^A$.

Table: 2.3 Different types of atomic species

Atomic species	Similarities	Differences	Examples
Isotopes (Soddy)	(i) Atomic No. (*Z*) (ii) No. of protons	(i) Mass No. (*A*) (ii) No. of neutrons	(i) ${}_1^1H, {}_1^2H, {}_1^3H$

	(iii) No. of electrons (iv) Electronic configuration (v) Chemical properties (vi) Position in the periodic table	(iii) Physical properties	(ii) $^{16}_{8}O, ^{17}_{8}O, ^{18}_{8}O$ (iii) $^{35}_{17}Cl, ^{37}_{17}Cl$
Isobars	(i) Mass No. (A) (ii) No. of nucleons	(i) Atomic No. (Z) (ii) No. of protons, electrons and neutrons (iii)Electronic configuration (iv) Chemical properties (v) Position in the perodic table.	(i) $^{40}_{18}Ar, ^{40}_{19}K, ^{40}_{20}Ca$ (ii) $^{130}_{52}Te, ^{130}_{54}Xe, ^{130}_{56}Ba$
Isotones	No. of neutrons	(i) Atomic No. (ii) Mass No., protons and electrons. (iii) Electronic configuration (iv) Physical and chemical properties (v) Position in the periodic table.	(i) $^{30}_{14}Si, ^{31}_{15}P, ^{32}_{16}S$ (ii) $^{39}_{19}K, ^{40}_{20}Ca$ (iii) $^{3}_{1}H, ^{4}_{2}He$ (iv) $^{13}_{6}C, ^{14}_{7}N$
Isodiaphers	Isotopic No. ($N - Z$) or ($A - 2Z$)	(i) At No., mass No., electrons, protons, neutrons. (ii) Physical and chemical properties.	(i) $_{92}U^{235}$, $_{90}Th^{231}$ (ii) $_{19}K^{39}$, $_{9}F^{19}$ (iii) $_{29}Cu^{65}$, $_{24}Cr^{55}$
Isoelectronic species	(i) No. of electrons (ii) Electronic configuration	At. No., mass No.	(i) $N_2O, CO_2, CNO^-(22e^-)$ (ii) $CO, CN^-, N_2(14e^-)$ (iii) $H^-, He, Li^+, Be^{2+}(2e^-)$ (iv) $P^{3-}, S^{2-}, Cl^-, Ar, K^+ and\ Ca^{2+}(18e^-)$
Isosters	(i) No. of atoms (ii) No. of electrons (iii) Physical and chemical properties.		(i) N_2 and CO (ii) CO_2 and N_2O (iii) HCl and F_2 (iv) CaO and MgS (v) C_6H_6 and $B_3N_3H_6$

Electromagnetic radiations

(1) Light and other forms of radiant energy propagate without any medium in the space in the form of waves are known as *electromagnetic radiations*. These waves can be produced by a charged body moving in a magnetic field or a magnet in a electric field. e.g. $\alpha -$ rays, $\gamma -$ rays, cosmic rays, ordinary light rays etc.

(2) **Characteristics**

(i) All electromagnetic radiations travel with the velocity of light.

(ii) These consist of electric and magnetic fields components that oscillate in directions perpendicular to each other and perpendicular to the direction in which the wave is travelling.

(3) A wave is always characterized by the following five characteristics,

(i) ***Wavelength*** **:** The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ (lambda) and is measured is terms of centimeter(cm), angstrom(Å), micron(μ) or nanometre (nm).

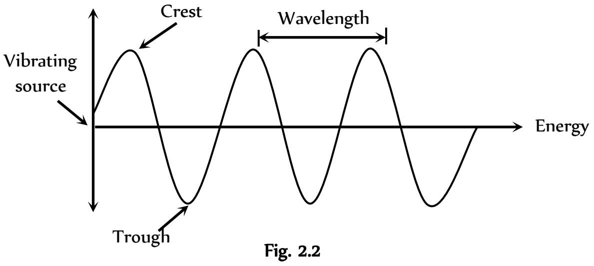


Fig. 2.2

$1Å = 10^{-8}\ cm = 10^{-10}\ m\ ; 1\mu = 10^{-4}\ cm = 10^{-6}\ m\ ;$

$1nm = 10^{-7}\ cm = 10^{-9}\ m\ ;\ \ 1cm = 10^{8}\ Å = 10^{4}\ \mu = 10^{7}\ nm$

(ii) ***Frequency*** **:** It is defined as the number of waves which pass through a point in one second. It is denoted by the symbol ν (nu) and is expressed in terms of cycles (or waves) per second (cps) or hertz (Hz).

