

Atomic Structure for JEE Main and Advanced (IIT-JEE)

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1. Dalton's Theory of Atom

John Dalton developed his atomic theory. According to this theory the Atom is considered to be hard, dense and smallest particle of matter, which is indivisible, the atoms belonging to a particular element, is unique. The properties of elements differ because of the uniqueness of the atoms belonging to particular elements. This theory provides a satisfactory basis for the laws of chemical combination. The atom can neither be created nor be destroyed i.e., it is indestructible.

Drawbacks: It fails to explain why atoms of different kinds should differ in mass and valency etc.

The discovery of isotopes and isobars showed that atoms of same elements may have different atomic masses (isotopes) and atoms of different kinds may have same atomic masses (isobars).

Sub-Atomic Particles: The discovery of various sub-atomic particles like electrons, protons etc. during late 19th century led to the ideal that the atom was no longer an indivisible and the smallest particle of the matter.

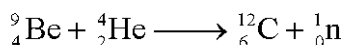
However, the researches done by various eminent scientists and the discovery of radioactivity have established beyond doubt, that atom is not the smallest indivisible particle but had a complex structure of its own and was made up of still smaller particles like electrons, protons, neutrons etc. At present about 35 different subatomic particles are known but the three particles namely electron, proton and neutron are regarded as the fundamental particles.

We shall now take up the brief study of these fundamental particles. The existence of electrons in atoms was first suggested, by J.J. Thomson, as a result of experimental work on the conduction of electricity through gases at low pressures and at high voltage, which produces cathode rays consisting of negatively charged particles, named as electrons. The e/m ratio for cathode rays is fixed whose value is $1.76 \times 10^8 \text{ C/g}$.

We know that an atom is electrically neutral, if it contains negatively charged electrons it must also contain some positively charged particles. This was confirmed by Goldstein in his discharge tube experiment with perforated cathode. On passing high voltage between the electrodes of a discharge tube it was found that some rays were coming from the side of the anode which passed through the holes in the cathode. These anode rays (canal rays) consisted of positively charged particles formed by ionization of gas molecules by the cathode rays. The charge to mass ratio (e/m value) of positively charged particles was found to be maximum when the discharge tube was filled with hydrogen gas as hydrogen is the lightest element. These positively charged particles are called protons.

e/m varies with the nature of gas taken in the discharge tube. The positive particles are positive residues of the gas left when the gas is ionized.

The electrically neutral charge particle, neutron was discovered by James Chadwick by bombarding boron or beryllium with α -particles.



Characteristics of the three fundamental particles are:

	Electron	Proton	Neutron
Symbol	e or e^{-1}	P	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	-1	+1	No charge
Mass in kg	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}
Mass in amu	5.485×10^{-4}	1.007	1.008
Actual charge (coulomb)	1.602×10^{-19}	1.602×10^{-19}	0
Actual charge (e.s.u.)	4.8×10^{-10}	4.8×10^{-10}	0

The atomic mass unit (amu) is 1/12 of the mass of an individual atom of ${}_6^{12}\text{C}$, i.e., 1.660×10^{-27} kg.

The neutron and proton have approximately equal masses of 1 amu and the electron is about 1836 times lighter, its mass can sometimes be neglected as an approximation.

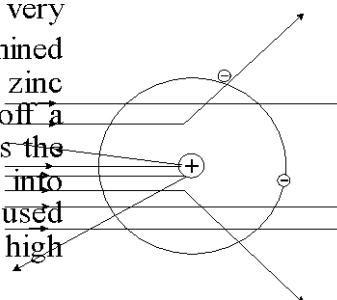
The electron and proton have equal, but opposite, electric charge while the neutron is not charged.

2. Models of Atom

Thomson's Model: Putting together all the facts known at that time, Thomson assumed that an atom is a sphere of positive charges uniformly distributed, with the electrons scattered as points throughout the sphere. This was known as plum-pudding model at that time. However this idea was dropped due to the success of α -particle scattering experiments studied by Rutherford and Mardson.

Rutherford's Model: α -particle emitted by radioactive substance were shown to be dipositive Helium ions (He^{++}) having a mass of 4 units and 2 units of positive charge.

Rutherford allowed a narrow beam of α -particles to fall on a very thin gold foil of thickness of the order of 4×10^{-4} cm and determined the subsequent path of these particles with the help of a zinc sulphide fluorescent screen. The zinc sulphide screen gives off a visible flash of light when struck by an α -particle, as ZnS has the remarkable property of converting kinetic energy of particle into visible light. [For this experiment, Rutherford specifically used α -particles because they are relatively heavy resulting in high momentum].



Observation

- Majority of the α -particles pass straight through the gold strip with little or no deflection.
- Some α -particles are deflected from their path and diverge.
- Very few α -particles are deflected backwards through angles greater than 90° .

- (iv) Some were even scattered in the opposite direction at an angle of 180° [Rutherford was very much surprised by it and remarked that “It was as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you”].

Conclusions

1. The fact that most of the α particles passed straight through the metal foil indicates the most part of the atom is empty.
2. The fact that few α particles are deflected at large angles indicates the presence of a heavy positively charged body i.e., for such large deflections to occur α -particles must have come closer to or collided with a massive positively charged body, and he named it nucleus.
3. The fact that one in 20,000 have deflected at 180° backwards indicates that volume occupied by this heavy positively charged body is very small in comparison to total volume of the atom.

Atomic model: On the basis of the above observation, and having realized that the rebounding α -particles had met something even more massive than themselves inside the gold atom, Rutherford proposed an atomic model as follows.

