

2. ATOMIC STRUCTURE

1. INTRODUCTION

The word atom in Greek means indivisible, i.e. an ultimate particle which cannot be further subdivided. This idea of all matter ultimately consisting of extremely small particles was conceived by ancient Indian and Greek philosophers. The old concept was put on firm footing by John Dalton with his atomic theory that was developed by him during the years 1803–1808.

1.1 Dalton's Atomic Theory

Dalton's atomic theory (1808) is based on the following two laws: law of conservation of mass and law of definite proportions. He also proposed law of multiple proportions, as a logical consequence of his theory.

- (a) Every element is composed of extremely small indestructible particles called atoms ('atom' in Greek means indivisible).
- (b) Atoms of any one element are all similar but they differ from atoms of another element.
- (c) Atoms of each element are fundamental particles, have a characteristic mass but do not have any structure.
- (d) Atoms of various elements take part in a chemical reaction to form compound (which is called molecule).
- (e) In any compound, the relative number and kinds of atoms are constant.

2. DISCOVERY OF FUNDAMENTAL PARTICLES

2.1 Cathode Rays – Discovery of Electron

- (a) In mid-1800s, scientists (William Crookes 1879, Julius Plucker 1889) started to study the discharge of electricity through partially evacuated tubes. Gases are normally poor conductor of electricity and they do not conduct electricity under normal pressure even with an applied potential of 1000 volt. However when the pressure was reduced to 10^{-2} mm at a potential of 1000 volt, Crookes and Plucker noticed that:

- (i) From the cathode surface a glow surrounding the cathode began and the space left between the glow and cathode was named Crookes dark space. Under this condition electric current starts to flow from one electrode to other.
- (ii) When the pressure is sufficiently low, the glow fills whole of the tube.

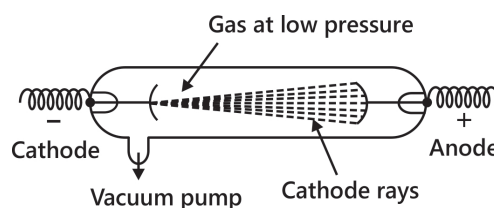


Figure 2.1: Cathode ray tube

Subsequently Thomson (1897) carried out the discharge through a vacuum tube which was filled with a gas at very low pressure (10^{-2} to 10^{-3} mm); he noticed the emission of invisible rays which produced fluorescence on the glass and influenced photographic plate. These rays were called cathode rays.

Important characteristics of cathode rays are as follows:

- (a) Cathode rays travel in straight lines with high speed of the order of 10^7 ms^{-1} , producing shadows of the objects placed in their path.
- (b) Cathode rays can pass through thin layers of matter.
- (c) Cathode rays are emitted from the surface of the cathode; their direction is not affected by the position of the anode.
- (d) Cathode rays have high kinetic energy and therefore:
 - (i) They can exert mechanical pressure on the object on which they fall.
 - (ii) They can produce heat when stopped by matter.
 - (iii) They can ionize a gas.
- (e) Cathode rays are deflected, both, by electric and magnetic fields.
- (f) Cathode rays produce fluorescence when they fall on certain substances like ZnS. The color of fluorescence varies with the chemical nature of substance.
- (g) Cathode rays can produce chemical changes and thus they affect photographic plates.
- (h) Cathode rays produce X-rays, when they strike a metal target of high atomic number such as tungsten, which are highly penetrating. In 1897 J. J. Thomson determined the e/m value (charge/mass) of the electron by studying the deflection of cathode rays in electric and magnetic fields. The value of e/m has been found to be $-1.7588 \times 10^8 \text{ coulomb/g}$.

2.1.1 Millikan's Oil-Drop Experiment

In 1909, the first precise measurement of the charge on an electron was made by Robert A. Millikan using his oil drop experiment. The charge on the electron was calculated to be $-1.6022 \times 10^{-19} \text{ coulomb}$. An electron has the smallest charge known; so it was, designated as unit negative charge.

Mass of the electron: The mass of the electron is calculated from the values of e/m .

$$e. m = e = \frac{e}{e/m} = \frac{-1.6022 \times 10^{-19}}{-1.7588 \times 10^8} = 9.1096 \times 10^{-28} \text{ g or } 9.1096 \times 10^{-31} \text{ kg}$$

This is known as the rest mass of the electron; that is, the mass of the electron when it is moving with low speed. For calculating the mass of a moving electron, the following formula is used.

$$\text{Mass of moving electron} = \frac{\text{rest mass of electron}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}, \text{ where } v \text{ is the velocity of the electron and } c \text{ is the velocity of}$$

light. When v is equal to c , mass of the moving electron is infinity and when the velocity of the electron becomes greater than c , the mass of the electron becomes imaginary.

Note: An electron can, thus be defined as a subatomic particle which carries charge $-1.60 \times 10^{-19} \text{ coulomb}$, that is, one unit negative charge and has mass $9.1 \times 10^{-31} \text{ g}$, that is, $\frac{1}{1837}$ the mass of the hydrogen atom (0.000549 amu).

2.2 Discovery of Protons – Positive Rays

- (a) Goldstein (1886) repeated the discharge tube experiment but he used perforated cathode and noticed the emission of positive rays or canal rays.

Note: These rays do not originate from anode, and so it is wrong to call them anode rays.

- (b) The specific charge (e/m) of canal rays particles varied with nature of gas and was found to be maximum if H_2 was used.
- (c) The positive rays particles were thus, called positively charged gaseous atoms left after the removal of electron or ionized gaseous atoms. However, if H_2 gas is used in discharges, the positive rays particles are named as protons (usually represented as P).
- (d) Thus, a subatomic particle, that is a fundamental constituent of all matter, is called a proton; it has a mass 1.673×10^{-27} kg and charge $+1.603 \times 10^{-19}$ C.

MASTERJEE CONCEPTS

- The specific charge (e/m) of proton is 9.58×10^7 C/kg.
- Mass of 1 mole proton = $N \times m_p = 6.023 \times 10^{23} \times 1.673 \times 10^{-27}$ kg = 1.0076×10^{-3} kg = 1.0076 g.
- The radius of proton = 1.53×10^{-13} cm.
- The volume of proton = $\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (1.53 \times 10^{-13})^3 = 1.50 \times 10^{-38}$ cm³.
- The charge on positive rays is usually +1 but it may have +2, +3 values.

Saurabh Gupta (JEE 2010, AIR 443)

The TV QUESTION

Q. What is the basic principle of a television picture tube or fluorescent light tubes?

Ans. The television picture tube is a cathode ray tube; the picture is produced due to fluorescence on the television screen coated with suitable material. Likewise fluorescent light tubes are also cathode ray tubes. These are coated inside with suitable materials which produce visible light when hit with cathode rays.

3. EARLIER MODELS OF ATOMS

3.1 Thomson's Model

After the discovery of protons and electrons, Thomson in 1898 proposed a watermelon model; the atom is considered as a sphere of positive charge with the electrons distributed within the sphere of radius of 10^{-10} m so as to give the most stable electrostatic agreement. In this model, the atom is visualized as a pudding or cake of positive charge with raisins (electrons) embedded in it. A major point of this model is that the mass of atom is considered to be spread uniformly over the atom.

3.2 Rutherford's Experiment

Rutherford conducted a series of experiments using α -particles. A beam of α -particles was directed against a thin foil of gold, platinum, silver, or copper. The foil was surrounded by a circular fluorescent zinc screen. Whenever an α -particle struck the screen, it produced a flash of light.

The following observations were made:

- (a) Most of the α -particles went straight without suffering any deflection.
- (b) Some of them were deflected through small angles.
- (c) A very small number (about 1 in 20,000) did not pass through the foil at all but suffered large deflections or even rebound.

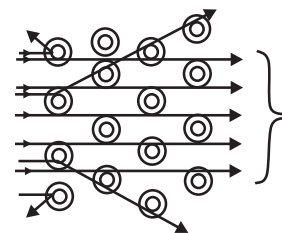


Figure 2.2: Gold leaf experiment

Following conclusions were drawn from these observations:

- (a) Many of the particles went straight through the metal foil undeflected, indicating that there must be very large empty space within the atom.
- (b) Some of the α -particles were deflected from their original paths through moderate angles, indicating that whole of the positive charge is concentrated in a space called nucleus. It is proposed to be present at the center of the atom.
- (c) A very small number of the α -particles suffered strong deflections or even rebound on their path indicating that the nucleus is rigid and α -particles recoil due to direct collision with the positively charged heavy mass.

Note: Information of Rutherford's scattering equation can be memorized by the following relations:

- (i) Kinetic energy of α -particles: $N = K_1 / [(1/2)mv^2]^2$
- (ii) Scattering angle ' θ ': $N = K_2 / [(\sin^4(\theta / 2))]$
- (iii) Nuclear charge: $N = K_3(Ze)^2$

Here, N = Number of α -particle striking the screen and K_1 , K_2 and K_3 are the constants.

3.3 Moseley's Experiment

Moseley studied the X-ray spectra of 38 different elements, starting from aluminium to gold by measuring the frequency of principal lines of a particular series (the α -lines in the k -series) of the spectra. He observed that the frequency of the particular spectral line was related to the serial number of the element in the periodic table which he termed atomic number (Z). He presented the following relationship

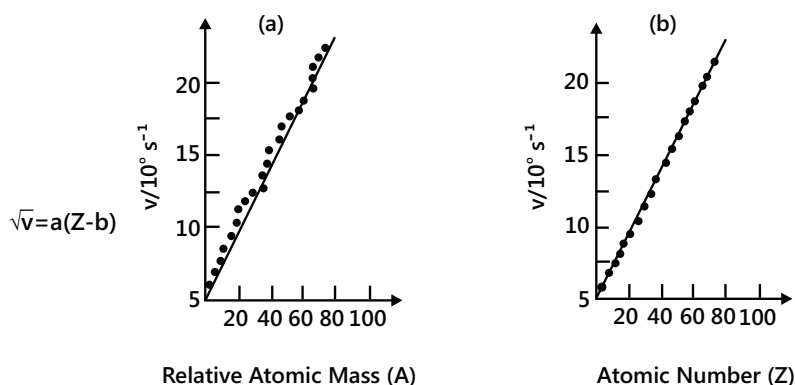


Figure 2.3: Moseley's plots

where ν = frequency of X-rays, Z = atomic number, a and b are constants. When the values of square roots of the frequency were plotted against atomic number of the element producing X-rays, a straight line was obtained. It was pointed out that the atomic number of an element is equal to the total positive charge of the nucleus.

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Atomic number of the element

= Serial number of the element in periodic table

= Charge on the nucleus of the atom of the element

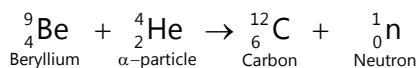
= Number of protons present in the nucleus of the atom of the element

= Number of extra nuclear electrons present in the atom of the element

Neeraj Toshniwal (JEE 2009, AIR 21)

3.4 Discovery of Neutron and Rutherford's Model

Chadwick bombarded beryllium with a stream of α -particles. He observed that the produced penetrations were not affected by electric and magnetic fields. These radiations consisted of neutral particles, which were called neutrons.



The mass of the neutron was determined to be 1.675×10^{-24} g, that is, nearly equal to the mass of proton.

Thus a neutron is a subatomic particle having a mass of 1.675×10^{-24} g, approximately 1 amu or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge. The e/m of neutron is zero.

Rutherford's Model of Atom: Rutherford proposed a model of the atom known as nuclear atomic model. As per this model,

- (a) An atom consists of a positively charged heavy nucleus where all the protons and neutrons are present. The number of the positive charge on the nucleus is different for different atoms.
- (b) The volume of the nucleus is very small and is only a very small fraction of the total volume of the atoms.

$$\frac{\text{Diameter of atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8} \text{ cm}}{10^{-13} \text{ cm}} = 10^5$$

Thus, the diameter of an atom is 100,000 times the diameter of the nucleus.