$\lambda\nu$ = distance travelled in one second = velocity = c

$$\nu = \frac{c}{\lambda}$$

(iii) ***Velocity*** **:** It is defined as the distance covered in one second by the wave. It is denoted by the letter 'c'. All electromagnetic waves travel with the same velocity, i.e., $3\times10^{10}\ cm/\sec$.

$$c = \lambda\nu = 3\times10^{10}\ cm/\sec$$

(iv) ***Wave number*** **:** This is the reciprocal of wavelength, i.e., the number of wavelengths per centimetre. It is denoted by the symbol $\bar{\nu}$ (nu bar). It is expressed in cm^{-1} or m^{-1}.

$$\bar{\nu} = \frac{1}{\lambda}$$

(v) ***Amplitude*** **:** It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'A'. It determines the intensity of the radiation.

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelengths or frequencies is known as ***electromagnetic spectrum***.

Table: 2.4

Name	Wavelength (Å)	Frequency (Hz)
Radio wave	$3\times10^{14}-3\times10^{7}$	$1\times10^{5}-1\times10^{9}$
Microwave	$3\times10^{7}-6\times10^{6}$	$1\times10^{9}-5\times10^{11}$
Infrared (IR)	$6\times10^{6}-7600$	$5\times10^{11}-3.95\times10^{16}$
Visible	$7600-3800$	$3.95\times10^{16}-7.9\times10^{14}$
Ultraviolet (UV)	$3800-150$	$7.9\times10^{14}-2\times10^{16}$
X-Rays	$150-0.1$	$2\times10^{16}-3\times10^{19}$
$\gamma-$ Rays	$0.1-0.01$	$3\times10^{19}-3\times10^{20}$
Cosmic Rays	0.01- zero	3×10^{20} – infinity

Atomic spectrum - Hydrogen spectrum

Atomic spectrum

Spectrum is the impression produced on a photographic film when the radiation (s) of particular wavelength (s) is (are) analysed through a prism or diffraction grating.

Types of spectrum

(1) **Emission spectrum :** Spectrum produced by the emitted radiation is known as emission spectrum. This spectrum corresponds to the radiation emitted (energy evolved) when an excited electron returns back to the ground state.

(i) ***Continuous spectrum*** **:** When sunlight is passed through a prism, it gets dispersed into continuous bands of different colours. If the light of an incandescent object resolved through prism or spectroscope, it also gives continuous spectrum of colours.

(ii) ***Line spectrum*** **:** If the radiation's obtained by the excitation of a substance are analysed with help of a spectroscope a series of thin bright lines of specific colours are obtained. There is dark space in between two consecutive lines. This type of spectrum is called line spectrum or atomic spectrum..

(2) **Absorption spectrum :** Spectrum produced by the absorbed radiations is called absorption spectrum.

Hydrogen spectrum

(1) Hydrogen spectrum is an example of line emission spectrum or atomic emission spectrum.

(2) When an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted.

(3) This light shows discontinuous line spectrum of several isolated sharp lines through prism.

(4) All these lines of H-spectrum have Lyman, Balmer, Paschen, Barckett, Pfund and Humphrey series. These spectral series were named by the name of scientist discovered them.

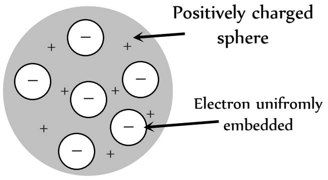
(5) To evaluate wavelength of various H-lines Ritz introduced the following expression,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Where R is universal constant known as Rydberg's constant its value is 109, 678 cm^{-1}.

Plum pudding model of Thomson

(1) He suggected that atom is a positively charged sphere having electrons embedded uniformly giving an overall picture of plum pudding.



Positive charge spreaded throughout the sphere

Fig. 2.3

(2) This model failed to explain the line spectrum of an element and the scattering experiment of Rutherford.

Rutherford's nuclear model

(1) Rutherford carried out experiment on the bombardment of thin (10^{-4} *mm*) *Au* foil with high speed positively charged $\alpha-$particles emitted from *Ra* and gave the following observations based on this experiment,

(i) Most of the $\alpha-$ particles passed without any deflection.

(ii) Some of them were deflected away from their path.

(iii) Only a few (one in about 10,000) were returned back to their original direction of propagation.

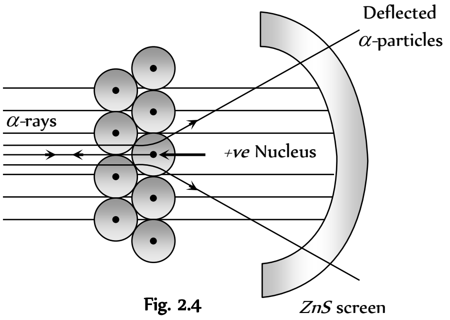


Fig. 2.4

(2) From the above observations he concluded that, an atom consists of

(i) ***Nucleus*** which is small in size but carries the entire mass i.e. contains all the neutrons and protons.