- (i) All the protons (+ve charge) and the neutrons (neutral charge) i.e. nearly the total mass of an atom is present in a very small region at the centre of the atom. The atom's central core is called nucleus.
- (ii) The size of the nucleus is very small in comparison to the size of the atom. Diameter of the nucleus is about 10^{-13} while the atom has a diameter of the order 10^{-8} of cm. So, the size of atom is 10^5 times more than that of nucleus.
- (iii) Most of the space outside the nucleus is empty.
- (iv) The electrons, equal in number to the net nuclear positive charge, revolve around the nucleus with high speed in various circular orbits.
- (v) The centrifugal force arising due to the high speed of an electron balances the columbic force of attraction of the nucleus and the electron remains stable in its path. Thus according to him atom consists of two parts (a) nucleus and (b) extra nuclear part.

Defects of Rutherford's atomic model

1. **Position of electrons:** The exact positions of the electrons from the nucleus are not mentioned.
2. **Stability of the atom:** Neils Bohr pointed out that Rutherford's atom should be highly unstable. According to the law of electro-dynamics, the electron should therefore, continuously emit radiation and lose energy. As a result of this a moving electron will come closer and closer to the nucleus and after passing through a spiral path, it should ultimately fall into the nucleus.

It was calculated that the electron should fall into the nucleus in less than 10^{-8} sec. But it is known that electrons keep moving outside the nucleus.

To solve this problem Neils Bohr proposed an improved form of Rutherford's atomic model.

Before going into the details of Neils Bohr model we would like to introduce you some important atomic terms.

3. Atomic Spectrum

If the atom gains energy the electron passes from a lower energy level to a higher energy level, energy is absorbed that means a specific wave length is absorbed. Consequently, a dark line will appear in the spectrum. This dark line constitutes the **absorption spectrum**.

Hydrogen Atom: If an electric discharge is passed through hydrogen gas taken in a discharge tube under low pressure, and the emitted radiation is analysed with the help of spectrograph, it is found to consist of a series of sharp lines in the UV, visible and IR regions. This series of lines is

known as line or atomic spectrum of hydrogen. The lines in the visible region can be directly seen on the photographic film.

Each line of the spectrum corresponds to a light of definite wavelength. The entire spectrum consists of six series of lines each series, known after their discoverer as the Balmer, Paschen, Lyman, Brackett, Pfund and Humphrey series. The wavelength of all these series can be expressed by a single formula.

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

$\bar{\nu}$ = wave number

λ = wave length

R = Rydberg constant (109678 cm^{-1})

n_1 and n_2 have integral values as follows

Series	n_1	n_2	Main spectral lines
Lyman	1	2, 3, 4, etc	Ultra-violet
Balmer	2	3, 4, 5 etc	Visible
Paschen	3	4, 5, 6 etc	Infra-red
Brackett	4	5, 6, 7 etc	Infra-red
Pfund	5	6, 7, 8, etc	Infra-red

Note: 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

The pattern of lines in atomic spectrum is characteristic of hydrogen.

Types of emission spectra

- Continuous spectra:** When white light from any source such as sun or bulb is analysed by passing through a prism, it splits up into seven different wide bands of colour from violet to red (like rainbow). These colour also continuous that each of them merges into the next. Hence the spectrum is called as continuous spectrum.
- Line spectra:** When an electric discharge is passed through a gas at low pressure light is emitted. If this light is resolved by a spectroscope, it is found that some isolated coloured lines are obtained on a photographic plate separated from each other by dark spaces. This spectrum is called line spectrum. Each line in the spectrum corresponds to a particular wavelength. Each element gives its own characteristic spectrum.

4. Planck's Quantum Theory

When a black body is heated, it emits thermal radiations of different wavelengths or frequency. To explain these radiations, Max Planck put forward a theory known as Planck's quantum theory. The main points of quantum theory are:

- Substances radiate or absorb energy discontinuously in the form of small packets or bundles of energy.
- The smallest packet of energy is called quantum. In case of light the quantum is known as photon.
- The energy of a quantum is directly proportional to the frequency of the radiation. $E \propto \nu$ (or $E = h\nu$ where ν is the frequency of radiation and h is Planck's constant having the value 6.626×10^{-27})

erg-sec or 6.626×10^{-34} J-sec.

- (iv) A body can radiate or absorb energy in whole number multiples of a quantum $h\nu$, $2h\nu$, $3h\nu$ $nh\nu$ where n is the positive integer.

Nelis Bohr used this theory to explain the structure of atom.

5. Bohr's Atomic Model

Bohr developed a model for hydrogen and hydrogen like atoms one-electron species (hydrogenic species). He applied quantum theory in considering the energy of an electron bond to the nucleus.

Important postulates: An atom consists of a dense nucleus situated at the center with the electron revolving around it in circular orbits without emitting any energy. The force of attraction between the nucleus and an electron is equal to the centrifugal force of the moving electron.

Of the finite number of circular orbits possible around the nucleus, and electron can revolve only in those orbits whose angular momentum (mvr) is an integral multiple of factor $h/2\pi$.

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

where, m = mass of the electron

v = velocity of the electron

n = orbit number in which electron is present

r = radius of the orbit

As long as an electron is revolving in an orbit it neither loses nor gains energy. Hence these orbits are called stationary states. Each stationary state is associated with a definite amount of energy and it is also known as energy levels. The greater the distance of the energy level from the nucleus, the more is the energy associated with it. The different energy levels are numbered as 1, 2, 3, 4, (from nucleus onwards) or K, L, M, N etc.

Ordinarily an electron continues to move in a particular stationary state without losing energy. Such a stable state of the atom is called as ground state or normal state.