The radius of a nucleus is proportional to the cube root of the mass number.

Radius of the nucleus = $1.33 \times 10^{-13} \times A^{1/3}$ cm where A is the mass number.

- (c) There is an empty space around nucleus called extra nuclear part, where electrons are present. The number of electrons in an atom is always equal to the number of protons present in the nucleus. The volume of the atom is about 10^{15} times the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = \frac{10^{-24}}{10^{-39}} = 10^{15}$$

- (d) The electrons revolve around the nucleus in closed orbits with high speeds. Centrifugal force is acting on the revolving electrons and is being counterbalanced by the force of attraction between electrons and the nucleus.

This model is similar to solar system; the nucleus representing the Sun and the electrons the Planets. The electrons are, therefore, generally referred to as planetary electrons.

Drawbacks of Rutherford's Model

- (a) According to wave theory, when a charged particle moves under the influence of an attractive force, it loses energy continuously in the form of electromagnetic radiations. Thus, the electron which moves in an attractive field (created by protons present in the nucleus) will emit radiations.

As result the electron will lose energy at every turn and move closer and closer to the nucleus following a spiral path and finally fall into the nucleus, thereby making the atom unstable. But the atom is quite stable meaning the electrons do not fall into nucleus, thus this model does not explain the stability of the atom.

- (b) If the electrons lose energy continuously, the observed spectra should be continuous. But the observed spectra consists of well-defined lines of definite frequency. Hence, in an atom, the loss of energy by the electrons is not continuous.

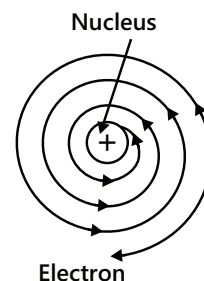


Figure 2.4: Spiral path of electron

3.5 Atomic Number and Mass Number

Atomic number of an element = Total number of protons present in the nucleus
 = Total number of electrons present in the neutral atom

Mass number of an element = No. of protons + No. of neutrons

3.6 Isotopes, Isobars, Isotones and Isoelectronic

Such atoms of the same element having the same atomic number but different mass numbers are known as isotopes. Such atoms of different elements having different atomic numbers, but same mass number, e.g.

$^{40}_{18}\text{Ar}$, $^{40}_{19}\text{K}$, $^{40}_{20}\text{Ca}$, are known as isobars. Such atoms of different elements containing the same number of neutrons,

e.g. $^{14}_6\text{C}$, $^{15}_7\text{N}$, $^{16}_8\text{O}$, are called isotones. Each of these atoms contains eight neutrons. They differ in atomic number as well mass number. Such species (atoms or ions) containing the same number of electrons, e.g. O^{2-} , F^{-} , Na^{+} , Mg^{2+} , Al^{3+} , Ne are called isoelectronic. Each of these contains 10 electrons each and so they are isoelectronic.

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- Retain in Memory:** Isotopes have same number of protons but different number of neutrons. Isobars have different number of protons as well as different number of neutrons. Isotones have different number of protons but same number of neutrons.
- Retain in Memory:** In a neutral atom (^A_ZX), No. of protons = No. of electrons = Atomic no.
 In a negative ion (X^{n-}), No. of electrons > No. of protons.
 No. of electrons = $Z + n$
 In a positive ion (M^{n+}), No. of electrons < No. of protons.
 No. of electrons = $Z - n$
 However, No. of protons is always = Z and No. of neutrons is always = $A - Z$.

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 1: Find out the atomic number, mass number, number of protons, electrons and neutrons present in the element with the notation $^{238}_{92}\text{U}$. (JEE MAIN)

Sol: Number of protons = Number of electrons = Atomic number (Z)

Number of neutrons = Mass number – Atomic number

Atomic number (Z) = 92

Mass number (A) = 238

∴ Number of protons = 92 and Number of electrons = 92

Further, $A - Z = 238 - 92 = 146$

Illustration 2: The nuclear radius is of the order of 10^{-13} cm while atomic radius is of the order 10^{-8} cm. If the nucleus and the atoms are assumed to be spherical, what is the fraction of the atomic volume occupied by the nucleus? **(JEE MAIN)**

Sol: Considering the spherical conditions, the volume of a sphere = $\frac{4\pi r^3}{3}$ where r is the radius of the sphere.

∴ Volume of the nucleus = $\frac{4\pi r^3}{3} = \frac{4\pi (10^{-13})^3}{3} \text{ cm}^3$

Similarly, volume of the atom = $\frac{4\pi r^3}{3} = \frac{4\pi (10^{-8})^3}{3} \text{ cm}^3$

∴ Fraction of the volume of atom occupied by the nucleus = $\frac{\frac{4\pi(10^{-13})^3}{3} \text{ cm}^3}{\frac{4\pi(10^{-8})^3}{3} \text{ cm}^3} = 10^{-15}$

4. ELECTROMAGNETIC RADIATIONS

Electromagnetic Radiations (EMR) are energy radiations which do not need any medium for propagation, e.g. visible, ultraviolet, X-rays, etc. Following are the important characteristics of EMR:

- (a) All electromagnetic radiations or waves travel with the velocity of light.
- (b) These consist of electric and magnetic fields that oscillate in directions perpendicular to each other and perpendicular to the direction in which the wave is travelling.

4.1 Characteristics of Waves

A wave is always characterized by the following six characteristics:

- (a) **Wavelength:** The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ (lambda) and is measured in units of centimetre (cm), angstrom (Å), micrometre, (μm) or nanometre (nm).

$$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

$$1 \mu\text{m} = 10^{-4} \text{ cm} = 10^{-6} \text{ m}$$

$$1 \text{ nm} = 10^{-7} \text{ cm} = 10^{-9} \text{ m}$$

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

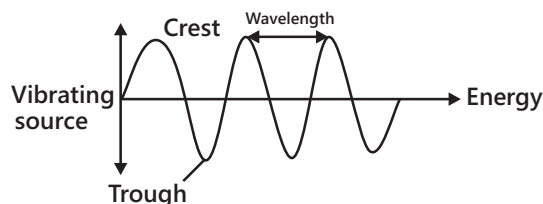


Figure 2.5: Representation of a wave and wavelength

- (b) **Frequency:** It is defined as the number of waves passing through a point in one second. It is denoted by the symbol (ν) and is measured in terms of cycles (or waves) per second (cps) or hertz (Hz).

$$\lambda \nu = \text{Distance travelled in one second} = \text{Velocity} = c \text{ or } \nu = \frac{c}{\lambda}$$

- (c) **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, that is, $3 \times 10^{10} \text{ cm/sec}$. $\lambda \nu = 3 \times 10^{10}$. Thus, a wave of higher frequency has shorter wavelength while a wave of lower frequency has a longer wavelength.

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

(e) **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.

(f) **Time period:** Time taken by one wave to complete a cycle or vibration is called time period. It is denoted by

$$T, T = \frac{1}{\nu}$$

Unit: Second per cycle.

4.2 Electromagnetic Spectrum

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

$$\nu \equiv 3 \times 10^7 \text{ (cycle/sec)} \xrightarrow{\text{Frequency}} 3 \times 10^{21}$$

$$\lambda(\text{cm}) = 10^3 \xrightarrow{\text{Wavelength}} 10^{-11}$$

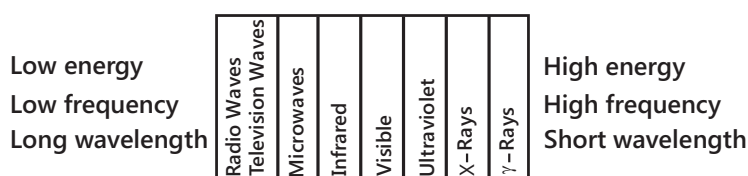


Figure 2.6: Electromagnetic spectrum

5. ATOMIC SPECTRA OF HYDROGEN

The impression produced on a screen when radiations of particular wavelengths are passed through a prism or diffraction grating is known as spectrum. It is broadly of two types: Emission spectra and Absorption spectra

Differences between emission spectrum and absorption spectrum

Emission spectrum	Absorptions spectrum
1. It gives bright lines (colored on the dark background).	1. It gives dark lines on the bright background.
2. Radiations from emitting source are analyzed by the spectroscope.	2. It is observed when the white light is passed through the substance and the transmitted radiations are analyzed by the spectroscope.
3. It may be continuous (if source emits white light) and may be discontinuous (if the source emits colored light).	3. These are always discontinuous.

5.1 Emission Spectra

It is obtained from the substances which emit light on excitation, that is, either by heating the substances on a film or by passing electric discharge through a thin filament of high melting point metal. Emission spectra are of two types:

(a) **Continuous spectra:** When white light is allowed to pass through a prism, the light gets resolved into several colours. This spectrum is a rainbow of colours, meaning violet merges into blue, blue into green and so on. This is a continuous spectrum.

(b) **Discontinuous spectra:** When gases or vapours of a chemical substance are heated in an electric arc or in a Bunsen flame, light is emitted. When a ray of this light is passed through a prism, a line spectrum is produced.

This spectrum consists of limited number of lines, each of which corresponds to a different wavelength of light. Each element has a unique line spectrum. Spectrum of hydrogen is an example of line emission spectrum or atomic emission spectrum. If an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted. If a ray of this light is passed through a prism, a discontinuous line spectrum of many isolated sharp lines is obtained. The wavelengths of the different lines show that these lines are in the visible, ultraviolet and infrared regions. The lines observed in the hydrogen spectrum can be classified into six series.

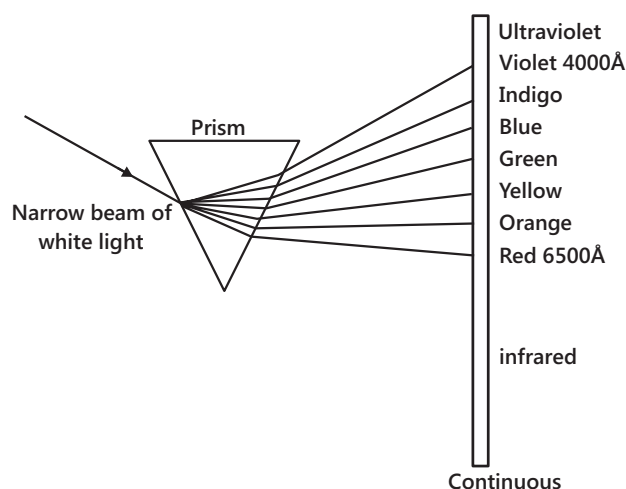


Figure 2.7: Continuous spectrum

Spectral series	Discovered by	Appearing in
Lyman series	Lyman	Ultraviolet region
Balmer series	Balmer	Visible region
Paschen series	Paschen	Infrared region
Brackett series	Brackett	Infrared region
Pfund series	Pfund	Infrared region
Humphrey series	Humphrey	Far-infrared region

5.2 Ritz Mathematical Formula

Ritz presented a mathematical formula to find the wavelengths of various hydrogen lines.

$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ where, R is universal constant, known as Rydberg constant. Its value is 0.9678 cm^{-1} , n_1 and

n_2 are integers (such that $n_2 > n_1$). For a given spectral series, n_1 remains constant while n_2 varies from line to line in the same series. The value of n_1 is 1, 2, 3, 4 and 5 for the Lyman, Balmer, Paschen, Brackett and Pfund series respectively. n_2 is greater than n_1 by at least 1.

Following are the values of n_1 and n_2 for various series:

Spectral series	Value of n_1	Value of n_2
Lyman series	1	2, 3, 4, 5,.....
Balmer series	2	3, 4, 5, 6,.....
Paschen series	3	4, 5, 6, 7,.....
Brackett series	4	5, 6, 7, 8,.....
Pfund series	5	6, 7, 8, 9,.....

