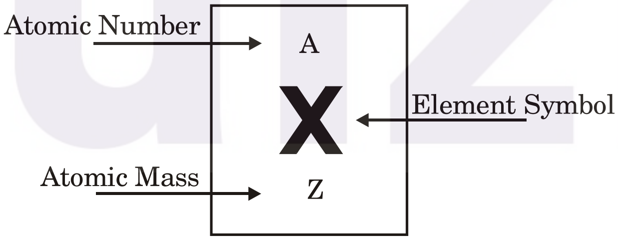
ATOMIC STRUCTURE

1. ATOMIC STRUCTURE

An atom is the smallest building block of matter. Atoms are made of neutrons, protons and electrons. The nucleus of an atom is extremely small in comparison to the atom.

Scientists use the Periodic Table in order to find out important information about various elements. Created by Dmitri Mendeleev (1834-1907), the periodic table orders all known elements in accordance to their similarities. When Mendeleev began grouping elements, he noticed the Law of Chemical Periodicity. This law states, "the properties of the elements are periodic functions of atomic number." The periodic table is a chart that categorizes elements by "groups" and "periods." All elements are ordered by their **atomic number.** The atomic number is the number of protons per atom. In a neutral atom, the number of electrons equals the number of protons. The periodic table represents neutral atoms. The atomic number is typically located above the element symbol. Beneath the element symbol is the **atomic mass.** Atomic mass is measured in Atomic Mass Units where 1 amu = (1/12) mass of carbon measured in grams. The atomic mass number is equal to the number of protons plus neutrons, which provides the average weight of all isotopes of any given element. This number is typically found beneath the element symbol. Atoms with the same atomic number, but different mass numbers are called isotopes. Below is a diagram of a typical cells on the periodic table.



1.1 Dalton's Atomic Theory

John Dalton ERS (6 September 1766 – 27 July 1844) was an English chemist meterologist and physicist. He is best known for his pioneering work in the development of modern atomic theory, and his research into colour blindness (sometimes referred to as Daltonism, in his honour).

Five main points of Dalton's Atomic Theory

- Elements are made of tiny particles called atoms.
- All atoms of a given element are identical.
- The atoms of a given element are different from those of any other element, the atoms of different elements can be distinguished from one another by their respective relative weights.
- Atoms of one element can combine with atoms of other elements to form chemical compounds; a given compound always has the same relative numbers of types of atoms.

- Atoms cannot be created, divided into smaller particles, nor destroyed in the chemical process; a chemical reaction simply changes the way atoms are grouped together.

1.1.1 Drawbacks of Dalton's atomic theory

- Ability of an atom was proved wrong, for, an atom can be further subdivided into protons, neutrons and electrons. However an atom is the smallest particle, which takes part in chemical ability.
- According to Dalton, the atoms of same element are similar in all respects. This is wrong because atoms of some elements vary in their mass and density. Such atoms of the same element having are called isotopes. For example, chlorine has two isotopes having mass numbers 35 and 37 a.m.u.
- Dalton also said atoms of different elements are different in all respects. This has been proved wrong in certain cases like Argon and Calcium atoms, which have the same atomic mass of 40. Such elements that have the same atomic mass are called **isobar.**
- According to Dalton, atoms of different elements combine in simple whole number ratio to form compounds. This is not seen in complex organic compounds like sugar $C_{12}H_{22}O_{13}$.
- The theory completely fails to explain the existence of allotropes. The difference in properties of charcoal, graphite, diamond went unexplained in spite of being made up of same kind of atoms.

1.1.2 Merits of Dalton's atomic theory

Despite the uncertainty at the heart of Dalton's atomic theory, the principles of the theory survived. To be sure, the conviction that atoms cannot be subdivided, created, or destroyed into smaller particles when they are combined, separated or rearranged in chemical reactions is inconsistent with the existence of nuclear fusion and nuclear fission, but such processes are nuclear reactions and not chemical reactions. In addition, the idea that all atoms of a given element are identical in their physical and chemical properties is not precisely true, as we know that different isotopes of an element have slightly varying weights.