If energy is supplied to an electron, it may jump (excite) instantaneously from lower energy (say 1) to higher energy level (say 2, 3, 4, etc) by absorbing one quantum of energy. This new state of electron is called as excited state. The quantum of energy absorbed is equal to the difference in energies of the two concerned levels.

Since the excited state is less stable, atom will lose its energy and come back to the ground state.

Energy absorbed or released in an electron jump, (ΔE) is given by

$$\Delta E = E_2 - E_1 = h\nu$$

Where E_2 and E_1 are the energies of the electron in the first and second energy levels, and ν is the frequency of radiation absorbed or emitted.

Note: If the energy supplied to hydrogen atom is less than 13.6 eV, it will accept 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 13.6 eV then all photons are absorbed and excess energy appear as kinetic energy of emitted photo electron.

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Merits of Bohr's theory

- (i) The experimental value of radii and energies in hydrogen atom are in good agreement with that calculated on the basis of Bohr's theory.
- (ii) Bohr's concept of stationary state of electron explains the emission and absorption spectra of hydrogen like atoms.
- (iii) The experimental values of the spectral lines of the hydrogen spectrum are in close agreement with the calculated by Bohr's theory.

Limitations of Bohr's Theory

- (i) It does not explain the spectra of atoms or ions having more than one electron.
- (ii) Bohr's atomic model failed to account for the effect of magnetic field (Zeeman effect) or electric field (Stark effect) on the spectra of atoms or ions. It was observed that when the source of a spectrum is placed in a strong magnetic or electric field, each spectral line further splits into a number of lines. This observation could not be explained on the basis of Bohr's model.
- (iii) de-Broglie suggested that electrons like light have dual character. It has particle and wave character. Bohr treated the electron only as particle.
- (iv) Another objection to Bohr's theory came from Heisenberg's Uncertainty Principle. According to this principle "it is impossible to determine simultaneously the exact position and momentum of a small moving particle like an electron". The postulate of Bohr, that electrons revolve in well defined orbits around the nucleus with well defined velocities is thus not attainable.

By Bohr's theory

- (i) **Radius and Energy levels of hydrogen atom:** Consider an electron of mass 'm' and charge 'e' revolving around a nucleus of charge Ze (where, Z = atomic number and e is the charge of the proton) with a tangential velocity v. r is the radius of the orbit in which electron is revolving.

By Coulomb's Law, the electrostatic force of attraction between the moving electron and nucleus is

$$\text{Coulombic force} = \frac{KZe^2}{r^2}$$

$$K = \frac{1}{4\pi\epsilon_0} \quad (\text{where } \epsilon_0 \text{ is permittivity of free space})$$

$$K = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$$

In C.G.S. units, value of $K = 1 \text{ dyne cm}^2(\text{esu})^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \quad \dots (i)$$

$$(\text{or}) \quad v^2 = \frac{KZe^2}{mr} \quad \dots (ii)$$

According to Bohr's postulate of angular momentum quantization, we have

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

$$v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad \dots \text{ (iii)}$$

Equating (2) and (3)

$$\frac{KZe^2}{mr} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

Solving for r we get $r = \frac{n^2 h^2}{4\pi^2 m K Z e^2}$

where $n = 1, 2, 3, \dots \infty$

Hence only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n, i.e., farther the level from the nucleus the greater is the radius.

The radius of the smallest orbit ($n = 1$) for hydrogen atom ($Z = 1$) is r_0 .

$$r_0 = \frac{n^2 h^2}{4\pi^2 m e^2 K} = \frac{1^2 \times (6.626 \times 10^{-34})^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9} = 5.29 \times 10^{-11} \text{ m}$$

$$r_0 = 0.529 \text{ \AA}$$

Radius of nth orbit for an atom with atomic number Z is simply written as

$$r_n = r_0 \frac{n^2}{Z} = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

- (ii) **Energy level of Hydrogen atom:** The total energy, E of the electron is the sum of kinetic energy and potential energy. Kinetic energy of the electron = $\frac{1}{2}mv^2$

$$\text{Potential energy} = \frac{-KZe^2}{r}$$

$$\text{Total energy} = \frac{1}{2}mv^2 - \frac{KZe^2}{r} \quad \dots \text{ (4)}$$

From equation (1) we know that

$$\frac{mv^2}{r} = \frac{KZe^2}{r}$$

$$\therefore \frac{1}{2}mv^2 = \frac{KZe^2}{2r}$$

Substituting this in equation (4)

$$\text{Total energy (e)} = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

$$KE = -\frac{1}{2}PE, KE = -TE$$

Substituting for r, gives us

$$E = \frac{2\pi^2 mZe^2 e^4 K^2}{n^2 h^2} \text{ where } n = 1, 2, 3, \dots$$

This expression shows that only certain energies are allowed to the electron. Since this energy expression consists so many fundamental constant, we are giving you the following simplified expressions.

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

$$= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J per atom} = -13.6 \times \frac{Z^2}{n^2} \text{ eV per atom}$$

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV per atom}$$

$$(1\text{eV} = 3.83 \times 10^{-23} \text{ Kcal})$$

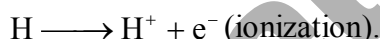
$$(1\text{eV} = 1.602 \times 10^{-12} \text{ erg})$$

$$(1\text{eV} = 1.602 \times 10^{-19} \text{ J})$$

$$E = -313.6 \times \frac{Z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J)}$$

The energies are negative since the energy of the electron in the atom is less than the energy of a free electron (i.e., the electron is at infinite distance from the nucleus) which is taken as zero. The lowest energy level of the atom corresponds to $n = 1$, and as the quantum number increases, E become less negative.