Note: (i) Atoms give line spectra while molecules give band spectra.

(ii) Balmer, Paschen, Brackett, Pfund series are found in emission spectrum.

5.3 Absorption Spectra

When the radiations from a continuous source like a hot body (sunlight) containing the quanta of all wavelengths pass through a sample of hydrogen gas, then the wavelength missing in the emergent light gives dark lines on the bright background. This type of spectrum that contains lesser number of wavelengths in the emergent light than in incident light is called absorption spectrum.

Illustration 3: Which has a higher energy, a photon of violet light with wavelength 400 Å or a photon of red light with wavelength 7000 Å? [$h = 6.62 \times 10^{-34}$ Js] **(JEE MAIN)**

Sol: Using photoelectric effect, $E = h\nu = h \frac{c}{\lambda}$

Given $h = 6.62 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms⁻¹

For a photon of violet light $\lambda = 4000 \text{ Å} = 4000 \times 10^{-10} \text{ m}$; $E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{4 \times 10^{-7}} = 4.96 \times 10^{-19}$

For a photon of red light, $L = 7000 \text{ Å} = 7000 \times 10^{-10} \text{ m}$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{7000 \times 10^{-10}} = 2.83 \times 10^{-19} \text{ J}$$

Hence, a photon of violet light has higher energy than a photon of red light.

Illustration 4: Calculate the wavelength of the spectral line, when the electron in the hydrogen atom undergoes a transition from the energy level 4 to energy level 2. **(JEE MAIN)**

Sol: According to Rydberg equation $\frac{1}{\lambda} = R \left(\frac{1}{x^2} - \frac{1}{y^2} \right)$

$$R = 109678 \text{ cm}^{-1}; x = 2; y = 4; \frac{1}{\lambda} = 109,678 \left[\frac{1}{4} - \frac{1}{16} \right] = 109,678 \times \frac{3}{16}$$

On solving, $\lambda = 486 \text{ nm}$.

6. QUANTUM THEORY OF RADIATION

In 1905, Einstein pointed out that light can be considered to consist of a stream of particles, called photons. The energy of each photon of light depends on the frequency of the light, that is, $E = h\nu$. According to Einstein, energy is also related as $E = mc^2$ where m is the mass of photon. Thus, he pointed out that light has wave as well as particle characteristics (dual nature).

Though the wave theory successfully explains many properties of electromagnetic radiations such as reflection, refraction, diffraction, interference, polarization etc. it fails to explain some phenomena like blackbody radiation, photoelectric effect etc. A new theory which is known as quantum theory of radiation was presented by Max Planck in 1901, to explain the blackbody radiation and photoelectric effect. According to this theory, a hot body emits radiant energy not continuously but discontinuously in the form of small packets of energy called quantum (quanta in plural). The energy associated with each quantum of a given radiation is proportional to the frequency of the emitted radiation. $E \propto \nu$ or $E = h\nu$ where h is a constant known as Planck's constant. Its numerical value is 6.624×10^{-27} erg/sec. The energy emitted or absorbed by a body can be either one quantum or any whole number multiple of $h\nu$, that is, $2h\nu, 3h\nu, 4h\nu, \dots, nh\nu$ quanta of energy.

6.1 Photoelectric Effect

The emission of electrons from a metal surface when exposed to light radiations of appropriate wavelength is called photoelectric effect. The emitted electrons are called photoelectrons. Work function or threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface. According to Einstein,

maximum kinetic energy of the ejected electron = Absorbed energy – Work function $\frac{1}{2}mv_{\max}^2 = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$,
 where ν_0 and λ_0 are threshold frequency and threshold wavelength respectively.

Stopping potential: Stopping potential is the minimum potential at which the photoelectric current becomes zero. If V_0 is the stopping potential, then $V_0 = h(\nu - \nu_0)$.

Laws of Photoelectric Effect

- Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.
- The maximum kinetic energy of photoelectrons is directly proportional to the frequency of incident radiation; also, it is independent of the intensity of light used.
- There is no time lag between incidence of light and emission of photoelectrons.
- For emission of photoelectrons, the frequency of incident light must be equal or greater than the threshold frequency.

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If kinetic energy of the emitted photoelectrons is plotted against the frequency of the absorbed photons, a straight line of slope h is obtained as shown in Fig. 2.8 A. If kinetic energy of the photoelectrons is plotted against intensity of the incident radiation (keeping frequency constant), a horizontal line is obtained as shown in Fig. 2.8 B.

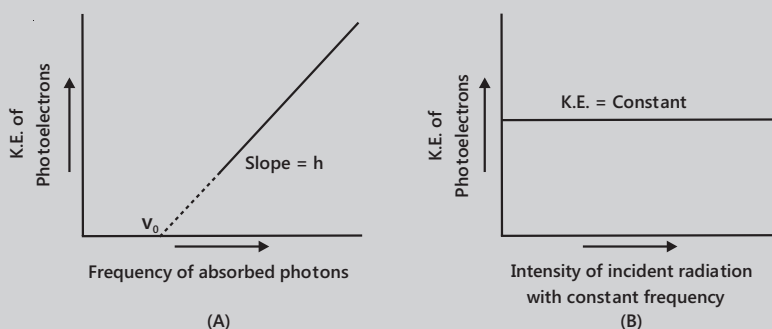


Figure 2.8: Plot of kinetic energy of photoelectrons emitted versus (A) frequency of absorbed photons and (B) intensity of the incident radiation with constant frequency

Aman Gour (JEE 2012, AIR 230)

The Heated Iron!!!

Q. When an iron bar is heated, it first becomes red, then yellow and finally begins to glow with white light and then blue light. Why?

Ans. The change in colour is because of increase in the frequency of radiation emitted on heating as red colour lies in the lower frequency region while blue colour lies in the high frequency region.

Illustration 5: When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium metal, electrons are emitted with a kinetic energy of $1.68 \times 10^5 \text{ J mol}^{-1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

(JEE MAIN)

Sol: The minimum energy needed to remove an electron is the threshold energy and the maximum wavelength would be obtained from the same equation. Thus, we use the following equations $E = h\nu = h\frac{c}{\lambda}$

For one electron, we multiply by the Avogadro's number, which gives us for one mole of photons, which is then subtracted from the kinetic energy and then divided by Avogadro's number again.

$$E = E_0 + KE$$

The maximum wavelength is found by the equation stated at the beginning.

Energy of a photon of radiation of wavelength 300 nm will be

$$E = h\nu = h\frac{c}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1})}{(300 \times 10^{-9} \text{ m})} = 6.626 \times 10^{-19} \text{ J}$$

$$\therefore \text{Energy of 1 mole of photons} = (6.626 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 3.99 \times 10^5 \text{ J mol}^{-1}$$

As $E = E_0 + KE$ of photoelectrons emitted.

$$\therefore \text{Minimum energy } (E_0) \text{ required to remove 1 mole of electrons from sodium} = E - KE$$

$$= (3.99 - 1.68) \times 10^5 \text{ J mol}^{-1} = 2.31 \times 10^5 \text{ J mol}^{-1}$$

$$\therefore \text{Minimum energy required to remove one electron} = \frac{2.31 \times 10^5 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.84 \times 10^{-19} \text{ J}$$

The wavelength corresponding to this energy can be calculated using the formula, $E = h\nu = h\frac{c}{\lambda}$

$$\therefore \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1})}{3.84 \times 10^{-19}} = 5.17 \times 10^{-7} \text{ m} = 517 \times 10^{-9} \text{ m} = 517 \text{ nm} \text{ which corresponds to green light.}$$

Illustration 6: O_2 undergoes photochemical dissociation into one normal oxygen atom and one excited oxygen atom. 1.976 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen requires 498 kJ mol⁻¹. What is the maximum wavelength effective for photochemical dissociation of O_2 ? **(JEE MAIN)**

Sol: Frame the dissociation reaction of oxygen and arrange the data. Calculate the energy required for the simple dissociation and then add it to the extra energy quoted in the question. Using this energy, solve for maximum wavelength.



$$\text{Energy required for simple dissociation of } \text{O}_2 \text{ into two normal atoms} = \frac{498 \times 10^3}{6.023 \times 10^{23}} = 8.268 \times 10^{-19} \text{ J mol}^{-1} \text{ Since,}$$

one atom has more energy (1.967 eV) in excited state when photochemical dissociation takes place, then energy

$$\text{required for photochemical dissociation of } \text{O}_2 = 8.268 \times 10^{-19} + 1.967 \times 1.602 \times 10^{-19} = 114.19 \times 10^{-20} \text{ J}$$

$$\text{Now using } E = \frac{hc}{\lambda}; 114.19 \times 10^{-20} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}; \lambda = 1740.52 \times 10^{-10} \text{ m} = 1740.52 \text{ \AA}$$

7. BOHR'S ATOMIC MODEL

Bohr proposed a quantum mechanical model of the atom, to overcome the objections of Rutherford's model and to explain the hydrogen spectrum. This model was based on the quantum theory of radiation and the classical laws of physics. The important postulates on which Bohr's model is based are the follows:

- (a) The atom has a nucleus where all the protons and neutrons are present. The size of the nucleus is very small. It is present at the center of the atom.

- (b) Negatively charged electrons are revolving around the nucleus in a similar way as the Planets are revolving around the Sun. The path of the electron is circular. The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

Force of attraction toward nucleus = Centrifugal force

- (c) Out of infinite number of possible circular orbits around the nucleus, the electron can revolve only on those orbits whose angular momentum is an integral multiple of $\frac{h}{2\pi}$, that is, $mvr = n\frac{h}{2\pi}$ where

m = Mass of the electron, v = Velocity of electron, r = Radius of the orbit and $n = 1, 2, 3, \dots$ number of the orbit. The angular momentum can have values such as, $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$, etc., but it cannot have

fractional value. Thus, the angular momentum is quantized. The specified or circular orbits (quantized) are called stationary orbits.

- (d) When the electron remains in any one of the stationary orbits, it does not lose energy. Such a state is called ground of normals.

In the ground state potential energy of electron will be minimum, hence it will be the most stable state.

- (e) Each stationary orbit is associated with a definite amount of energy. The greater is the distance of the orbit from the nucleus, more shall be the energy associated with it. These orbits are also called energy levels and are numbered as 1, 2, 3, 4, ... or K, L, M, N, ... from nucleus outward, i.e. $E_1 < E_2 < E_3 < E_4 \dots$ ($E_2 - E_1 > E_3 - E_2 > E_4 - E_3$).

- (f) The emission or absorption of energy in the form of radiation can occur only when an electron jumps from one stationary orbit to another. $\Delta E = E_{\text{high}} - E_{\text{low}} = h\nu$; energy is absorbed when the electron jumps from an inner to an outer orbit and it is emitted when the electron moves from an outer to an inner orbit.

When the electron moves from an inner to an outer orbit by absorbing definite amount of energy, the new state of the electron is said to be excited state.