- It has enabled us to explain the laws of chemical combination.
- Dalton was the first person to recognize a workable distinction between the ultimate particle of an element (atom) and that of a compound (molecule).

1.2 Thomson's Cathode Ray Experiment

Even without consciously realizing it, most of us are already aware of what a cathode ray tube is. Looking at any glowing neon sign or any 'old fashioned' television set, and you are looking at the modern descendents of the cathode ray tube.

Physicists in the 19th century found out that if they constructed a glass tube with wires inserted in both ends, and pumped out as much of the air as they could, an electric charge passed across the tube from the wires would create a fluorescent glow. This cathode ray also became known as an 'electron gun'.

Later and improved cathode ray experiments found that certain types of glass produced a fluorescent glow at the positive end of the tube. William Crookes discovered that a tube coated in a fluorescing material at the positive end, would produce a focused 'dot' when rays from the electron gun hit it.

With more experimentation, researchers found that the 'cathode rays' emitted from the cathode could not move around solid objects and so traveled in straight lines, a property of waves. However, other researchers, notably Crookes, argued that the focused nature of the beam meant that they had to be particles.

Physicists knew that the ray carried a negative charge but were not sure whether the charge could be separated from the ray. They debated whether the rays were waves or particles, as they seemed to exhibit some of the properties of both. In response, JJ Thomson constructed some elegant experiments to find a definitive and comprehensive answer about the nature of cathode rays.

1.2.1 Thomson's First Cathode Ray Experiment

- Thomson had an inkling that the 'rays' emitted from the electron gun were inseparable from the latent charge, and decided to try and prove this by using a magnetic field.
- His first experiment was to build a cathode ray tube with a metal cylinder on the end. This cylinder had two slits in it, leading to electrometers, which could measure small electric charges.
- He found that by applying a magnetic field across the tube, there was no activity recorded by the electrometers and so the charge had been bent away by the magnet. This proved that the negative charge and the ray were inseparable and interwined.

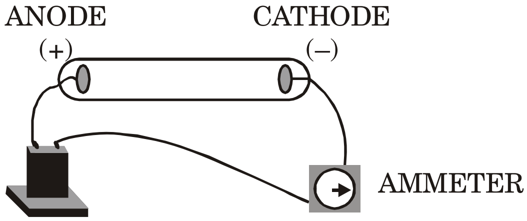
1.2.2 Thomson's Cathode Ray Second Experiment

- Like all great scientists, he did not stop there, and developed the second stage of the experiment, to prove that the rays carried a negative charge. To prove this hypothesis, he attempted to deflect them with an electric field.
- Earlier experiments has failed to back this up, but Thomson thought that the vacuum in the tube was not good enough, and found ways to improve greatly the quality.
- For this, he constructed a slightly different cathode ray tube, with a fluorescent coating at one end and a near perfect vacuum. Halfway down the tube were two electric plates, producing a positive anode and a negative cathode, which he hoped would deflect the rays.
- As he expected, the rays were deflected by the electric charge, proving beyond doubt that the rays were made up of charged particles carrying a negative charge. This result was a major discovery in itself, but Thomson resolved to understand more about the nature of these particles.

1.2.3 Thomson's Third Experiment

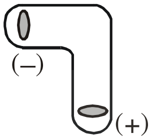
- The third experiment was a brilliant piece of scientific deduction and shows how a series of experiments can gradually uncover truths. Many great scientific discoveries involve performing a series of interconnected experiments, gradually accumulating data and proving a hypothesis.
- He decided to try to work out the nature of the particles. They were too small to have their mass or charge calculated directly, but he attempted to deduce this from how much the particles were bent by electrical currents, of varying strengths.
- He found out that the mass to charge ratio was so high that the particles either carried a huge charge, or were a thousand time smaller than a hydrogen ion. He decided upon the later and came up with the idea that the cathode rays were made of particles that emanated from within the atoms themselves, a very bold and innovative idea.
- Julius Plucker and his student Johann Hittorf were experimenting with a Geissler tube. Plucker and Hittorf placed two electrodes at each end of the tube.