When $n = \infty$, $E = 0$ which corresponds to an ionized atom i.e., the electron and nucleus are infinitely separated.



(iii) **Velocity of electron**

$$\text{We know that, } mvr = \frac{nh}{2\pi}; v = \frac{nh}{2\pi mr}$$

By substituting for r we are getting

$$v = \frac{2\pi KZe^2}{nh}$$

Where excepting n and z all are constant, $v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/sec.}$

Further application of Bohr's work was made, to other one electron species (Hydrogenic ion) such as He^+ and Li^{2+} . In each case of this kind, Bohr's prediction of the spectrum was correct.

(iv) **Explanation for hydrogen spectrum by Bohr's theory:** According to the Bohr's theory electron neither emits nor absorbs energy as long as it stays in a particular orbit. However, when an atom is subjected to electric discharge or high temperature, and electron in the atom may jump from the normal energy level, i.e., ground state to some higher energy level i.e., excited state. Since the life time of the electron in excited state is short, it returns to the ground state in one or more jumps. During each jumps, energy is emitted in the form of a photon of light of definite wavelength or frequency. The frequency of the photon of light thus emitted depends upon the energy difference of the two energy levels concerned (n_1, n_2) and is given by

$$h\nu = E_2 - E_1 = \frac{-2\pi^2 m Z^2 e^4 K^2}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\nu = \frac{2\pi^2 m Z^2 e^4 K^2}{h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The frequencies of the spectral lines calculated with the help of above equation are found to be in good agreement with the experimental values. Thus, Bohr's theory elegantly explains the line spectrum of hydrogen and hydrogenic species.

Bohr had calculated Rydberg constant from the above equation.

$$\nu = \frac{c}{\lambda} = \frac{2\pi^2 m Z^2 e^4 K^2}{h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{\lambda} = \bar{\nu} = \frac{2\pi^2 m Z^2 e^4 K^2}{h^3 c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{where } \frac{2\pi^2 m e^4 K^2}{h^3 c} = 1.097 \times 10^{-7} \text{ m}^{-1} \text{ or } 109678 \text{ cm}^{-1}$$

$$\text{i.e. Rydberg constant (R)} \quad \therefore \quad \bar{\nu} = \frac{1}{\lambda} = R Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$\bar{\nu}$ = wave number.

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6. Electromagnetic Energy

Newton was first person to comment on the nature of light in terms of Corpuscular. Theory of Light. According to this theory light is a stream of particles commonly known as corpuscles of light. He was able to explain reflection and refraction, the most common phenomenon of light. But the other phenomenon like diffraction and interference could not be explained on the basis of this theory.

Maxwell, in 1956 proposed that radiant energy (light) has wave characteristics. Light according to him is Electromagnetic Wave arising due to the disturbance created by electric and magnetic fields oscillating perpendicular to each other in space. Like all other mechanical waves, it is characterised by velocity c , frequency ν , wavelength λ which are related as :

$$c = \nu \lambda. \text{ The value of } c \text{ is constant and equal to } 3 \times 10^8 \text{ m/s.}$$

7. Electromagnetic Spectrum

Electromagnetic wave or radiation is not a single wavelength radiation, but a mixture of various wavelength or frequencies. All the frequencies have same speed.

If all the components of Electromagnetic Radiation (EMR) are arranged in order of decreasing or increasing wavelengths or frequencies, the pattern obtained is known as Electromagnetic Spectrum.

The following table shows all the components of light.

S.No.	Name	Wavelength	Frequency(Hz)	Source
1.	Radio wave	$3 \times 10^{14} - 3 \times 10^7$	$1 \times 10^5 - 1 \times 10^9$	Alternating current of high frequency
2.	Microwave	$3 \times 10^7 - 6 \times 10^6$	$1 \times 10^9 - 5 \times 10^{11}$	Klystron tube
3.	Infrared (IR)	$6 \times 10^6 - 7600$	$5 \times 10^{11} - 3.95 \times 10^{16}$	Incandescent objects
4.	Visible	7600–3800	$3.95 \times 10^{16} - 7.9 \times 10^{14}$	Electric bulbs, sun rays
5.	Ultraviolet(UV)	3800–150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, arc lamps with mercury vapours
6.	X-Rays	150–0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
7.	γ -Rays	0.1–0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Secondary effect of radioactive decay
8.	Cosmic Rays	0.01–zero	3×10^{20} –Infinity	Outer space

Continuous Spectrum: When sunlight (white light) is passed through a prism, it is dispersed or resolved into a continuous spectra of colours. It extends from RED (7600 Å) at one end to the VIOLET (3800Å) at other end. In this region, all the intermediate frequencies between red and violet are present. The type of spectrum is known as Continuous Spectrum., Hence continuous spectra is one which contains radiation of all the frequencies.

Discontinuous Spectrum: Light emitted from atoms heated in a flame or excited electrically in gas discharge tube, does not contain a continuous spread of wavelengths (or frequencies). It contains only certain well-defined wavelength (or frequencies). The spectrum pattern appears as a series of bright lines (separated by gaps of darkness) and hence called as Line-Spectrum.

One notable feature observed is, that each element emits a characteristic spectrum, suggesting that there is discrete relation between the spectrum characteristics and the internal atomic structure of an atom.

8. Photoelectric Effect

It was observed by Hertz and Lenard around 1880 that when a clean metallic surface is irradiated by monochromatic light of proper frequency, electrons are emitted from it. This phenomenon of ejection of the electrons from metal surface was called as Photoelectric Effect.