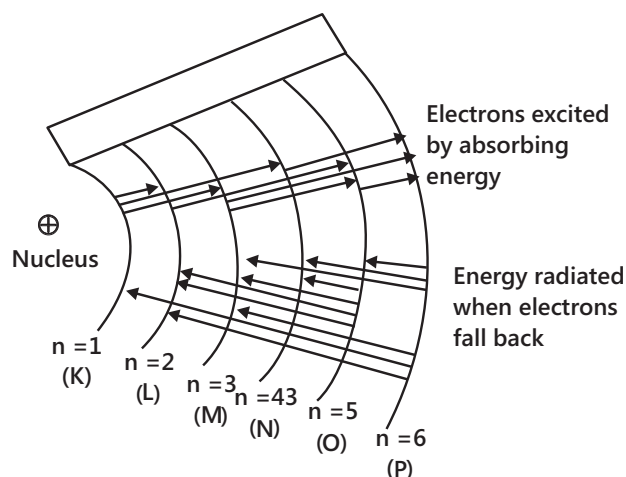


Figure 2.9: Excitation and De- excitation

7.1 Some Important Results of Bohr's Equation

Consider a H-atom in which an electron of mass ' m ', charge ' e ' revolving round a nucleus of charge $1p$ (unit + ve) with a tangential velocity ' v ' at a distance ' r ' from the nucleus. The necessary centripetal force required to keep the electron moving is provided by the electrostatic attraction between the electron and the nucleus,

$$\text{i.e. } \frac{e^2}{r^2} = \frac{mv^2}{r} \quad \dots (i)$$

$$\text{Since } mvr = \frac{nh}{2\pi} \quad \dots (ii)$$

- (a) **The radius:** Therefore, by Eqs. (1) and (2),

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

$$\text{or } r_n = n^2 \times r_1 \quad \dots (iv)$$

$$\text{Also, } r_1 = \frac{h^2}{4\pi^2 m e^2}$$

$$\text{For H-atom; } r_{1H} = \frac{(6.626 \times 10^{-27})^2}{4 \times (3.14)^2 \times (9.108 \times 10^{-28}) \times (4.803 \times 10^{-10})^2}; r_{1H} = 0.529 \times 10^{-8} \text{ cm} = 0.529 \text{ \AA}$$

$$\text{For H like atoms; (He}^+, \text{Li}^{2+}, \text{Be}^{3+}, \dots, \text{etc.). The charge on nucleus is } +Z \text{ and therefore, } \frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

Similarly, we get

$$r_n = \frac{n^2 h^2}{4\pi^2 m Z e^2} \quad \dots \text{ (v)}$$

$$\text{Or } r_{\text{nH-like atom}} = r_{\text{nH}} / Z \quad \dots \text{ (vi)}$$

where Z is atomic number of atom

(b) Velocity: The velocity of an electron in nth orbit of H-atom can be derived by Eqs. (1) and (2), as

$$v_n = \frac{2\pi e^2}{nh} \quad \dots \text{ (vii)}$$

$$= \frac{2 \times 3.14 \times (4.803 \times 10^{-10})^2}{n \times 6.626 \times 10^{-27}} = \frac{2.18 \times 10^8}{n} \text{ cm sec}^{-1}; \therefore v_{1H} = 2.18 \times 10^8 \text{ cm sec}^{-1} \quad \dots \text{ (viii)}$$

$$\text{Also, } v_n = \frac{v_1}{n} \text{ For H like atom; } v_n = \frac{2\pi Z e^2}{nh} \quad \dots \text{ (ix)}$$

$$\text{Or } v_{\text{nH like atom}} = v_{\text{nZ-atom}} \times Z \quad \dots \text{ (x)}$$

(c) Time required to complete one revolution by an electron round nucleus in an orbit: Let $2\pi r_n$ be the circumference of orbit and v_n is velocity of electron in that orbit T for one revolution in an orbit = $\frac{2\pi r_n}{v_n}$... (xi)

(d) Number of revolutions per second made by an electron round the nucleus in an orbit:

$$\text{Number of revolutions} = \frac{v_n}{2\pi r_n} \quad \dots \text{ (xii)}$$

(e) Energy: Total energy ET of an electron for H-atom in a shell can be given by,

$$E_T = \text{Potential energy} + \text{Kinetic energy}; E_T = \left(-\frac{e^2}{r_n} \right) + \left(\frac{1}{2} \cdot \frac{e^2}{r_n} \right) = -\frac{e^2}{2r_n} \quad \dots \text{ (xiii)}$$

$$\text{By Eqs. (3) and (13), } E_T = \frac{2\pi^2 m e^4}{n^2 h^2} \quad \dots \text{ (xiv)}$$

$$= -\frac{2 \times (3.14)^2 \times 9.108 \times 10^{-28} \times (4.803 \times 10^{-10})^4}{n^2 \times (6.625 \times 10^{-27})^2} \text{ erg} = -\frac{21.77 \times 10^{-12}}{n^2} \text{ erg} = -\frac{21.77 \times 10^{-19}}{n^2} \text{ J (107 erg = 1 J)}$$

$$E_T = -\frac{13.6}{n^2} \text{ eV (1.602} \times 10^{-19} \text{ J = 1 eV); } E_{1H} = -13.6 \text{ eV} \quad \dots \text{ (xv)}$$

For H like atom; $E_T = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$

$$E_T = \frac{-21.77 \times 10^{-12}}{n^2} \times Z^2 \text{ erg} \quad \dots \text{(xvi)}$$

Also, for H-atom: $E_n \propto -\frac{1}{n^2}$ and $E_n = \frac{E_1}{n^2}$; E_1 for H-atom $= -\frac{13.6}{1^2} = -13.6 \text{ eV}$

$$E_2 \text{ for H-atom} = -\frac{13.6}{2^2} = -3.4 \text{ eV}; E_3 \text{ for H-atom} = -\frac{13.6}{3^2} = -1.51 \text{ eV}$$

$$E_\infty \text{ for H-atom} = -\frac{13.6}{\infty^2} = 0 \text{ eV}; E_1 \text{ for H like atom} = E_1 \text{ for H} \times Z^2 = -13.6 \times Z^2 \text{ eV} \quad \dots \text{(xvii)}$$

(f) Frequency (ν), wavelength (λ) and wave number ($\bar{\nu}$) during electron transition:

$$\text{Furthermore, } \Delta E = h\nu = E_{n_2} - E_{n_1} \quad \dots \text{(xviii)}$$

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{2\pi^2 me^4}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots \text{(xix)}$$

$$\text{Or } \bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 me^4}{ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1} \quad \dots \text{(xx)}$$

where $\bar{\nu}$ is wave number, λ is wavelength of light involved during electronic transition.

$$\frac{1}{\lambda} = 1.096 \times 10^5 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1} \quad \dots \text{(xxi)}$$

7.2 Interpretation of Hydrogen Spectrum

Maximum number of lines produced when an electron jumps from n^{th} level to ground level is equal to $\frac{n(n-1)}{2}$.

For example, in the case of $n = 4$, the number of lines produced is six ($4 \rightarrow 3$, $4 \rightarrow 2$, $4 \rightarrow 1$, $3 \rightarrow 2$, $3 \rightarrow 1$, $2 \rightarrow 1$). When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$.

If the electron returns from energy level having energy E_2 to energy level having energy E_1 , then the difference may be expressed in terms of energy of photon as: $E_2 - E_1 = \Delta E = h\nu$.

Or the frequency of the emitted radiation is given by $\nu = \frac{\Delta E}{h}$.

Since, ΔE can be only definite values depending on the definite energies of E_2 and E_1 , ν will have only fixed values

in an atom, or $\nu = \frac{c}{\lambda} = \frac{\Delta E}{h}$ or $\lambda = \frac{hc}{\Delta E}$.

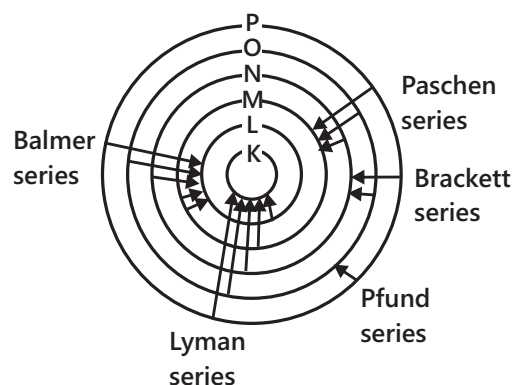


Figure 2.10: Interpretation of Hydrogen Spectrum

Since, h and c are constants, ΔE corresponds to definite energy; thus, each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom. Thus, the different spectral lines in the spectra of atoms correspond to different transitions of electrons from higher energy levels to lower energy levels.

7.3 Derivation of Rydberg Equation

Let an excited electron from n_2 shell come to the n_1 shell with the release of radiant energy. The wave number $\bar{\nu}$ of the corresponding spectral line may be calculated in the following manner:

$$\Delta E = E_2 - E_1 = (-)\frac{2\pi^2 m Z^2 e^4}{n_2^2 h^2} - (-)\frac{2\pi^2 m Z^2 e^4}{n_1^2 h^2}; \frac{hc}{\lambda} = \frac{2\pi^2 m Z^2 e^4}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{Where } \Delta E = h\nu = \frac{hc}{\lambda}; \therefore \bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 m Z^2 e^4}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ Or } \bar{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{where } R = \frac{2\pi^2 m e^4}{ch^3} = \text{Rydberg constant} = 109,743 \text{ cm}^{-1}$$

This value of R is in agreement with experimentally determined value $109,677.76 \text{ cm}^{-1}$. Rydberg equation for

$$\text{hydrogen may be given as, } \bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

7.4 Modification of Rydberg's Equation

$$\text{According to the Rydberg's equation: } \bar{\nu}_{\text{wave number}} = \frac{2\pi^2 m Z^2 e^4}{ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

It can be considered that the electron and the nucleus revolve around their common center of mass. Therefore, instead of the mass of the electron, the reduced mass of the system was introduced and the equation becomes

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

$$\text{Reduced mass } \mu \text{ can be calculated as, } \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

$$\text{Where } m = \text{Mass of electron and } M = \text{Mass of nucleus. } \therefore \mu = \frac{mM}{m+M}$$

Some Important Points to be Remembered

First Line of a Series

(a) First line of a series: It is the line of longest wavelength' or 'line of shortest energy'

$$n_2 = (n_1 + 1); \bar{\nu} = \frac{1}{\lambda_{\text{first}}} = R \left[\frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} \right]$$

Similarly for second, third and fourth lines, $n_2 = n_1 + 2$; $n_2 = n_1 + 3$ and $n_2 = n_1 + 4$ respectively

$$\therefore \text{Rydberg's equation may be written as, } \bar{\nu} = \frac{1}{\lambda} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{(n_1 + x)^2} \right] \text{ where } x = \text{Number of line in the spectrum.}$$

e.g. $x = 1, 2, 3, 4, \dots$ for first, second, third and fourth lines in the spectrum respectively.

Series Limit or Last Line of a Series

(b) Series limit or last line of a series: It is the line of shortest wavelength or line of highest energy.

$$\text{For last line, } n_2 = \infty; \bar{\nu}_{\text{last}} = \frac{1}{\lambda_{\text{Last}}} = \frac{R}{n_1^2}$$

$$\text{Lyman limit} = \frac{R}{1^2}; \text{ Balmer limit} = \frac{R}{2^2}$$

$$\text{Paschen limit} = \frac{R}{3^2}; \text{ Brackett limit} = \frac{R}{4^2}$$

$$\text{Pfund limit} = \frac{R}{5^2}; \text{ Humphrey limit} = \frac{R}{6^2}$$

Intensity of Spectral Lines

(c) The intensities of spectral line in a particular series decrease with increase in the value of n_2 , i.e. higher state e.g. **Lyman series** $(2 \rightarrow 1) > (3 \rightarrow 1) > (4 \rightarrow 1) > (5 \rightarrow 1)$,

$$(n_2 \rightarrow n_1)$$

Balmer series $(3 \rightarrow 2) > (4 \rightarrow 2) > (5 \rightarrow 2) > (6 \rightarrow 2)$

$$(n_2 \rightarrow n_1)$$

Decreasing intensity of the spectral lines \longrightarrow

7.5 Ionization Energy, Excitation Energy and Separation Energy

$$\text{Excitation potential for } n_1 \rightarrow n_2 = \frac{E_{n_2} - E_{n_1}}{\text{Electronic charge}}$$

$$\text{Ionization potential for } n_1 \rightarrow \infty = \frac{E_{n_1}}{\text{Electronic charge}}$$

The energy required to remove an electron from the ground state to form cation, i.e. to take the electron to infinity, is called ionization energy.

$$\text{IE} = E_{\infty} - E_{\text{ground}}; \text{IE} = 0 - E_1(\text{H}) = 13.6 \text{ eV atom}^{-1} = 2.17 \times 10^{-18} \text{ J atom}^{-1}$$

$$\text{IE} = \frac{Z^2}{n^2} \times 13.6 \text{ eV}; \frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}; (\text{IE})Z = \frac{(\text{IE})_{\text{H}} \times Z^2}{n^2}$$

If an electron is already present in the excited state, then the energy required to remove that electron is called separation energy. $E_{\text{separation}} = E_{\infty} - E_{\text{excited}}$

7.6 Limitations of Bohr's Model

- (a) It does not explain the spectra of multi-electron atoms.
- (b) By using a high resolving power spectroscope it is observed that a spectral line in the hydrogen spectrum is not a simple line but a collection of several lines which are very close to one another. This is known as fine spectrum. Bohr's theory does not explain the fine spectra of even the hydrogen atom.
- (c) Spectral lines split into a group of inner lines under the influence of magnetic field (Zeeman effect) and electric field (Stark effect); but, Bohr's theory does not explain this.
- (d) Bohr's theory is not in agreement with Heisenberg's uncertainty principle.