  - The positive plate was called the anode
  - The negative plate was called the cathode
- Pumped all the air from the tube, creating a vacuum
- Connected wires from the electrodes to a battery



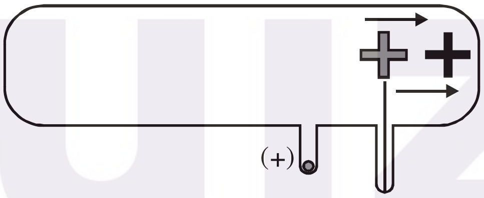
Plucker and Hittorf discovered that when electricity flowed through the Geissler tube, a mysterious greenish glow was produced around the tube.

Sir William Crookes gained more knowledge about the mysterious green glow when he created a bent Geissler tube in 1875. He noticed that the glow was the most intense opposite to the negative electrode, also called the cathode. Crookes reasoned that rays traveled from the cathode and then hit the end of the tube. Because of this, Crookes named these rays cathode rays.



Bent Geisster Tube

In later experiments Crookes placed barriers in the path of cathode rays :



Crookes Tube with Maltese Cross

Because a shadow was produced behind the barrier, Crookes reasoned that cathode rays.

  - Acted like light
  - Seemed to travel in straight lines

Next, Crookes was able to change the path of the rays with a magnet. This meant

  - The cathode rays were NOT light (light is not affected my magnets or magnetic fields)
  - Cathode rays had some sort of charge.

After further experiments, Crookes proved :

(1) All cathode rays have identical properties-the material the cathode is made of does not matter.

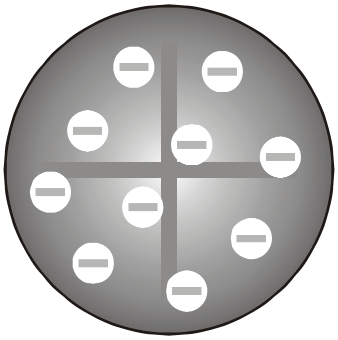
(2) Cathode rays normally travel in straight lines perpendicular to the cathode.

(3) Magnetic fields change the path of the cathode rays. (Crookes suspected that any charged object, not just magnets, could change the path of cathode rays.)

(4) Rays caused reactions similar to those caused by light.

(5) Scientists could not decide if cathode rays were electromagnetic waves or negatively charged particles.