It was observed that if the frequency of incident radiation is below a certain minimum value (threshold frequency), no emission takes place however high the intensity of light may be.

Another important feature observed was that the kinetic energy of the electrons emitted is independent of the Intensity of the light. The kinetic energy of the electrons increases linearly with the frequency of incident light radiation. This was highly contrary to the laws of Physics at that time i.e. the energy of the electrons should have been proportional to the intensity of the light, not on the frequency.

These features could not be properly explained on the basis of Maxwell's concept of light i.e. light as electromagnetic wave.

In 1905, Einstein applied Planck's quantum theory of light to account for the extraordinary features of the photoelectric effect. He introduced a new concept that light shows dual nature. In phenomenon like reflection, refraction and diffraction it shows wave nature and in phenomenon like photoelectric effects, it shows particle nature. According to the particle nature, the energy of the light is carried in discrete units whose magnitude is proportional to the frequency of the light wave. These units were called as photons (or quanta).

According to Einstein, when a quantum of light (photon) strikes a metal surface, it imparts its energy to the electrons in the metal. In order for an electron to escape from the surface of the metal, it must overcome the attractive force of the positive ions in the metal. So a part of the photon's energy is absorbed by the metal surface to release the electron, this is known as work function of the surface and is denoted by ϕ . The remaining part of the energy of the photon goes into the kinetic energy of the electron emitted. If E is the energy of the photon, KE is the kinetic energy of the electron and ϕ be the work function of the metal then we have;

$$\phi = h\nu_0 \text{ and } E_i = h\nu$$

$$\Rightarrow KE = E_i - \phi \Rightarrow KE = h\nu - h\nu_0 = h(\nu - \nu_0)$$

Also, if m be the mass and v be the velocity of the electron ejected then

$$KE = \frac{1}{2}mv^2 = h(\nu - \nu_0).$$

Note: The electromagnetic Radiation (or wave) now emerges as an entity which shows dual nature i.e., sometimes as Wave and sometimes as Particle (quantum aspect).

9. Quantum Mechanical Model of Atom

The atomic model which is based on the particle and wave nature of the electron is known as wave or quantum mechanical model of the atom. This was developed by Schrodinger in 1926. This model describes the electron as a three dimensional wave in the electronic field of positively charged nucleus. Schrodinger derived an equation which describes wave motion of positively charged nucleus. Schrodinger derived an equation which describes wave motion of an electron. The differential equation is

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

where x, y, z are certain coordinates of the electron, m = mass of the electron, E = total energy of the electron, V = potential energy of the electron; h = Planck's constant and ψ (psi) = wave function of the electron.

Significance of ψ : The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z . The wave function may have positive or negative values depending upon the value of coordinates. The main aim of Schrodinger equation is to give solution for probability approach. When the equation is solved, it is observed that for some regions of space the value of ψ is negative. But the probability must be always positive and cannot be negative, it is thus, proper to use ψ^2 in favour of ψ .

Significance of ψ^2 : ψ^2 is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is

termed as orbital. The important point of the solution of the wave equation is that it provides a set of numbers called quantum numbers which describe energies of the electron in atoms, information about the shapes and orientations of the most probable distribution of electrons around nucleus.

10. Quantum Numbers

To understand the concept of Quantum Numbers, we must know the meaning of some terms clearly so as to avoid any confusion.

Energy Level: The non-radiating energy paths around the nucleus are called as Energy Levels or Shells. These are specified by numbers having values 1, 2, 3, 4, ... or K, L, M, N, ... in order of increasing energies. The energy of a particular energy level is fixed.

Sub-Energy Level: The phenomenon of splitting of spectral lines in electric and magnetic fields reveals that there must be extra energy levels within a definite energy level. These were called as Sub-Energy Levels or Sub-Shells. There are four types of sub-shells namely; **s**, **p**, **d**, **f**.

First energy level (K or 1) has one sub-shell designated as 1s, the second energy level (L or 2) has two sub-shell as 2s & 2p, the third energy level (M or 3) has three sub-shell as 3s, 3p and 3d, and the fourth energy level (N or 4) has four sub-shells as 4s, 4p, 4d and 4f. The energy of sub-shell increases roughly in the order: $s < p < d < f$.

Orbital: Each sub-energy level (sub-shell) is composed of one or more orbitals. These orbitals belonging to a particular sub-shell have equal energies and are called as degenerate orbitals. **s**-sub-shell has one orbital, **p** has three orbitals, **d** has five orbitals and **f** has seven orbitals.

To describe or to characterize the electrons around the nucleus in an atom, a set of four numbers is used, called as Quantum Numbers. These are specified such that the states available to the electrons should follow the laws of quantum mechanics or wave mechanics.

Principal Quantum Number: (n): This quantum number represents the main energy levels (principal energy levels) designated as $n = 1, 2, 3, \dots$ or the corresponding shells are named as K, L, M, N, ... respectively. It gives an idea of position and energy of an electron. The energy level $n = 1$ corresponds to minimum energy and subsequently $n = 2, 3, 4, \dots$, are arranged in order of increasing energy.

Higher is the value of n , greater is its distance from the nucleus, greater is its size and also greater is its energy.

It also gives the total electrons that may be accommodated in each shell, the capacity of each shell is given by the formula $2n^2$, where n : principal quantum number.

Azimuthal Quantum Number: (l): This number determines the energy associated with the angular momentum of the electron about the nucleus. It is also called as the angular momentum quantum number. It accounts for the appearance of groups of closely packed spectral lines in electric field.