Illustration 7: Find out the number of waves made by a Bohr-electron in one complete revolution in its third Bohr orbit of H-atom. **(JEE MAIN)**

Sol: These 3 formulas need to be considered.

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2}; v_n = \frac{2\pi e^2}{nh}; \text{ number of waves in one round} = \frac{2\pi r_3}{\lambda} = \frac{2\pi r_3}{h/mv_3} \left(\because \lambda = \frac{h}{mv} \right)$$

Number of waves made by an electron in Bohr's orbit is equal to number of orbits.

$$\therefore \text{No. of waves in one round} = \frac{2\pi r_3 \times v_3 \times m}{h} = \frac{2\pi \times n^2 h^2}{4\pi^2 m e^2} \times \frac{2\pi e^2}{nh} \times \frac{m}{h}; n = 3$$

Illustration 8: Calculate the shortest and longest wavelengths in hydrogen spectrum of Lyman series.

Or

calculate the wavelengths of the first line and the series limit for the Lyman series for hydrogen. ($R_H = 109678 \text{ cm}^{-1}$)

Sol: (a) For Lyman series, $n_1 = 1$

For shortest wavelength in Lyman series (i.e. series limit), the energy difference in two states showing transition should be maximum, i.e. $n = \infty$.

$$\text{So, } \frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = R_H; \lambda = \frac{1}{109678} = 9.117 \times 10^{-6} \text{ cm} = 911.7 \text{ \AA}$$

(b) For longest wavelength in Lyman series (i.e. first line), the energy difference in two states showing transition should be minimum, i.e. $n_2 = 2$

$$\text{So, } \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4} R_H \text{ or } \lambda = \frac{4}{3} \times \frac{1}{R_H} = \frac{4}{3 \times 109678} = 1215.7 \times 10^{-8} \text{ cm} = 1215.7 \text{ \AA}$$

Illustration 9: Calculate the ratio of the time required for an electron taking one round of second orbit of H-atom and He^+ ion. **(JEE MAIN)**

Sol: Use the time formula $\frac{2\pi r_n}{v_n}$. This is the time required to complete one round in nth orbit where v is the velocity of electron.

$$\text{For H-like atom, } T_{\text{He}^+} = \frac{2\pi r_1 \times n^2}{Z} \times \frac{n}{v_1 \times Z} \text{ needs to be used.}$$

For second orbit of H-atom: When r_n and r_1 are radii of H-atom: v_n and v_1 are velocities of electron in nth and first orbit of H-atom. Time required to complete one round in nth orbit is $\frac{2\pi r_n}{v_n}$ where v_n is velocity of electron in nth orbit of H-atom

Time required to complete one round in n^{th} orbit is $\frac{2\pi r_n}{v_n}$ where v_n is velocity of electron in n^{th} orbit and r_n is radius

$$\text{of } n^{\text{th}} \text{ orbit. } T_H = \frac{2\pi r_n}{v_n} \quad (\because r_n = r_1 \times n^2 \text{ and } v_n = \frac{v_1}{n})$$

$$= \frac{2\pi r_1 \times n^2 \times n}{v_1} \left(\because v_1 = \frac{2\pi e^2}{h} \right) = \frac{2\pi r_1 \times n^3 \cdot h}{2\pi e^2} \quad T_H = \frac{r_1 n^3 h}{e^2} \quad \dots(i)$$

For second orbit of He^+ : $T_{\text{He}^+} = \frac{2\pi r_{n\text{He}^+}}{v_{n\text{He}^+}}$; $[r_{n\text{He}^+} = \frac{r_{1\text{H}} \times n^2}{Z}; v_{n\text{He}^+} = v_{n\text{H}} \times Z \text{ and } v_{n\text{H}} = \frac{v_1}{n}]$

$$T_{\text{He}^+} = \frac{2\pi r_1 \times n^2}{Z} \times \frac{n}{v_1 \times Z}; T_{\text{He}^+} = \frac{2\pi r_1 n^3 \times h}{Z^2 \times 2\pi e^2} = \frac{r_1 n^3 h}{e^2 \cdot Z^2}; \therefore \frac{T_{\text{H}^+}}{T_{\text{He}^+}} = Z^2 = 4 \quad (Z = 2 \text{ for } \text{He}^+)$$

Illustration 10: Find out the quantum number 'n' corresponding the excited state of He^+ ion if on de-excitation to the ground state that ion emits only two photons in succession with wavelength 1023.7 and 304 Å ($R_{\text{H}} = 1.097 \times 10^7 \text{ m}^{-1}$) **(JEE MAIN)**

Sol: For two successive transitions say from n to n_1 and n_1 to 1.

$$\Delta E = (E_n - E_{n_1})(E_{n_1} - E_1) = E_n - E_1 = \frac{hcR_{\text{H}}Z^2}{n^2} + \frac{hcR_{\text{H}}Z^2}{1^2} = hcR_{\text{H}}Z^2 \left[\frac{n^2 - 1}{n^2} \right] \quad \dots (i)$$

$$\text{Also given, } \Delta E_1 = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2} = hc \left[\frac{\lambda_1 + \lambda_2}{\lambda_1 \cdot \lambda_2} \right] \quad \dots (ii)$$

$$\therefore \text{By Eqs. (i) and (ii)} \quad \frac{n^2 - 1}{n^2} = \left[\frac{\lambda_2 + \lambda_1}{\lambda_1 \lambda_2} \right] \times \frac{1}{R_{\text{H}} \cdot Z^2} = \frac{1}{1.097 \times 10^7 \times 4} \left[\frac{(1026.7 + 304) \times 10^{-10}}{1026.7 \times 304 \times 10^{-20}} \right] = 0.9716; \therefore n = 6$$

8. SOMMERFIELD'S EXTENSION OF BOHR'S THEORY

To explain the fine spectrum of hydrogen atom, Sommerfield in 1915 proposed that the moving electron might describe elliptical orbits in addition to circular orbits and the nucleus is situated at one of the foci. In a circular motion only the angle of revolution changes while the distance from the nucleus remains the same but in an elliptical motion both the angle of revolution and the distance of the electron from the nucleus change. The distance from the nucleus is termed as radius vector and the angle revolution is known as azimuthal angle. The tangential velocity of the electron at a particular instant can be resolved into two components: one along the radius vector called radial velocity and the other perpendicular to the radius vector called transverse or angular velocity. These two velocities give rise to radial momentum and angular or azimuthal momentum. Sommerfeld proposed

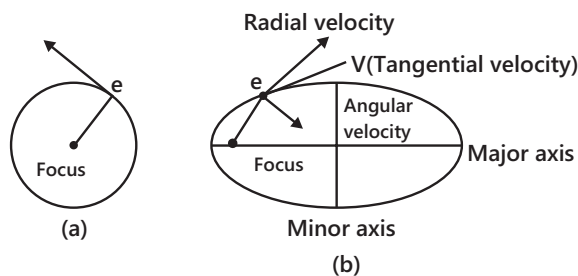


Figure 2.11: Sommerfield's extension

that both the moments must be integral multiples of $\frac{h}{2\pi}$

$$\text{Radial momentum} = n_r \frac{h}{2\pi};$$

$$\text{azimuthal momentum} = n_\phi \frac{h}{2\pi}$$

n_r and n_ϕ are related to the main orbit 'n' as:

$$n = n_r + n_\phi \text{ or}$$

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

(i) ' n_ϕ ' cannot be zero because under this condition, ellipse shall take the shape of a straight line.

(ii) ' n_ϕ ' cannot be more than ' n ' because the minor axis is always smaller than major axis; when the major axis becomes equal to minor axis the ellipse takes the shape of a circle. Thus, n_2 can have all integral values up to ' n ' but not zero. When the values are less than ' n ', orbits are elliptical and when it becomes equal to ' n '. The orbit becomes circular in nature.

For $n = 1$, n_ϕ can have only one value, i.e. 1. Therefore, the first orbit is circular in nature.

For $n = 2$, n_ϕ can have two values 1 and 2, i.e. the second orbit has two sub orbits; one is elliptical and the other is circular in nature.

For $n = 3$, n_ϕ can have three values 1, 2 and 3, i.e. the third orbit has three sub orbits, two are elliptical and one is circular in nature. For $n = 4$, n_ϕ can have four values 1, 2, 3 and 4, i.e. fourth orbit has four sub-orbits, three are elliptical and fourth one is circular in nature (Fig.2.12). Sommerfield thus introduced the concept of sub-energy shells. In a main energy shell, the energies of sub-shells differ slightly from one another. Hence, the jumping of an electron from one energy shell to another energy shell will involve slightly different amount of energy as it will depend on sub-shell also. This explains to some extent the fine structure of hydrogen atom. However, Sommerfield extension fails to explain the spectra of multi-electron atoms.

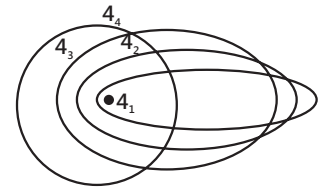


Figure 2.12: Elliptical path

9. PARTICLE AND WAVE NATURE OF ELECTRON

In 1924, **Louis de Broglie** proposed that an **electron**, like light behaves both as a material particle and as wave. This proposal gave birth to a new theory as **wave mechanical theory of matter**. According to this theory, the electrons, protons and even atoms, when in motion, possess wave properties.

De Broglie derived an expression for calculating the wavelengths of the wave associated with the electron. Using

$$\text{Planck's equation, } E = h\nu = h \cdot \frac{c}{\lambda} \quad \dots(i)$$

$$\text{On the basis of Einstein's mass-energy relationship the energy of a photon is } E = mc^2 \quad \dots(ii)$$

where c is the velocity of the electron

$$\text{Equating both the equations, we get } h \frac{c}{\lambda} = mc^2; \lambda = \frac{h}{mc} = \frac{h}{p}$$

Momentum of the moving electron is inversely proportional to its wavelengths.

$$\text{Let kinetic energy of the particle of mass 'm' is } E. E = \frac{1}{2}mv^2; 2Em = m^2v^2$$

$$\sqrt{2Em} = mv = p(\text{momentum}); \lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}}$$

9.1 Davisson and Germer Modification

Davisson and German made the following modification to de Broglie equation:

When a charged particle say an electron is accelerated with a potential of V ; then the kinetic energy is given as:

$$\frac{1}{2}mv^2 = eV; m^2v^2 = 2eVm; mv^2 = \sqrt{2eVm} = p; \lambda = \frac{h}{\sqrt{2eVm}}$$

$$\lambda = \frac{h}{\sqrt{2qVm}} \quad \text{for charged particles of charge } q$$

De Broglie waves are not radiated into space, i.e. they are always associated with electron. Since the wavelength decreases if the value of mass (m) increases, in the case of heavier particles the wavelength is too small to be measured. De Broglie equation is applicable in the case of smaller particles like electron and has no significance for larger particles.