(ii) ***Extra nuclear part*** which contains electrons. This model was similar to the solar system.

(3) **Properties of the nucleus**

(i) Nucleus is a small, heavy, positively charged portion of the atom and located at the centre of the atom.

(ii) All the positive charge of atom (i.e. protons) are present in nucleus.

(iii) Nucleus contains neutrons and protons, and hence these particles collectively are also referred to as ***nucleons.***

(iv) The ***size*** of nucleus is measured in ***Fermi*** (1 Fermi = 10^{-13} *cm*).

(v) The ***radius*** of nucleus is of the order of $1.5\times10^{-13}\,cm.$ to $6.5\times10^{-13}\,cm.$ i.e. 1.5 to 6.5 Fermi. Generally the radius of the nucleus (r_n) is given by the following relation,

$$r_n = r_o(=1.4\times10^{-13}\,cm)\times A^{1/3}$$

This exhibited that nucleus is 10^{-5} times small in size as compared to the total size of atom.

(vi) The ***Volume*** of the nucleus is about $10^{-39}\,cm^3$ and that of atom is $10^{-24}\,cm^3$, i.e., volume of the nucleus is 10^{-15} times that of an atom.

(vii) The **density** of the nucleus is of the order of $10^{15}\,g\,cm^{-3}$ or 10^8 tonnes cm^{-3} or $10^{12}\,kg/cc$. If nucleus is spherical than,

$$\text{Density} = \frac{\text{mass of the nucleus}}{\text{volume of the nucleus}} = \frac{\text{mass number}}{6.023\times10^{23}\times\frac{4}{3}\pi r^3}$$

(4) **Drawbacks of Rutherford's model**

(i) It does not obey the ***Maxwell theory of electrodynamics,*** according to it "A small charged particle moving around an oppositely charged centre continuously loses its energy". If an electron does so, it should also continuously lose its energy and should set up spiral motion ultimately failing into the nucleus.

(ii) It could not explain the line spectra of $H-$ atom and discontinuous spectrum nature.

Planck's quantum theory

When black body is heated, it emits thermal radiation's of different wavelengths or frequency. To explain these radiations, max planck put forward a theory known as planck's quantum theory.

(i) The radiant energy which is emitted or absorbed by the black body is not continuous but discontinuous in the form of small discrete packets of energy, each such packet of energy is called a '**quantum**'. In case of light, the quantum of energy is called a '**photon**'.

(ii) The energy of each quantum is directly proportional to the frequency (ν) of the radiation, i.e.

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

Where, $h =$ Planck's constant = 6.62×10^{-27} *erg. sec.* or 6.62×10^{-34} *Joules* sec.

(iii) The total amount of energy emitted or absorbed by a body will be some whole number quanta. Hence $E = nh\nu$, where n is an integer.

Photoelectric effect

(1) When radiations with certain minimum frequency (ν_0) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomenon is called *photoelectric effect* and the electrons emitted are called *photo-electrons.* The current constituted by photoelectrons is known as photoelectric current.

(2) The electrons are ejected only if the radiation striking the surface of the metal has at least a minimum frequency (ν_0) called *Threshold frequency.* The minimum potential at which the plate photoelectric current becomes zero is called *stopping potential.*

(3) The velocity or kinetic energy of the electron ejected depend upon the frequency of the incident radiation and is independent of its intensity.

(4) The number of photoelectrons ejected is proportional to the intensity of incident radiation.

(5) **Einstein's photoelectric effect equation**

According to Einstein,

Maximum kinetic energy of the ejected electron = absorbed energy – threshold energy

$$\frac{1}{2}mv^2_{\max} = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

Where, ν_0 and λ_0 are threshold frequency and threshold wavelength.

Bohr's atomic model

Bohr retained the essential features of the Rutherford model of the atom. However, in order to account for the stability of the atom he introduced the concept of the stationary orbits. The Bohr postulates are,

(1) An atom consists of positively charged nucleus responsible for almost the entire mass of the atom (This assumption is retention of Rutherford model).

(2) The electrons revolve around the nucleus in certain permitted circular orbits of definite radii.

(3) The permitted orbits are those for which the angular momentum of an electron is an intergral multiple of $h/2\pi$ where h is the Planck's constant. If m is the mass and v is the velocity of the electron in a permitted orbit of radius r, then

$$L = mvr = \frac{nh}{2\Pi};\; n = 1, 2, 3, \ldots\ldots \infty$$

Where L is the orbital angular momentum and n is the number of orbit. The integer n is called the principal quantum number. This equation is known as the Bohr quantization postulate.

(4) When electrons move in permitted discrete orbits they do not radiate or lose energy. Such orbits are called stationary or non-radiating orbits. In this manner, Bohr overcame Rutherford's difficulty to account for the stability of the atom. Greater the distance of energy level from the nucleus, the more is the energy associated with it. The different energy levels were numbered as 1,2,3,4 .. and called as $K, L, M, N,$ .... etc.