It can assume all integral values from 0 to $n-1$. The possible values of l are :

$$0, 1, 2, 3, \dots, n-1.$$

Each value of l describes a particular sub-shell in the main energy level and determines the shape of the electron cloud.

When $n = 1$, $l = 0$, i.e., its energy level contains one sub-shell which is called as a **s**-sub-shell. So for $l = 0$, the corresponding sub-shell is a **s**-sub-shell. Similarly when $l = 1, 2, 3$, the sub-shells are called **p**, **d**, **f** sub-shells respectively.

As you know for $n = 1$, $l = 0$, there is only one sub-shell. It is represented by 1s. Now for $n = 2$, l can take two values (the total number of values taken by l is equal to the value of n in a particular energy level). The possible values of l are 0, 1. The two sub-shell representing the IInd energy level are 2s, 2p. In the same manner, for $n = 3$, three sub-shells are designated as 3s, 3p, 3d corresponding to $l = 0, 1, 2$, and for $n = 4$, four sub-shells are designated as 4s, 4p, 4d, 4f corresponding to $l = 0, 1, 2, 3$.

The orbital Angular momentum of electron = $\sqrt{\ell(\ell+1)} \frac{h}{2\pi}$.

Note that its value does not depend upon value of n .

Magnetic Quantum Number (m): An electron with angular momentum can be thought as an electric current circulating in a loop. A magnetic field due to this current is observed. This induced magnetism is determined by the magnetic quantum number. Under the influence of magnetic field, the electrons in a given sub-energy level prefer to orient themselves in certain specific regions in space around the nucleus. The number of possible orientations for a sub-energy level is determined by possible values of m corresponds to the number of orbitals in a given sub-energy level).

m can have any integral values between $-l$ to $+l$ including 0, i.e., $m = -l, 0, +l, \dots, 0, 1, 2, 3, 4, \dots, l-1, +l$. We can say that a total of $(2l + 1)$ values of m are there for a given value of l — 2, -1, 0, 1, 2, 3.

In s sub-shell there is only one orbital [$l = 0, \Rightarrow m = (2l + 1) = 1$].

In p sub-shell there are three orbitals corresponding to three values of m : -1, 0 +1. [$l = 1 \Rightarrow m = (2l + 1) = 3$]. These three orbitals are represented as p_x, p_y, p_z along X, Y, Z axes perpendicular to each other.

In d sub-shell, there are five orbitals corresponding to -2, -1, 0 +1, +2, [$l = 2 \Rightarrow m = (2 \times 2 + 1) = 5$]. These five orbitals are represented as $d_{xy}, d_{zx}, d_{x^2-y^2}, d_{z^2}$.

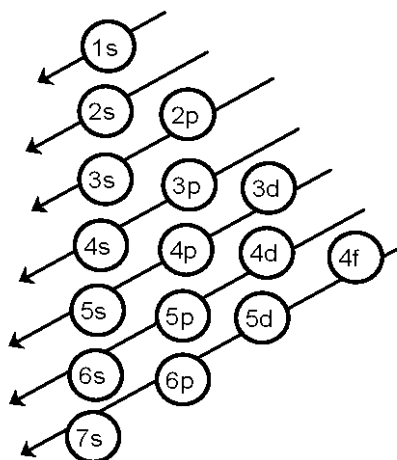
In f sub-shell there are seven orbitals corresponding to -3, -2, -1, 0, +1, +2, +3 [$l = 3 \Rightarrow m = (2 \times 3 + 1) = 7$].

Spin quantum Number (s): When an electron rotates around a nucleus it also spins about its axis. If the spin is clockwise, its spin quantum number is $+1/2$ and is represented as \uparrow . If the spin is anti-clockwise, its value is $-1/2$ and is represented as \downarrow . If the value of s is $+1/2$, then by convention, we take that electron as the first electron in that orbital and if the value of s is $-1/2$, it is taken as second electron.

11. Aufbau Principle

Aufbau is a German word meaning 'building up'. This gives us a sequence in which various sub-shells are filled up depending on the relative order of the energy of the sub-shells. The sub-shell with minimum energy is filled up first and when this obtains maximum quota of electrons, then the next sub-shell of higher energy starts filling.

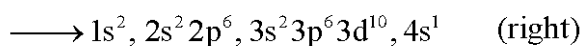
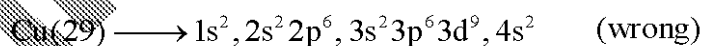
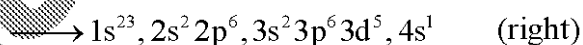
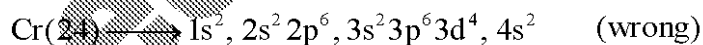
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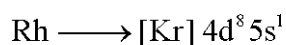
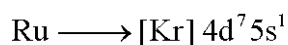
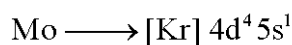
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

Sub-shell	n	l	(n+l)	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	Lowest value of n
3s	3	0	3	
3p	3	1	4	Lowest value of n
4s	4	0	4	
3d	3	2	5	Lowest value of n
4p	4	1	5	
5s	5	0	5	
4d	4	2	6	Lowest value of n
5p	5	1	6	
6s	6	0	6	
4f	4	3	7	Lowest value of n
5d	5	2	7	
6p	6	1	7	
7s	7	0	7	
5f	5	3	8	Lowest value of n
6d	6	2	8	
7p	7	1	8	

Exceptions to Aufbau Principle: In some cases it is seen that actual electronic arrangement is slightly different from arrangement given by Aufbau principle. A simple reason behind this is that half-filled and full-filled sub-shell have got extra stability.