(a) de Broglie wavelengths associated with charged particles

$$(i) \text{ For electron: } \lambda = \frac{12.27}{\sqrt{V}} \text{ \AA} \quad (ii) \text{ For proton: } \lambda = \frac{0.286}{\sqrt{V}} \text{ \AA}$$

$$(iii) \text{ For } \alpha\text{- particles: } \lambda = \frac{0.101}{\sqrt{V}} \text{ \AA} \text{ where } V = \text{acceleration potential of these particles}$$

(b) de Broglie wavelength associated with uncharged particles

$$(i) \text{ For neutrons: } \lambda = \frac{h}{\sqrt{2Em}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times E}} = \frac{0.286}{\sqrt{E(\text{eV})}} \text{ \AA}$$

$$(ii) \text{ For gas molecules: } \lambda = \frac{h}{m \times v_{\text{rms}}} = \frac{h}{\sqrt{3mkT}} \text{ where, } k = \text{Boltzmann constant}$$

9.2 Bohr's Theory vs. de Broglie Equation

Bohr's Theory versus de Broglie equation: Bohr's theory postulates that angular momentum of an electron is an integral multiple of $h/2\pi$. This postulate can be derived with the help of de Broglie concept of wave nature of electron.

Consider an electron moving in a circular orbit around nucleus. The wave train would be associated with the circular orbit as shown in the figure. If the two ends of an electron wave meet to give a regular series of crests and troughs, the electron wave is said to be in phase, i.e. the circumference of Bohr orbit is equal to whole number multiple of the wavelength of the electron wave.

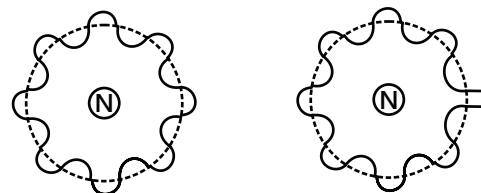


Figure 2.13: Wave in phase and out of phase

$$\text{So, } 2\pi r = n\lambda \text{ Or } \lambda = \frac{2\pi r}{n} \quad \dots(i)$$

$$\text{From de Broglie equation, } \lambda = \frac{h}{mv} \quad \dots(ii)$$

$$\text{Thus, } \frac{h}{mv} = \frac{2\pi r}{n} \text{ or } mvr = n \frac{h}{2\pi} \quad (v = \text{velocity of electron and } r = \text{radii of the orbit})$$

$$\text{i.e. Angular momentum} = n \frac{h}{2\pi} \quad \dots(iii)$$

This proves that the concepts of de Broglie and Bohr are in perfect agreement with each other.

Illustration 11: With what velocity must an electron travel so that its momentum is equal to that of a photon of wavelength of $\lambda = 5200 \text{ \AA}$ **(JEE MAIN)**

Sol: Momentum = mv and $\lambda = h/mv$. They are the momentum of an electron and photon respectively. Thus, by equating them would give the velocity.

$$\therefore \lambda = h/mv \therefore \text{Momentum of photon} = mv = h/\lambda = \frac{6.626 \times 10^{-34}}{5200 \times 10^{-10}} \text{ kg m sec}^{-1}$$

$$\text{Also, momentum of electron} = mv = 9.108 \times 10^{-31} \times v \text{ kg m sec}^{-1}$$

Since, both are same and thus equating the two $9.108 \times 10^{-31} \times v = \frac{6.626 \times 10^{-34}}{5200 \times 10^{-10}}$
 $\therefore v = 1400 \text{ m sec}^{-1}$

Illustration 12: The wavelength of an electron moving in second orbit of H-atom is an integral multiple of its circumference. **(JEE MAIN)**

Calculate:

- (a) Number of wave in the second orbit,
- (b) Speed of electron in the second orbit.
- (c) How much potential must be applied to an electron so that the electron becomes stationary at a point?

Sol: Circumference is $2\pi r$ and it is said that the wavelength is an integral multiple of the circumference. Thus, $n\lambda = 2\pi r$. Moreover, number of waves made by an electron in Bohr's orbit is equal to number of orbits.

(a) No. of waves (n) in the second orbit = 2

(b) Also $2\pi r_2 = 2 \times 3.14 \times 0.529 \times 10^{-8} \times 4 = 13.28 \times 10^{-8} \text{ cm}$

Since, $n\lambda = 2\pi r \therefore \lambda = \frac{13.28 \times 10^{-8}}{2} = 6.64 \times 10^{-8} \text{ cm} = 6.64 \times 10^{-10} \text{ m}$

$\therefore v = \frac{h}{\lambda m} = \frac{6.626 \times 10^{-34}}{6.64 \times 10^{-10} \times 9.108 \times 10^{-31}} = 1.09 \times 10^6 \text{ m/s}$

(c) Also $eV_0 = \frac{1}{2}mv^2 \therefore V_0 = \frac{9.108 \times 10^{-31} \times (1.09 \times 10^6)^2}{2 \times 1.602 \times 10^{-19}} = 3.38 \text{ V}$

10. HEISENBERG'S UNCERTAINTY PRINCIPLE

We see around us all moving particles, 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. Likewise is it possible to measure the position and velocity for the subatomic particle also?

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

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 ($\Delta p = m\Delta v$ 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 readily written as $\Delta x \cdot \Delta p \geq h/4\pi$

Explanation of Heisenberg's uncertainty principle: Let us attempt to measure both the position and momentum of an electron; to pinpoint 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, both the position and the velocity of the electron are disturbed. 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 $\pm \lambda$. 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 a moving macroscopic particle. Hence Heisenberg's uncertainty principle does not apply to macroscopic particles.

Illustration 13: Why cannot the electron exist inside the nucleus according to Heisenberg's uncertainty principle? **(JEE MAIN)**

Sol: Following the Heisenberg's Uncertainty principle, the location of the electron is justified. Use $\Delta x \cdot \Delta p \geq h/4\pi$ or $\Delta x \cdot \Delta p = h/4\pi$.

Diameter of the atomic nucleus is of the order of 10^{-15} m

The maximum uncertainty in the position of electron is 10^{-15}

Mass of electron = 9.1×10^{-31} kg.;

$\Delta x \cdot \Delta p = h/4\pi$;

$\Delta x \times (m \cdot \Delta v) = h/4\pi$;

$\Delta v = h/4\pi \times 1/\Delta x$. $M = 6.53 \times 10^{-34}/4\pi \times 1/10^{-15} \times 9.1 \times 10^{-31}$; $\Delta v = 5.80 \times 10^{10} \text{ ms}^{-1}$

The value is much higher than the velocity of light and hence not possible.

Illustration 14: What is the uncertainty in the position of electron, if uncertainty in its velocity is 0.0058 m/s? **(JEE MAIN)**

Sol: $\Delta x \times \Delta v = h/4\pi m$; $\Delta x = 6.62 \times 10^{-34} / 4\pi \times 3.14 \times 9.1 \times 10^{-31} \times 0.0058$; $\Delta x = 0.01$ m

11. WAVE MECHANICAL MODEL OF ATOMS

Erwin Schrodinger in 1920 put forward this model by taking into account the de Broglie concept of dual nature of matter and Heisenberg's uncertainty principle. In this model, the discrete energy levels or orbits proposed by Bohr's model are replaced by mathematical function ψ (psi) which is related with probability of finding electrons around the

nucleus. The wave equation for an electron wave propagating in 3-D space 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 ψ is the amplitude of the electron wave at point with coordinates x, y, z , E = total energy and V = potential energy of the electron; ψ is also called wave function and ψ^2 gives the probability of finding the electron at (x, y, z) . The acceptable solutions of the above equation for the energy E are called Eigen values and the corresponding wave functions are called **Eigen functions**.

Every function is not an Eigen function. An acceptable solution for Schrodinger wave equation must satisfy the following conditions:

1. The function should be finite.
2. It should always bear a single value at a particular point in space.
3. It should be a continuous function. Schrodinger wave equation can be written as

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0; \text{ or } \nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is called Laplacian operator This equation can be rewritten as $\nabla^2 \psi = -\frac{8\pi^2 m}{h^2} (E - V) \psi$;

$$\text{or } \left(-\frac{h^2}{8\pi^2 m} \nabla^2 + V \right) \psi = E \psi; \text{ or } H \psi = E \psi, \text{ where } H = -\frac{h^2}{8\pi^2 m} \nabla^2 + V, \text{ is called Hamiltonian operator}$$

In this operator, the first term represents kinetic energy operator (T) and the second term represents potential energy operator (V).

Significance of ψ : It represents the amplitude of an electron wave. It can be positive or negative. It has no physical value.

Significance of ψ^2 : It is a probability function. It determines the probability of finding an electron within a smaller region of space around nucleus. The space in which there is maximum probability of finding an electron is termed as orbital.

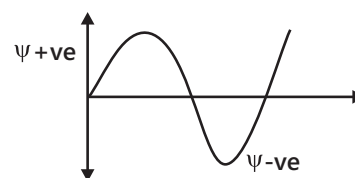


Figure 2.14: Significance of ψ

12. QUANTUM NUMBERS

An atom contains large number of shells and sub-shells. These are distinguished from one another on the basis of their size, shape and orientation (direction) in space. The parameters are given in terms of different numbers called **quantum numbers**.

Quantum numbers may be defined as a set of four numbers with the help of which we can get complete information about all the electrons in an atom. It tells us the address of the electron i.e. location, energy, the type of orbital occupied and orientation of that orbital.

12.1 Principal Quantum Number

- (a) This is denoted by n , an integer.
- (b) The values of n are from 1 to n .

$n = 1$	K shell;	$n = 2$	L shell
$n = 3$	M shell;	$n = 4$	N shell
- (c) ' n ' represents the major energy shell to which an electron belongs.
- (d) The values of ' n ' signify the size and energy level of major energy shells.
- (e) As the value of ' n ' increases, the energy of the electron increases and thus, the electron is less tightly held with nucleus.
- (f) Angular momentum can be calculated using principal quantum number: $mvr = nh/2\pi$

12.2 Azimuthal Quantum Number

This is denoted by l .

- (a) The values of l are from 0 to $(n - 1)$
- (b) $l = 0$, s-sub-shell, spherical (The representation is independent of the value of n)
 $l = 1$, p-sub-shell, dumbbell
 $l = 2$, d-sub-shell, double dumbbell or like leaf
- (c) The letters s, p, d, f designate old spectral terms.
 Sharp (s), principal (p), diffuse (d), fundamental (f)
- (d) For a given value of n , total values of ' l ' are n .
- (e) The values of l signify the shape and energy level of sub-shells in a major energy shell.
- (f) The angular momentum of an electron in an orbital is given by $nh/2\pi$.
- (g) The energy level for sub-shells of a shell shows the order: $s < p < d < f$

12.3 Magnetic Quantum Number

- (a) Denoted by m_l , an integer.
- (b) Zeeman effect: Zeeman studied the fine spectrum of H using a spectroscope of high resolving power as well as putting the source under the influence of magnetic field. He noticed that the spectral line splits up to more than one component

- (c) Each frequency of radiation emitted by the atom in the presence of magnetic field splits up into components if the angular momentum of the electron along the magnetic field are restricted to the value, $m_l = \frac{h}{2\pi}$
- (d) The values of m_l lie from $\pm l$ through zero.
- (e) The positive values of magnetic quantum number m_l represent the angular momentum component of the orbital in the direction of the applied magnetic field whereas the negative values of m_l account for the angular momentum component of orbital in the opposite direction of applied magnetic field.
- (f) Total values of m_l for a given value of $n = n^2$.
- (g) Total values of m_l for a given value of $l = (2l + 1)$
- (h) The values of m_l signify the possible numbers of orientations of a sub-shell.
- (i) In the absence of magnetic field, the three p-orbitals are equivalent in energy and are said to be threefold degenerate, i.e. sub sub-shell (orbitals) having same energy level are known as **degenerate orbitals**.