(5) Ordinarily an electron continues to move in a particular stationary state or orbit. Such a state of atom is called ground state. When energy is given to the electron it jumps to any higher energy level and is said to be in the excited state. When the electron jumps from higher to lower energy state, the energy is radiated.

Advantages of Bohr's theory

(i) Bohr's theory satisfactorily explains the spectra of species having one electron, *viz.* hydrogen atom, He^{+}, Li^{2+} etc.

(ii) ***Calculation of radius of Bohr's orbit*** **:** According to Bohr, radius of n^{th} orbit in which electron moves is

$$r_n = \left[\frac{h^2}{4\pi^2 me^2 k}\right] . \frac{n^2}{Z}$$

Where, $n =$ Orbit number, $m =$ Mass number $\left[9.1\times 10^{-31} kg\right]$, $e =$ Charge on the electron $\left[1.6\times 10^{-19}\right]$ $Z =$ Atomic number of element, k = Coulombic constant $\left[9\times 10^{9}\, Nm^2c^{-2}\right]$

After putting the values of *m,e,k,h,* we get.

$$r_n = \frac{n^2}{Z}\times 0.529 Å$$

(iii) ***Calculation of velocity of electron***

$$V_n = \frac{2\pi e^2 ZK}{nh}, V_n = \left[\frac{Ze^2}{mr}\right]^{1/2}; V_n = \frac{2.188\times 10^8\, Z}{n} cm.\sec^{-1}$$

(iv) ***Calculation of energy of electron in Bohr's orbit***

Total energy of electron = K.E. + P.E. of electron $= \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$

Substituting of *r*, gives us $E = \frac{-2\pi^2 mZ^2e^4k^2}{n^2h^2}$ Where, n=1, 2, 3.......... ∞

Putting the value of m, e, k, h, π we get

$$E = 21.8\times 10^{-12}\times \frac{Z^2}{n^2} erg\ per\ atom$$

$$= -21.8\times 10^{-19}\times \frac{Z^2}{n^2} J\ per\ atom (1J = 10^7 erg)$$

$$E = -13.6\times \frac{Z^2}{n^2} eV\ per\ atom (1\text{eV} = 1.6\times 10^{-19} J)$$

$$= -13.6\times \frac{Z^2}{n^2} k.cal/mole\ \ (1\ cal = 4.18J)$$

or $\frac{-1312}{n^2} Z^2 kJmol^{-1}$

When an electron jumps from an outer orbit (higher energy) n_2 to an inner orbit (lower energy) n_1, then the energy emitted in form of radiation is given by

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2k^2me^4Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \Delta E = 13.6 Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV/atom$$

As we know that $E = h\bar{\nu}$, $c = \nu\lambda$ and $\bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E}{hc}$,

$$= \frac{2\pi^2k^2me^4Z^2}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

This can be represented as $\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Where, $R = \frac{2\pi^2k^2me^4}{ch^3}$; *R* is known as Rydberg constant. Its value to be used is $109678 cm^{-1}$.

The negative sign in the above equations shows that the electron and nucleus form a bound system, *i.e.,* the electron is attracted towards the nucleus. Thus, if electron is to be taken away from the nucleus, energy has to be supplied. The energy of the electron in $n = 1$ orbit is called the ground state energy; that in the $n = 2$ orbit is called the first excited state energy, etc. When $n = \infty$ then $E = 0$ which corresponds to ionized atom *i.e.,* the electron and nucleus are infinitely separated $H \rightarrow H^{+} + e^{-}$ (ionization).

(6) **Spectral evidence for quantisation** (Explanation for hydrogen spectrum on the basisof bohr atomic model)

(i) The light absorbed or emitted as a result of an electron changing orbits produces characteristic absorption or emission spectra which can be recorded on the photographic plates as a series of lines, the optical spectrum of hydrogen consists of several series of lines called **Lyman, Balmar, Paschen, Brackett, Pfund** and **Humphrey.** These spectral series were named by the name of scientist who discovered them.

(ii) To evaluate wavelength of various H-lines Ritz introduced the following expression,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Where, R is $= \frac{2\pi^2 me^4}{ch^3} =$ Rydberg's constant

It's theoritical value = 109,737 cm^{-1} and It's experimental value = $109,677.581 cm^{-1}$

This remarkable agreement between the theoretical and experimental value was great achievment of the Bohr model.

(iii) Although *H*-atom consists of only one electron yet it's spectra consist of many spectral lines.

(iv) *Comparative study of important spectral series of Hydrogen is shown in following table.*

(v) If an electron from *n* excited state comes to various energy states, the maximum spectral lines obtained will be $= \frac{n(n-1)}{2}$. *n*= principal quantum number.