Similarly the following elements have slightly different configurations than expected.

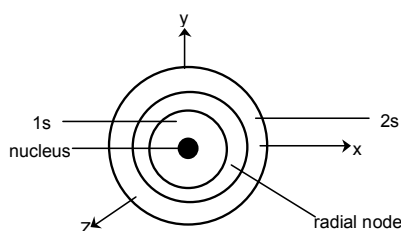




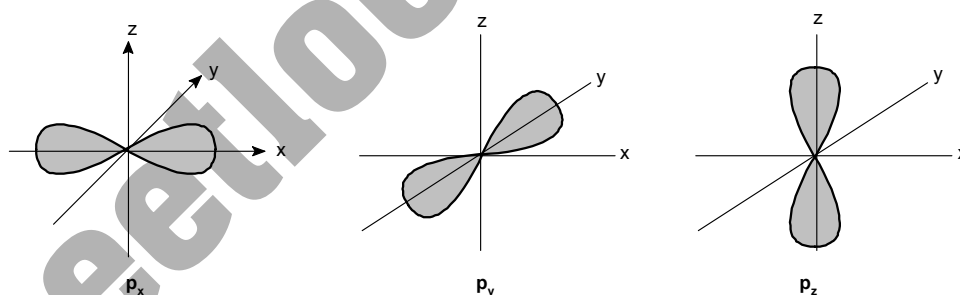
Shapes of Atomic Orbitals

- (i) **S-orbital:** An electron is considered to be immersed out in the form of a cloud. The shape of the cloud is the shape of the orbital. The cloud is not uniform but denser in the region where the probability of finding the electron is maximum.

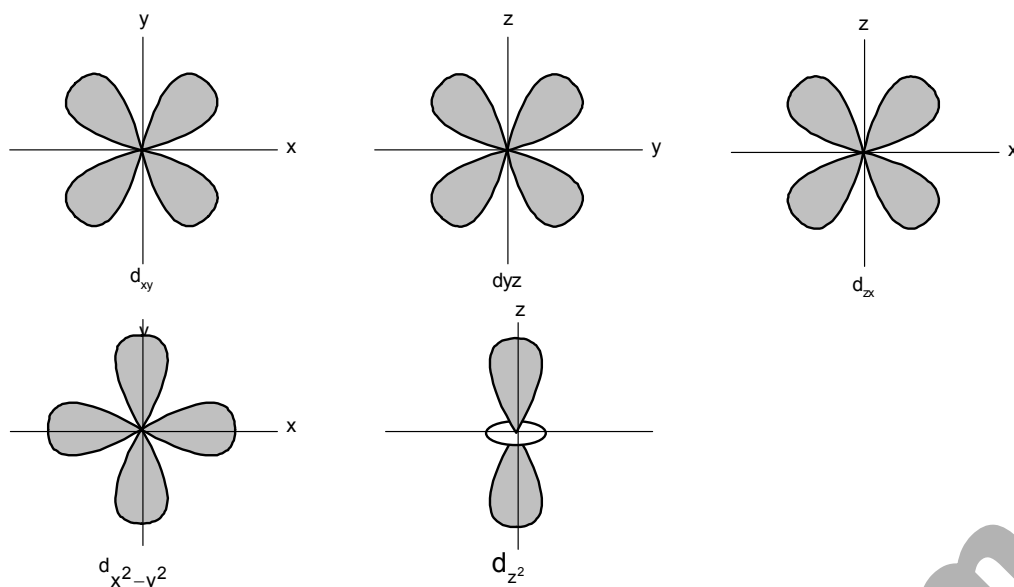
The orbital with the lowest energy is the 1s orbital. It is a sphere with its center of the nucleus of the atom. The s-orbital is said to be spherically symmetrical about the nucleus, so that the electronic charge is not concentrated in any particular direction. 2s orbital is also spherically symmetrical about the nucleus, but it is larger than (i.e., away from) the 1s orbit.



- (ii) **p-orbitals:** There are three p-orbitals: p_x , p_y and p_z . They are dumb-bell shaped, the two lobes being separated by a nodal plane, i.e., a plane where there is no likelihood of finding the electron. The p-orbitals have a marked direction character, depending as to whether p_x , p_y and p_z orbital is being considered. The p-orbitals consist of two lobes with the atomic nucleus lying between them. The axis of each p-orbital is perpendicular to the other two. The p_x , p_y and p_z orbitals are equivalent except for their directional property. They have the same energy; orbitals having the same energy are said to be degenerated.



- (iii) **d-orbitals:** There are five d-orbitals. The shapes of four d-orbitals resemble four leaf clovers. The fifth d-orbital has a different shape. The shapes of these orbitals are given below.



12. Dual Character

In case of light some phenomenon like diffraction and interference can be explained on the basis of its wave character. However, the certain other phenomenon such as black body radiation and photoelectric effect can be explained only on the basis of its particles nature. Thus, light is said to have a dual character. Such studies on light were made by Einstein in 1905.

Louis de-Broglie, in 1942 extended the ideal of photons to material particles such as electron and he proposed that matter also has a dual character-as wave and as particle.

Derivation of de-Broglie equation: The wavelength of the wave associated with any material particle was calculated by analogy with photon. In case of photon, if it is assumed to have wave character, its energy is given by

$$E = h\nu \dots (i) \text{ (according to the Planck's quantum theory)}$$

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

If the photon is supposed to have particle character, its energy is given by

$$E = mc^2 \dots (ii) \text{ according to Einstein's equation)}$$

where 'm' is the mass of photon, 'c' is the velocity of light.