1.3.1 Plum-Pudding Model



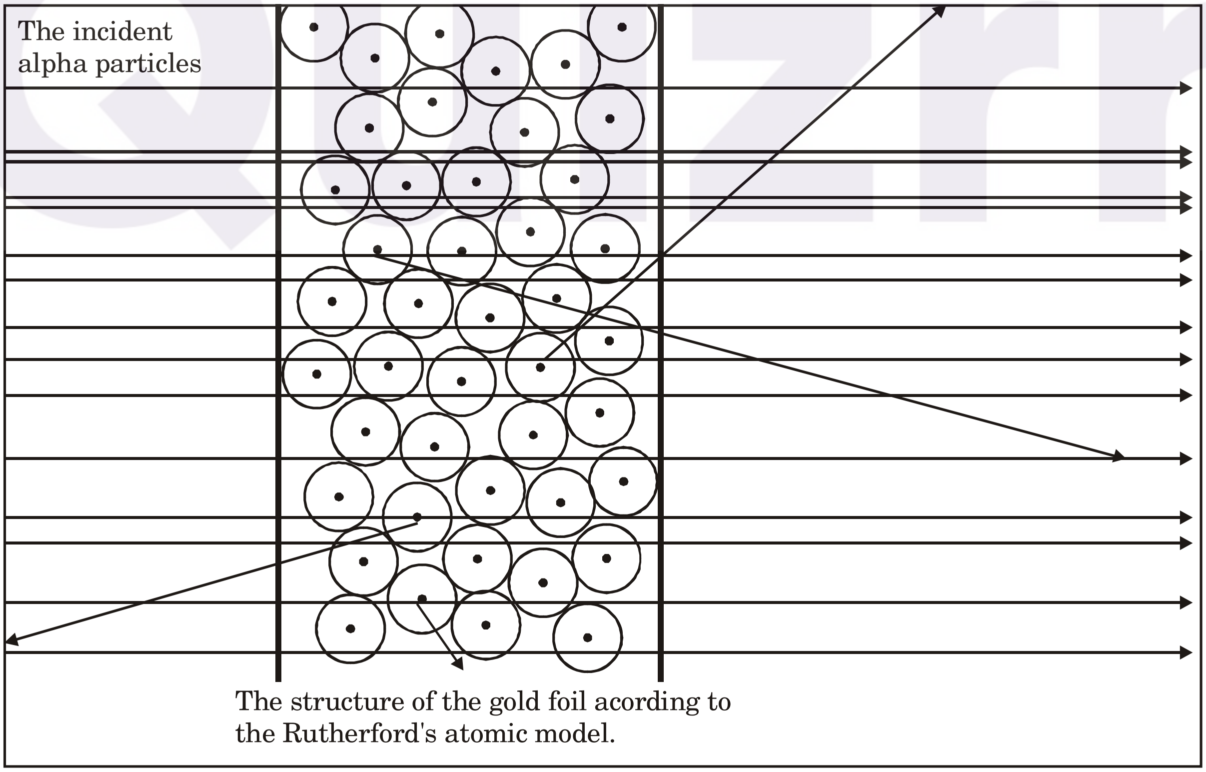
The Plum pudding model of the atom by JJ Thomson, who discovered the electron in 1897, was proposed in 1904 before the discovery of the atomic nucleus. In this model, the atom is compared of electrons (which Thomson still called "corpuscles," though G.J. Stoney had proposed that atoms of electricity be called electrons in 1894), surrounded by a soup of positive charge to balance the electron's negative charge, like negatively-charged "plums" surrounded by positively-charged "pudding". The electrons (as we know then today) were thought to be positioned throughout the atom, but with many structures possible for positioning multiple electrons.

A schematic representation of the plum pudding model of the atom. In Thomson's mathematical model the "corpuscles" (or modern electrons) were arranged non-randomly, in rotating rings.

1.3.2 Rutherford's Model

In the year 1898 Thomson created the idea of atom as the positive charged ball in which there are negative charges placed-the "plum cake" model. So summing up the whole atom were to be neutral.

In the years 1909-1911 Ernest Rutherford and his students-Hans Geiger (1882-1945) and Ernest Marsden conducted some experiment to search the problem of alpha particles scattering by the thin gold-leaf. Rutherford knew that the particles contain the 2e charge. The experiment caused the creation of the new model of atom-the "planetary" model. Rutherford suggested to hit the gold-leaf with fast alpha particles from the source ^{214}Po. (The source R was in the lead lining F). The particles felt from the



The alpha particles propagated on the atomic nucleuses of the gold foil source on the gold-leaf E and were observed by the microscope M. The whole experiment was in the metal lining A and was covered with the glass plate P. The instrument was attached to the footing B. The gold leaf was about $5*10^{-7}$ meter thick. The scientist knew that reckoning the scattering angle could say much about the structure of atoms of the gold-leaf.

Rutherford made a theoretical analysis of angles of scattering in accordance with **Thomson's** theory of atom in accordance with his own theory. He assumed that atom consisted of positive charged nucleus and negative charged electrons circling around the nucleus. Then his theoretic calculations he compared with the experiment result. Alpha particles going through atom created in accordance with the **"plum cake"** model wouldn't be strong abberated because the electric field in that atom wouldn't be strong. In the model created by Rutherford the field is much stronger near to the nucleus, so some of alpha particles are much more abberated. The other going in the far distance to the nucleus are almost at all abberated. The probability that any alpha particle will hit the nucleus is small but there is such a chance.