As *n*=6 than total number of spectral lines $= \frac{6(6-1)}{2} = \frac{30}{2} = 15.$

(vi) Thus, at least for the hydrogen atom, the Bohr theory accurately describes the origin of atomic spectral lines.

(7) **Failure of Bohr model**

(i) Bohr theory was very successful in predicting and accounting the energies of line spectra of hydrogen i.e. one electron system. It could not explain the line spectra of atoms containing more than one electron.

(ii) This theory could not explain the presence of multiple spectral lines.

(iii) This theory could not explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.

(iv) This theory was unable to explain of dual nature of matter as explained on the basis of De broglies concept.

(v) This theory could not explain uncertainty principle. (vi) No conclusion was given for the concept of quantisation of energy.

Table: 2.5

S.No.	**Spectral series**	**Lies in the region**	**Transition** $n_2 > n_1$	$\lambda_{\max} = \frac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R}$	$\lambda_{\min} = \frac{n_1^2}{R}$	$\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{n_2^2}{n_2^2 - n_1^2}$
(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 $n_2 = \infty$ $\lambda_{\min} = \frac{1}{R}$	$\frac{4}{3}$
(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 $n_2 = \infty$ $\lambda_{\min} = \frac{4}{R}$	$\frac{9}{5}$
(3)	Paschen series	Infra red region	$n = 3$ $n_2 = 4,5,6....\infty$	$n_1 = 3$ and $n_2 = 4$ $\lambda_{\max} = \frac{144}{7R}$	$n_1 = 3$ and $n_2 = \infty$ $\lambda_{\min} = \frac{9}{R}$	$\frac{16}{7}$
(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 $n_2 = \infty$ $\lambda_{\min} = \frac{16}{R}$	$\frac{25}{9}$
(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 $n_2 = \infty$ $\lambda_{\min} = \frac{25}{R}$	$\frac{36}{11}$
(6)	Humphrey series	Far infrared region	$n_1 = 6$ $n_2 = 7,8....\infty$	$n_1 = 6$ and $n_2 = 7$ $\lambda_{\max} = \frac{36 \times 49}{13R}$	$n_1 = 6$ and $n_2 = \infty$ $\lambda_{\min} = \frac{36}{R}$	$\frac{49}{13}$

Bohr–Sommerfeild's model

It is an extension of Bohr's model. The electrons in an atom revolve around the nuclei in elliptical orbit. The circular path is a special case of ellipse. Association of elliptical orbits with circular orbit explains the fine line spectrum of atoms.

Dual nature of electron

(1) In 1924, the French physicist, ***Louis de Broglie*** suggested that if light has both particle and wave like nature, the similar duality must be true for matter. Thus an electron, behaves both as a material particle and as a wave.

(2) This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

(3) According to de-broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation

$$\lambda = \frac{h}{mv},$$ where h = Planck's constant.

(4) This can be derived as follows according to Planck's equation,

$$E = h\nu = \frac{h.c}{\lambda} \quad \left(\because \ \nu = \frac{c}{\lambda}\right)$$

energy of photon (on the basis of Einstein's mass energy relationship), $E = mc^2$

Equating both $\frac{hc}{\lambda} = mc^2$ or $\lambda = \frac{h}{mc}$ which is same as de-Broglie relation. $(\because \ mc = p)$

(5) This was experimentally verified by ***Davisson and Germer*** by observing diffraction effects with an electron beam. Let the electron is accelerated with a potential of V than the Kinetic energy is

$$\frac{1}{2}mv^2 = eV \ ; \quad m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = P \ ; \quad \lambda = \frac{h}{\sqrt{2eVm}}$$

(6) If Bohr's theory is associated with de-Broglie's equation then wave length of an electron can be determined in bohr's orbit and relate it with circumference and multiply with a whole number

$$2\pi r = n\lambda \ or \ \lambda = \frac{2\pi r}{n}$$

From de-Broglie equation, $\lambda = \frac{h}{mv}$.

Thus $\frac{h}{mv} = \frac{2\pi r}{n}$ or $mvr = \frac{nh}{2\pi}$

(7) The de-Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. Since, we come across macroscopic objects in our everyday life, de-broglie relationship has no significance in everyday life.

Heisenberg's uncertainty principle

This principle states "It is impossible to specify at any given moment both the position and momentum (velocity) of an electron".

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

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 $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

In terms of uncertainty in energy, ΔE and uncertainty in time Δt, this principle is written as, $\Delta E \,.\, \Delta t \geq \frac{h}{4\pi}$

Schrödinger wave equation

(1) Schrodinger wave equation is given by ***Erwin Schrödinger*** in 1926 and based on dual nature of electron.

(2) In it electron is described as a three dimensional wave in the electric field of a positively charged nucleus.