By equating (i) and (ii)

$$h\nu = mc^2$$

$$\text{But } \nu = c / \lambda$$

$$h \frac{c}{\lambda} = mc^2$$

$$(\text{or}) \lambda = h / mc$$

The above equation is applicable to material particle if the mass and velocity of photon is replaced by the mass and velocity of material particle. Thus for any material particle like electron.

$$\lambda = h / mv \text{ (or) } \lambda = \frac{h}{p}$$

where $mv = p$ is the momentum of the particle.

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13. Heisenberg's Uncertainty Principle

All moving objects that we see around us e.g., a car, a ball thrown in the air etc, move along definite paths. Hence their position and velocity can be measured accurately at any instant of time. Is it possible for subatomic particle also?

As a consequence of dual nature of matter. Heisenberg, in 1927 gave a principle about the uncertainties in simultaneous measurement of position and momentum (mass \times velocity) of small particles. This principle states.

It is impossible to measure simultaneously the position and momentum of a small microscopic moving particle with absolute accuracy or certainty i.e., if an attempt is made to measure any one of these two quantities with higher accuracy, the other becomes less accurate.

The product of the uncertainty in position (Δx) and the uncertainty in the momentum ($\Delta p = m \cdot \Delta v$ where m is the mass of the particle and Δv is the uncertainty in velocity) is equal to or greater than $h/4\pi$ where h is the Planck's constant.

Thus, the mathematical expression for the Heisenberg's uncertainty principle is simply written as

$$\Delta x \cdot \Delta p \geq h/4\pi \quad \text{or} \quad \Delta E \times \Delta t \geq \frac{h}{4\pi}$$

Explanation of Heisenberg's uncertainty Principle: Suppose we attempt to measure both the position and momentum of an electron, to pin point the position of the electron we have to use light so that the photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the hitting, the position as well as the velocity of the electron is distributed. The accuracy with which the position of the particle can be measured depends upon the wavelength of the light used. The uncertainty in position is $+\lambda$. The shorter the wavelength, the greater is the accuracy. But shorter wavelength means higher frequency and hence higher energy. This high energy photon on striking the electron changes its speed as well as direction. But this is not true for macroscopic moving particle. Hence Heisenberg's uncertainty principle is not applicable to macroscopic particles.

Electronic Configuration of Elements: Quantum numbers can now characterize the electrons in an atom. To describe the arrangements and distribution of electrons for different elements, following rules and selective principles are used. The distributions of electrons in an atom is known as the electronic configuration of that element.

Aufbau Principle: An atom in its lowest state of energy is said to be in ground state. The ground state is the most stable in an atom. According to Aufbau principle.

"Electrons are added progressively to the various orbitals in their order of increasing energy starting with the orbital of lowest energy".

The order of increasing energy may be summed up as follows

$$1s, 2s, 2p, 3s, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, \dots$$

As a working rule, a new electron enters an empty orbital for which the value of $(n + l)$ is minimum. If the value $(n + l)$ is same for two or more orbitals, the new electron enters an orbital having lower value of n .

Pauli's Exclusion Principle: According to this principle

No two electrons in an atom can have the same set of all the quantum numbers or one can say that no two electrons can have the same quantised states.

Consider an electronic arrangement in 1st energy level ($n = 1$). For $n = 1$, $l = 0$, and $m = 0$. Now s can have two values corresponding to each value of m i.e. $s = +1/2, -1/2$ (n, l , possible designation of an electron in a state with $n = 1$ is $1, 0, 0, +1/2$ and $1, 0, 0, -1/2$ (n, l, m, s) i.e., two quantised states. This implies that an orbital can accommodate (for $n = 1, m = 0, \Rightarrow$ one orbital) maximum of two electrons having opposite spins.

The maximum number of electrons in the different subshells = $2(2l + 1)$.

s -sub-shell = 2, p -sub-shell = 6, d -sub-shell = 10 and f -sub-shell = 14.

Hund's Rule of maximum Multiplicity

According to this rule: "Electrons never pair until no available empty degenerate orbitals are left to him."

This means an electron always occupies a vacant orbital in the same sub-shell (degenerate orbital) and pairing starts only when all of the degenerate orbitals are filled up. This means that the pairing starts with 2nd electron in a sub-shell, 4th electron in p -sub-shell, 6th electron in d -sub-shell and 8th electron in f -sub-shell.

By doing this, the electrons stay as far away from each other as possible. This is highly reasonable if we consider the electron-electron repulsion. Hence electrons obey Hund's rule as it results in lower energy state and hence more stability.

Extra Stability of Half and fully Filled Orbitals: A particularly stable system is obtained when a set of equivalent orbitals (degenerate orbitals) is either fully filled or half filled, i.e., each containing one or a pair of electrons. This effect is more dominant in d and f sub-shells.

This means three or six electrons in p -sub-shell, five or ten electrons in d -sub-shell, and seven or fourteen electrons in f -sub-shell forms a stable arrangement. Note this effect when filling of electrons takes place in d sub-shells (for atomic number $Z = 24, 25$, and $29, 30$).

In the following table you should analyse how to employ the above rules to write electronic configuration of various elements.

Electronic configuration of an element is represented by the notation $n l^x$.

x : number of electrons present in an orbital

l : denotes the sub-shell

n : principal quantum number.

14. Node and Nodal Plane

Node is defined as a region where the probability of finding an electron is zero.

The planes passing through the angular nodal points are called nodal planes.

Nodes

No. of radial or spherical nodes = $n - l - 1$

No. of angular nodes = l , Total no. of nodes = $n - 1$

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