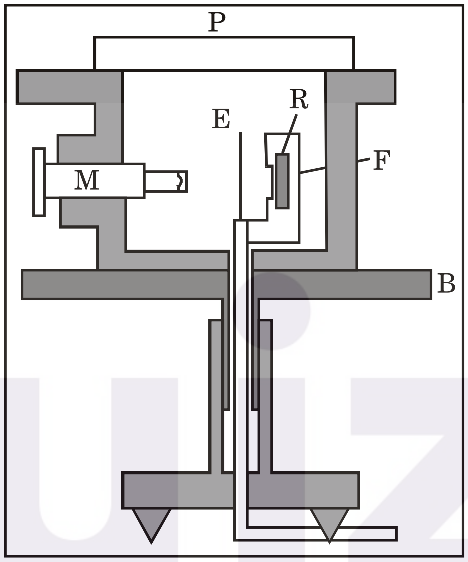
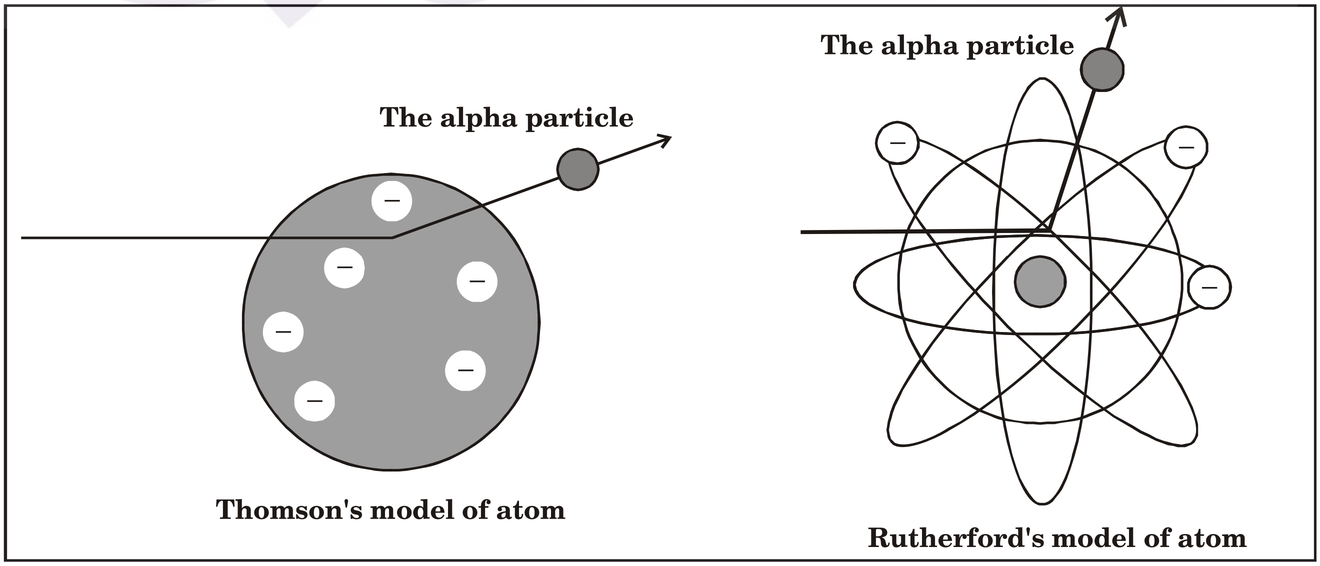


Fig. 1. Marsden-Geiger experiment



The models of the Thomson's atom and Rurtherford's atom; and the expected aberration of alpha particle in both cases

The experiment showed that there are some not much abberated alpha particles but also some abberated of a very big angle (135-150 degree). That occurrence couldn't be explained by some small, added aberrations. Experiment data proved the "planetary" model of atom.