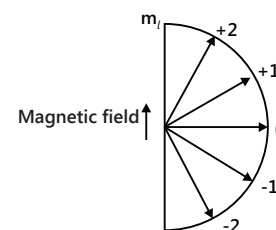


Figure 2.15: Magnetic quantum number

12.4 Spin Quantum Number

- (a) Wave mechanical treatment required no more than three quantum number n , l and m . The existence of multiple, i.e. doublet structure led to the introduction of a spin quantum number m_s .
- (b) The values of m_s are $+\frac{1}{2}$ and $-\frac{1}{2}$. This is due to the fact of the doublet structures of spectral lines which can be explained by proposing only two directions of spin of electron along its own axis.
- (c) The values of m_s signify the direction of rotation or spin of an electron in its axis during its motion.
- (d) Spin angular momentum is given by $\frac{h}{2\pi} \sqrt{m_s(m_s + 1)} = \frac{h}{2\pi} \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} = \frac{\sqrt{3}}{4} \frac{h}{\pi} = \frac{\sqrt{3}}{2} h$.
- (e) The spin may be clockwise $\left(+\frac{1}{2} \text{ or } -\frac{1}{2} \right)$ or anticlockwise $\left(-\frac{1}{2} \text{ or } +\frac{1}{2} \right)$
- (f) Spin multiplicity of an atom = $\sqrt{s(s + 1)}$.

12.5 Shapes of Orbitals

The electron cloud represents the shape of the orbital. It is not uniform but it is dense where the probability for finding the electron is maximum.

- (a) s-orbitals do not vary with angles, i.e. they do not have directional dependence. Thus, all s-orbitals are called spherically symmetrical. Their size increases with increases in the value of n . 1s-orbital has no nodal plane (the plane at which zero electron density is noticed). 2s-orbital has one nodal plane; 3s-orbital has two nodal planes. Thus it is evident that the number of nodal planes increases with increasing value of principal quantum number.
- (b) All orbitals with $l \neq 0$ have angular dependence. Therefore, p and d and other higher angular momentum orbitals are not spherically symmetrical. p-orbitals consist of two lobes to form dumbbell shaped structure. The three p-orbitals along x, y, z-axes named as p_x , p_y , p_z orbitals are perpendicular to each other. All the three p-orbitals of a sub-shell have the same size and shape but differ from each other in orientation. The subscripts x, y and z indicate the axis along which the orbitals are oriented and possess maximum electron density. Also, the orbitals of a sub-shell having same energy are referred as **degenerate orbitals**.

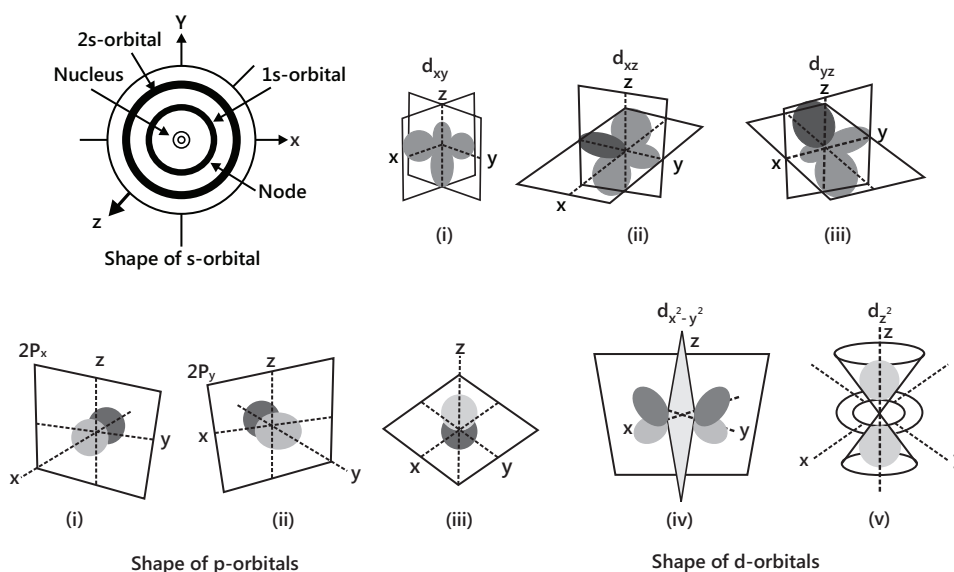


Figure 2.16: Shapes of orbitals

Illustration 15: Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

(JEE MAIN)

- | | | | |
|-------------|-------------|---------------|---------------|
| (a) $n = 2$ | (b) $n = 4$ | (c) $n = 3$ | (d) $n = 4$ |
| $l = 1$ | $l = 2$ | $l = 1$ | $l = 2$ |
| $m_l = 2$ | $m_l = 0$ | $m_l = \pm 1$ | $m_l = \pm 2$ |

Sol: (a) $\because n = 2$ and $l = 1 \therefore 2p$ Since, $m_l = -1 \therefore 2p_y$ or $2p_x$ similarly for others

- (b) $4d_{z^2}$ (c) $3p_x$ or $3p_y$ (d) $4d_{x^2-y^2}$ or $4d_{xy}$

Illustration 16: For $n = 6$ suggest

(JEE MAIN)

- Total number of electrons that it can have
- Total number of sub-shells which can exist
- Total number of sub sub-shells (orbitals) which can exist.

Sol: Having the knowledge of quantum numbers and the existing combinations, the following can be predicted.

- (a) 72 (b) 6 (c) 36

13. SCHRODINGER WAVE EQUATION FOR H-ATOM

Since the electron in the hydrogen atom seems to be a spherically symmetric potential spherical polar coordinates are used to solve the equation. The potential energy is simply that of a point charge, $U(r) = -e^2/4\pi\epsilon_0 r$. When the value of potential energy is substituted in the equation and is solved in polar coordinate form, the total energy is found to be $E = -me^4/8\epsilon^2 n^2 h^2$, which is the same as given by the Bohr's model. The solutions of Schrodinger wave equation is obtained by separating the variables so that the wave function is represented by the product – $\psi(r, \theta, \phi) = \underbrace{R(r)}_{\text{Radial part}} \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$. Since the function R depends only on r_1 , it describes the distribution of the

electron as function of r from the nucleus. These two functions, Θ and Φ depend upon two quantum numbers, n and l and taken together give the angular distribution of the electron. The radial part of the wave function for some

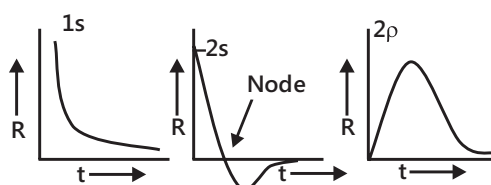
orbitals may be given as,

n	l	R_n	
1s	0	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Z/a_0}$;
2s	0	0	$\frac{1}{\sqrt{3}}\left(\frac{Zr}{2a_0}\right)^{3/2} e^{-Zr/2a_0}$

where Z = atomic number, a_0 = radius of first Bohr orbit of hydrogen

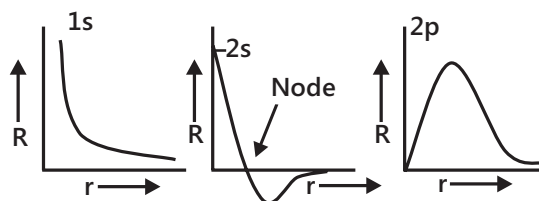
14. PLOTS OF GRAPHS

14.1 Plots of Graphs of R (Radial Wave Function) vs. r (Radius of Atom)



Note: The point where the wave function changes its sign is called node. The number of radial nodes can be determined by the formula: $(n - l - 1)$.

14.2 Plots of Graphs of R^2 (Radial Probability Density) vs. r (Radius of Atom)



- (a) For 1s and 2s orbitals, the function is not defined at $r = 0$ (asymptotic behaviour) as the probability of finding electron inside nucleus is not known but there can be a probability of finding electron just outside the nucleus as s orbital lies very closer to nucleus.
- (b) For 2p orbital, at $r = 0$, probability is zero.

14.3 Plots of Graphs of R^2r (Radial Probability Distribution) vs. r (Radius of Atom)

In order to visualize the electron cloud, consider the space around nucleus divided into a large number of small concentric spherical shells of radius dr . The volume of such a shell can be –

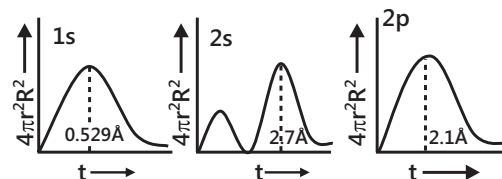
$$dv = 4\pi r^2 dr \quad \text{So,} \quad dv = 4\pi r^2 dr$$

This volume is called radial volume and the probability of finding an electron within this shell is called radial probability distribution function.

$$\text{R.P.F.} = (\text{Volume of spherical shell}) \times \text{probability density}$$

$$= (4\pi r^2 dr) \times R$$

$$\text{Radial probability distribution} = 4\pi r^2 dr R^2$$



MASTERJEE CONCEPTS

- For 1s orbital, radial probability increases with increase in distance from the nucleus, reaches a maximum and then decreases. The maxima are the maximum probability of finding an electron which is also called 'radius of maximum probability' and is also same as Bohr's radius.
- For 2s, the graph has two maxima. In between these two maxima, the curve passes through a zero value indicating that there is zero probability of finding the electron at that distance. This point is a nodal point which can be a radial/spherical node.

Neeraj Toshniwal (JEE 2009, AIR 21)**14.4 Angular Node/Nodal Plane**

The probability of finding an electron in nucleus is zero; so it is called a nodal point. Any plane passing through that point where the probability of finding an electron is zero is called a nodal plane.

MASTERJEE CONCEPTS

- s orbital doesn't have any nodal plane.
- p orbital has one nodal plane. Nodal plane for p_x is YZ plane, for p_y is XZ plane and for p_z is XY plane.
- d orbital has two nodal planes. Nodal planes for d_{xy} are XZ and YZ, for d_{xz} are YZ and XY, for d_{yz} are XY and XZ, for $d_{x^2-y^2}$ are the lines inclined at 45° with X and Y axes.
- So, number of angular nodes = l

Saurabh Gupta (JEE 2010, AIR 443)**Important Points: Key Take-Away**

Type of information	Principal Quantum No. (n)	Azimuthal Quantum No. (l)	Magnetic Quantum m_l	Spin Quantum No. m_s
1. Why is it required?	To explain the main lines of a spectrum	To explain the line structure of the line spectrum	To explain the splitting of lines in a magnetic field	To explain the magnetic properties of substances
2. What does it tell?	(i) Main shell in which the electron resides	(i) No. of sub-shells present in any main shell	No. of orbitals present in any sub-shell or the number of orientation of each sub-shell	Direction of electron spin, i.e. clockwise or anti clockwise
	(ii) Approx distance of the electron from the nucleus	(ii) Relative energies of the sub-shell		
	(iii) Energy of the shell	Shapes of orbitals		
	(iv) Max. no. of electrons present in the shell ($2n^2$)			
3. What are the symbols?	n	l	m or m_l	s or m_s
4. What are the values?	1, 2, 3, 4 etc. i.e. any integer	For a particular value of n, $l = 0$ to $n - 1$	For a particular value of i.e. = -1 to +1 including zero	For a particular value of m ,
5. Other designations?	K, L, M, N, etc.	$l = 0$, s-sub-shell; $l = 1$, p-sub-shell; $l = 2$, d-sub-shell; $l = 3$, f-sub-shell	For p-sub-shell $m_l = -1, 0, +1$, designated as p_x, p_y and p_z	Two arrows pointing in opposite directions, i.e. \uparrow and \downarrow

MASTERJEE CONCEPTS

- Number of radial nodes = $(n - l - 1)$
- Number of angular nodes = l
- Total number of nodes = $(n - l)$
- Number of nodal planes = l

Aman Gour (JEE 2012, AIR 230)**15. PAULI'S EXCLUSION PRINCIPLE**

The principle states that no two electrons in an atom can have the same set of all the numbers. In other words, no orbital can have more than two electrons.