(3) The probability of finding an electron at any point around the nucleus can be determined by the help of Schrodinger wave equation which is,

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

Where x, y and z are the 3 space co-ordinates, m = mass of electron, h = Planck's constant, E = Total energy, V = potential energy of electron, Ψ = amplitude of wave also called as wave function, ∂ = for an infinitesimal change.

(4) The Schrodinger wave equation can also be written as,

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2}(E - V)\,\Psi = 0$$

Where ∇ = laplacian operator.

(5) **Physical significance of Ψ and Ψ^2**

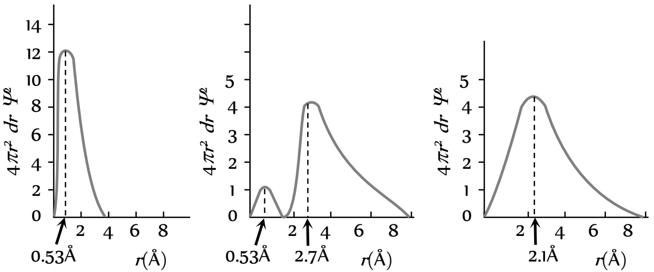
(i) The wave function Ψ represents the amplitude of the electron wave. The amplitude Ψ is thus a function of space co-ordinates and time i.e. $\Psi = \Psi(x, y,\, z......\, times)$

(ii) For a single particle, the square of the wave function (Ψ^2) at any point is proportional to the probability of finding the particle at that point.

(iii) If Ψ^2 is maximum than probability of finding e^- is maximum around nucleus and the place where probability of finding e^- is maximum is called *electron density*, electron cloud or an atomic orbital. It is different from the Bohr's orbit.

(iv) The solution of this equation provides a set of number called *quantum numbers* which describe specific or definite energy state of the electron in atom and information about the shapes and orientations of the most probable distribution of electrons around the nucleus.

Radial probability distribution curves : Radial probability is $R = 4\pi r^2 dr \psi^2$. The plats of R distance from nucleus as follows



1s 2s 2s

Fig. 2.5

Quantum numbers

Each orbital in an atom is specified by a set of three quantum numbers (*n, l, m*) and each electron is designated by a set of four quantum numbers (*n, l, m* and *s*).

(1) **Principle quantum number (*n*)**

(i) It was proposed by *Bohr* and denoted by '*n*'.

(ii) It determines the average distance between electron and nucleus, means it denotes the size of atom.

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

(iv) 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.

(v) It gives the information of orbit *K, L, M, N*------------.

(vi) Angular momentum can also be calculated using principle quantum number

(2) **Azimuthal quantum number (*l*)**

(i) Azimuthal quantum number is also known as angular quantum number. Proposed by *Sommerfield* and denoted by '*l*'.

(ii) It determines the number of sub shells or sublevels to which the electron belongs.

(iii) It tells about the shape of subshells.

(iv) It also expresses the energies of subshells $s < p < d < f$ (increasing energy).

(v) The value of $l = (n - 1)$ always. Where '*n*' is the number of principle shell.

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

(vii) It represent the orbital angular momentum. Which is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$

(viii) The maximum number of electrons in subshell $= 2(2l+1)$

$s-\text{subshell} \rightarrow 2\,\text{electrons} \quad d-\text{subshell} \rightarrow 10\,\text{electrons}$

$p-\text{subshell} \rightarrow 6\,\text{electrons} \quad f-\text{subshell} \rightarrow 14\,\text{electrons}.$

(ix) For a given value of '*n*' the total values of '*l*' is always equal to the value of '*n*'.

(3) **Magnetic quantum number (*m*)**

(i) It was proposed by *Zeeman* and denoted by '*m*'.

(ii) It gives the number of permitted orientation of subshells.

(iii) The value of *m* varies from –*l* to +*l* through zero.

(iv) It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proves the Zeeman effect.

(v) For a given value of '*n*' the total value of '*m*' is equal to n^2.

(vi) For a given value of '*l*' the total value of '*m*' is equal to $(2l+1)$.

(vii) *Degenerate orbitals* : Orbitals having the same energy are known as degenerate orbitals. e.g. for *p* subshell p_x p_y p_z

(viii) The number of degenerate orbitals of *s* subshell =0.

(4) **Spin quantum numbers (*s*)**

(i) It was proposed by *Goldshmidt & Ulen Back* and denoted by the symbol of 's'.

(ii) The value of 's' is $+1/2$ and $-1/2$, which signifies the spin or rotation or direction of electron on it's axis during movement.

(iii) The spin may be clockwise or anticlockwise.

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

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

(vi) This quantum number is not the result of solution of schrodinger equation as solved for *H*-atom.

Table : 2.6 Distribution of electrons among the quantum levels

n	*l*	*m*	Designation of orbitals	Number of Orbitals in the subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	–1, 0, +1	2p	3
3	0	0	3s	1
3	1	–1, 0, +1	3p	3
3	2	–2, –1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	–1, 0, +1	4p	3
4	2	–2, –1, 0, +1, +2	4d	5
4	3	–3, –2, –1, 0, +1, +2, +3	4f	7

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) *s*-orbitals known as radial node or modal surface. But there is no radial node for 1s orbital since it is starting from the nucleus.

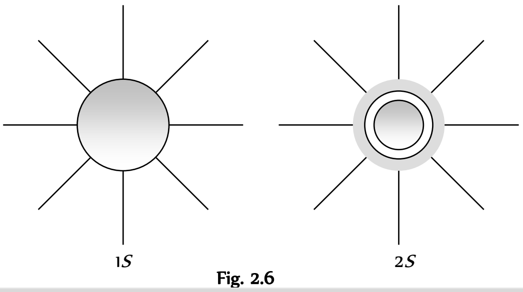


Fig. 2.6

(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.

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

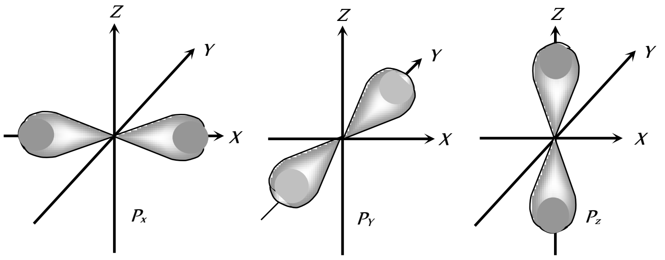


Fig. 2.7

(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.

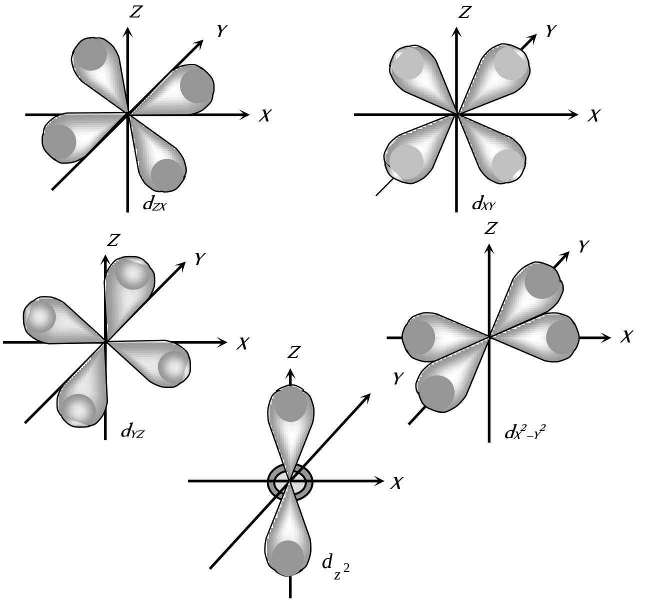


Fig. 2.8

(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 $f_{x(x^2-y^2)}, f_{y(x^2-y^2)}, f_{z(x^2-y^2)}, f_{xyz}, f_{z^3}, f_{yz^2}$ and f_{xz^2}.

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

Rules for filling of electrons in various orbitals

The atom is built up by filling electrons in various orbitals according to the following rules,

(1) **Aufbau's principle**

This principle states that the electrons are added one by one to the various orbitals in order of their increasing energy starting with the orbital of lowest energy. The increasing order of energy of various orbitals is

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

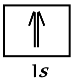
(2) **(*n*+*l*) Rule**

In neutral isolated atom, the lower the value of $(n + l)$ for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of $(n + l)$, the orbitals with lower value of n has lower energy.

(3) **Pauli's exclusion principle**

According to this principle "no two electrons in an atom will have same value of all the four quantum numbers".

If one electron in an atom has the quantum numbers $n = 1$, $l = 0$, $m = 0$ and $s = +1/2$, no other electron can have the same four quantum numbers. In other words, we cannot place two electrons with the same value of s in a $1s$ orbital.

The orbital diagram  does not represent a possible arrangement of electrons

Because there are only two possible values of s, an orbital can hold not more than two electrons.

(4) **Hund's Rule of maximum multiplicity**

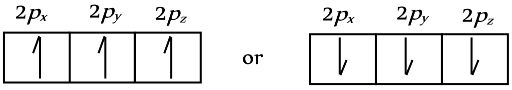
This rule deals with the filling of electrons in the orbitals having equal energy (degenerate orbitals). According to this rule,

"Electron pairing in p, d and f orbitals cannot occur until each orbitals of a given subshell contains one electron each or is singly occupied".