Conclusion:

- The maximum capacity of a main energy shell is equal to $2n^2$ electrons.
- The maximum capacity of a sub-shell is equal to $2(2l + 1)$ electrons.
- Number of sub-shells in a main energy shell is equal to the value of n .
- Number of orbitals in a main energy shell is equal to n^2 .
- One orbital cannot have more than two electrons. If two electrons are present, their spins should be in opposite directions.

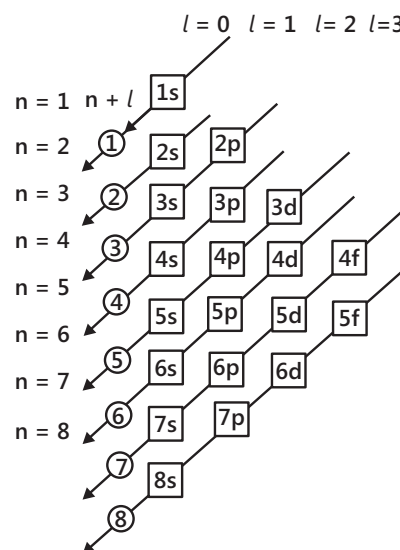
16. AUFBAU PRINCIPLE

The word 'aufbau' originates from the German word 'Aufbauen' which means 'to build'. 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 of the lowest energy is filled up first, then the next sub-shell of higher energy starts filling. The sequence in which various sub-shells are filled is the following:

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

Using $(n + l)$ Value:

The sequence in which various sub-shells are filled up can also be determined with the help of $(n + l)$ value. When two or more sub-shells have same $(n + l)$ value, the sub-shell with the lowest value of ' n ' is filled up first.

**Figure 2.17:** Aufbau rule

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

The principal quantum number solely determines the energy of the electron in a hydrogen atom and other single electron species like He^+ , Li^{2+} and Be^{3+} . The energy of orbitals in hydrogen and hydrogen like species increases as follows: $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$

Exceptions to Aufbau Principle: In some instances it is noted that actual electronic arrangement is slightly different from the arrangement expected by Aufbau principle. A simple reason behind this is that half-filled and full-filled sub-shells have got extra stability.

$\text{Cr}_{24} \rightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4, 4s^2$ (wrong)

$\rightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$ (right)

$\text{Cr}_{29} \rightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$ (wrong)

$\rightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$ (right)

Similarly the following elements have slightly different configurations than expected:

$\text{Nb}_{41} \longrightarrow [\text{Kr}]4d^4 5s^1$

$\text{Mo}_{42} \longrightarrow [\text{Kr}]4d^5 5s^1$

$\text{Ru}_{44} \longrightarrow [\text{Kr}]4d^7 5s^1$

$\text{Rh}_{45} \longrightarrow [\text{Kr}]4d^8 5s^1$

$\text{Pd}_{46} \longrightarrow [\text{Kr}]4d^{10} 5s^0$

$\text{Ag}_{47} \longrightarrow [\text{Kr}]4d^{10} 5s^1$

$\text{Pt}_{78} \longrightarrow [\text{Xe}]4f^{14} 5d^9 6s^1$

$\text{Au}_{79} \longrightarrow [\text{Xe}]4f^{14} 5d^{10} 6s^1$

$\text{La}_{57} \longrightarrow [\text{Kr}]4d^{10} 5s^2 5p^6 5d^1 6s^2$

$\text{Ce}_{58} \longrightarrow [\text{Kr}] 4d^{10} 5s^2 5p^6 5d^0 6s^2$

$\text{Gd}_{64} \longrightarrow [\text{Kr}] 4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$

17. HUND'S RULE OF MAXIMUM MULTIPLICITY (ORBITAL DIAGRAMS)

It states that electrons are distributed among the orbitals of sub-shell in such a way as to give the maximum number of unpaired electrons with parallel spins. This means that the orbitals available in a sub-shell are first filled singly before they begin to pair i.e. the pairing of electrons occurs with the introduction of the second electron in the s-orbital, the fourth electron in the p-orbitals, the sixth electron in the d-orbitals and the eighth electron in the f-orbitals. The rule is based on the fact that electrons have the same charge and repel each other and hence try to keep further apart from each other as much as possible. The electrons thus occupy different orbitals of the sub-shell as to minimize the inter-electronic repulsion and increase the stability of the atom. Orbitals tend to become half-filled or completely filled since such an arrangement will be more stable on account of symmetry.

Illustration 18: Write the electronic configurations of the elements with the following atomic numbers: 3, 8, 14, 17, 21, 38, 57. Also mention the groups of the periodic table to which they belong. **(JEE MAIN)**

Atomic No.	Electronic configuration	Group of periodic Table
22	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^2$	2
57	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 5d^1, 6s^2$	2

Note: Here one electron enters the 5d orbital before filling up of the 4f begins.

Rules for finding the group number

- (i) If the last shell contains one, two electrons, then the group number is 1, 2 respectively.
- (ii) If the last shell contains more than two electrons, then the group number is the total number of electrons in the last shell plus 10.
- (iii) If electrons are present in $(n-1)d$ orbital in addition to those in the ns orbital, then the group number is equal to the total number of electrons present in the $(n-1)d$ orbital and ns orbital.

Illustration 19: Give the electronic configuration of the following ions:

- (i) Cu^{2+} (ii) Cr^{3+} (iii) Fe^{2+} and Fe^{3+} (iv) H^- (v) S^{2-}

(JEE MAIN)

Sol: During the formation of cations, electrons are lost while in the formation of anions, electrons are added to the valence shell. The number of electrons added or lost is equal to the numerical value of the charge present on the ion.

Following this general concept, we can write the electronic configurations of all the ions given in the equation.

(i) $\text{Cu}^{2+} = {}_{29}\text{Cu} - 2e^- = 1s^2 2s^2 3s^2 3p^6 3d^{10} 4s^1 - 2e^- = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

(ii) $\text{Cr}^{3+} = {}_{24}\text{Cr} - 3e^- = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1 - 3e^- = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

$\text{Fe}^{3+} = {}_{26}\text{Fe} - 3e^- = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2 3d^5$

(iii) $\text{H}^- = {}_1\text{H} + 1e^- = 1s^1 + 1e^- = 1s^2$

(iv) $\text{S}^{2-} = {}_{16}\text{S} + 2e^- = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1 + 2e^- = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$

POINTS TO REMEMBER

Representation of a chemical symbol	${}_Z^AX^{A-Z+n}$	X = Element, A = Mass number = No. of protons (p) + No. of neutrons (n) Z = Atomic number = No. of protons
Millikan's oil drop experiment	$m = \frac{m_0}{[1 - (v/c)^2]^{1/2}}$	m = Moving mass of an electron m_0 = Rest mass of an electron
Reduced mass (μ) $\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m} = \frac{mM}{m+M}$	Radius of the nucleus (R_n) $R_n = R_1(A)^{1/3}$, $R_1 = 1.33 \times 10^{-13} \text{ cm}$ A = Mass number	
Moseley's experiment $\sqrt{\nu} = a(Z - b)$ where ν = Frequency of X-rays, Z = atomic number, a and b are constants,	Ritz mathematical formula $\frac{1}{\lambda_{\text{vac}}} = \bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ Where $\bar{\nu}$ = Wave number, R = Rydberg's constant, n_1 and n_2 are integers (such that $n_2 > n_1$) integers or energy levels.	Maximum kinetic energy of the ejected electron Max. KE = Absorbed energy - Work function $\frac{1}{2}mv_{\text{max}}^2 = h\nu - h\nu_0 = hc \left[\frac{1}{\lambda} - \frac{1}{\lambda_0} \right]$

Bohr's model inputs Radius of an atom = $r_a = \frac{n^2}{Z} \times \frac{h^2}{4\pi^2 e^2 m}$ Velocity of an electron = $v = \frac{Z}{n} \times \frac{2\pi e^2}{h}$ Energy of an electron = $E_n = \frac{E_1}{n^2} Z^2 = -\frac{2\pi^2}{n^2}$ Orbital angular momentum $L = \frac{h}{2\pi} \sqrt{l(l+1)}$	De Broglie's hypothesis $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}}$ where λ = wavelength, p = Momentum, h = Planck's constant, E = Kinetic energy	Heisenberg's uncertainty principle $\Delta x \Delta p \geq \frac{h}{4\pi}$ Δx = Change in position, Δp = Change in momentum
Some important points to be remembered	Spin angular momentum $S = \frac{h}{2\pi} \sqrt{S(S+1)}$ Total no. of e^- in an energy level = $2n^2$ Total no. of e^- in a sublevel = $2(2l+1)$ Maximum no. of e^- in an orbital = 2 Total no. of orbitals in a sublevel = $(2l+1)$ No. of sub-shells in main energy shell = n No. of orbitals in a main energy shell = n^2 $l = \begin{matrix} 0 & 1 & 2 & 3 & 4 \\ s & p & d & f & g \end{matrix}$	Magnetic moment (μ) = $\mu \sqrt{n(n+2)}$ B.M. n = Number of unpaired e^-

Solved Examples

JEE Main/Boards

Example 1: When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. Calculate ν_0 for the metal.

Sol: Threshold frequency needs to be calculated. The incident frequency has been given and a condition of photons emission has been given.

Applying photoelectric equation,

$$KE = h\nu - h\nu_0$$

It can be also written as $(\nu - \nu_0) = \frac{KE}{h}$; Given

$$KE_2 = 2KE_1$$

$$\nu_2 - \nu_0 = \frac{KE_2}{h} \quad \dots (i)$$

$$\text{and } \nu_1 - \nu_0 = \frac{KE_1}{h} \quad \dots (ii)$$

Dividing equation (i) by equation (ii)

$$\frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} = \frac{KE_2}{KE_1} = \frac{2KE_1}{KE_1} = 2; \text{ or } \nu_2 - \nu_0 = 2\nu_1 - 2\nu_0$$

$$\text{or } \nu_0 = 2\nu_1 - \nu_2 = 2(2.0 \times 10^{16}) - (3.2 \times 10^{16}) \\ = 8.0 \times 10^{15} \text{ Hz}$$

Example 2: An electron moves in an electron field with a kinetic energy of 2.5 eV. What is the associated de Broglie wavelength?

Sol: The de-Broglie equation is $\lambda = \frac{h}{p} = \frac{h}{mv}$. Modifying

the equation according to the given data and taking the help of kinetic energy, we solve it.

$$\text{Kinetic energy} = \frac{1}{2}mv^2 \left(v = \frac{h}{m\lambda} \right) \\ = \frac{1}{2}m \left(\frac{h}{m\lambda} \right)^2 = \frac{1}{2} \frac{h^2}{m\lambda^2} \text{ or } \lambda^2 = \frac{1}{2} \frac{h^2}{m \times KE} \\ \lambda = \frac{h}{\sqrt{2m \times KE}} \left(\begin{matrix} m = 9.108 \times 10^{-28} \text{ g} \\ h = 6.626 \times 10^{-27} \text{ erg.sec} \\ 1\text{eV} = 1.602 \times 10^{-12} \text{ erg} \end{matrix} \right)$$