This is due to the fact that electrons being identical in charge, repel each other when present in the same orbital. This repulsion can however be minimised if two electrons move as far apart as possible by occupying different degenerate orbitals. All the unpaired electrons in a degenerate set of orbitals will have same spin.

As we now know the Hund's rule, let us see how the three electrons are arranged in p orbitals.

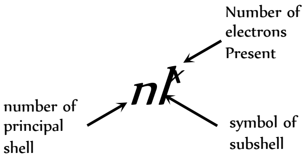
The important point ot be remembered is that all the singly occupied orbitals should have electrons with parallel spins i.e in the same direction either-clockwise or anticlockwise.



Electronic configurations of elements

On the basis of the elecronic configuration principles the electronic configuration of various elements are given in the following table :

The above method of writing the electronic configurations is quite cumbersome. Hence, usually the electronic configuration of the atom of any element is simply represented by the notation.



Some Unexpected Electronic Configuration

Some of the exceptions are important though, because they occur with common elements, notably chromium and copper.

Cu has 29 electrons. Its excepted electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$ but in reality the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ as this configuration is more stable. Similarly Cr has the configuration of $1s^2 2s^2 sp^6 3s^2 3p^6 4s^1 3d^5$ instead of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$.

Factors responsible for the extra stability of half-filled and completely filled subshells,

(i) *Symmetrical distribution* : It is well known fact that symmetry leads to stability. Thus the electronic configuration in which all the orbitals of the same subshell are either completely filled or are exactly half filled are more stable because of symmetrical distribution of electrons.

(ii) *Exchange energy* : The electrons with parallel spins present in the degenerate orbitals tend to exchange their position. The energy released during this exchange is called exchange energy. The number of exchanges that can take place is maximum when the degenerate orbtials (orbitals of same subshell having equal energy) are exactly half-filled or completely. As a result, the exchange energy is maximum and so it the stability.

Tips & Tricks

- All lines in the visible region are of Balmer series but reverse is not true i.e., all Balmer lines will not fall in visible region.
- A part of an atom up to penultimate shell is a kernel or atomic core.
- If the energy supplied to hydrogen atom is less than 13.6 eV it will awpt or absorb only those quanta which can take it to a certain higher energy level i.e., all those photons having energy less than or more than a particular energy level will not be absorbed by hydrogen atom, but if energy supplied to hydrogen atom is more than 13.6eV then all photons are absorbed and excess energy appear as kinetic energy of emitted photo electron.
- No of nodes in any orbital $=(n-l-1)$
- No of nodal planes in an orbitals $=l$
- The d orbital which does not have four lobes is d_{z^2}
- The d orbital whose lobes lie along the axis is $d_{x^2-y^2}$
- Spin angular momentum $=\sqrt{s(s+1)}\frac{h}{2\pi}$
- Total spin $=\pm\frac{n}{2}$; where n is no of unpaired e^-
- Magnetic moment $=\sqrt{n(n+2)}$ B.M. (Bohr magnetron) of n unpaired e^-
- Ion with unpaired electron in d or f orbital will be coloured.
- Exception of E.C. are $Cr(24)$, $Cu(29)$, $Mo(42)$, $Ag(47)$, $W(74)$, $Au(79)$.
- No. of waves $n=\frac{2\pi r}{\lambda}$ (where $\lambda=\frac{h}{mv}$)
- No. of revolutions of e^- per second is $=\frac{v}{2\pi r}$.
- The solution of schrodinger wave equation gives principal, azimuthal and magnetic quantum numbers but not the spin quantum number.
- In the Rydberg formula, when $n_2=\infty$ the line produced is called the limiting line of that series.
- Among various forms of visible light, violet colour has shortest wavelength, highest frequency and highest energy.
- Red coloured light has largest wavelength, least frequency and lowest energy in visible light.
- Elements give line spectra. The line spectrum is characteristic of the excited atom producing it. No two elements have identical line spectrum.
- The line spectrum results from the emission of radiations from the atoms of the elements and is therefore called as atomic spectrum.
- Atoms give line spectra (known as atomic spectrum) and the molecules give band spectra (known as molecular spectrum).
- The negative potential at which the photoelectric current becomes zero is called cut off potential or stopping potential.
- When energy or frequency of scattered ray is lesser than the incident ray, it is known as Compton effect.
- The instrument used to record solar spectrum is called spectrometer or spectrograph developed by Bunsen and Kirchoff in 1859.
- The intensities of spectral lines decreases with increase in the value of n. For example, the intensity of first Lyman line $(2\rightarrow 1)$ is greater than second line $(3\rightarrow 1)$ and so on.
- In Balmer series of hydrogen spectrum the first line $(3\rightarrow 2)$ is also known as L_α line. The second line $(4\rightarrow 2)$ is L_β line. The line from infinity energy shell is called limiting line.