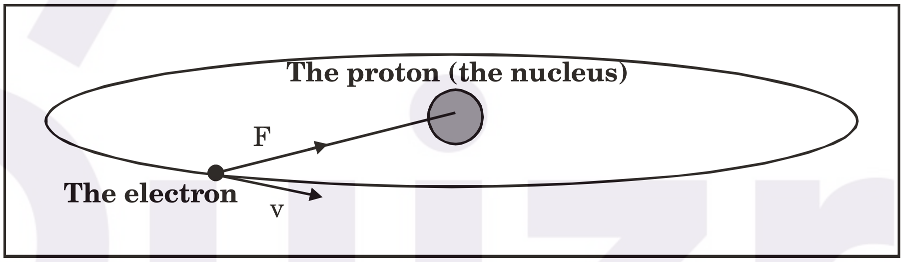
Between an alpha particle and an atomic nucleus there subsist an interaction - the repulsing - according to Coulomb force :

$$F = \frac{1}{4.\prod . \in_0} . \frac{2.Z\ e^2}{r^2} \quad (1)$$

where (2*e)-alpha particle charged, (Ze)-atomic nucleus charged, $\in_0$ -permittivity of free space, r-distance between the nucleus and the particle.

1.3.2.1 Conclusions

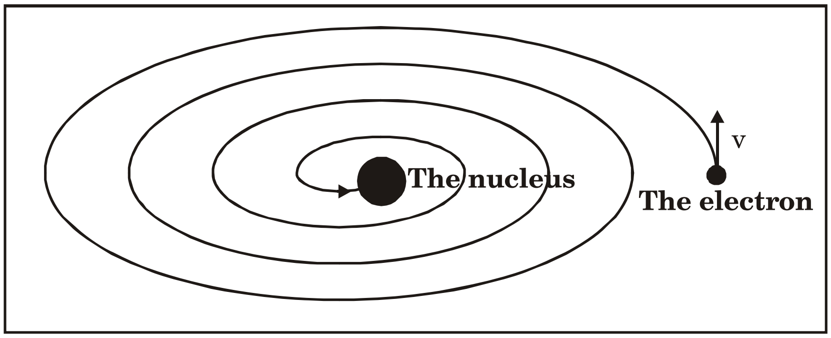
Summarising the results of his work Rutherford came to the opinion that atom consisted of a nucleus (of size 10^{-15} to 10^{-14} meter). The nucleus contains the whole positive charge and almost the whole atom's mass. Around the nucleus, on the area of the size of the order of 10^{-10} meter, light electrons are circling. Electrons have to circle around the nucleus on orbits, not to fell down on the nucleus. The orbits depend on electrons energy. In atoms of the same element, electrons circle on the same characteristic, for that element, orbits i.e. the optical spectrum of atoms of the same element is the same.



The Rutherford's atomic model. The electron circulating on the orbit around the nucleus with the velocity v is attracted by it with the force F

1.3.2.2 Drawbacks

The model created by Rutherford had still some serious discordance. According to the classic science, electron moving around the nucleus should emit an electromagnetic wave. That kind of emission is connected with the escape of some energy from the electron-ion circuit. Electron should then move not by the circle but helical and finally collide with the nucleus. But atom is stable. Other discordance regarded the radiation-it were to be constant (because the time of electron's cycle in accordance with the lost of energy should change constantly) and spectral lines shouldn't occur.



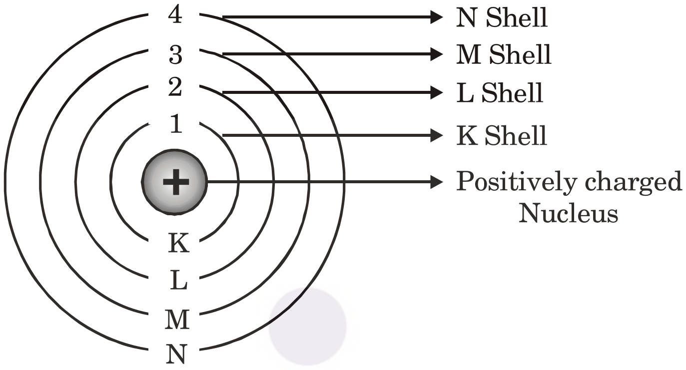
In the planetary model of atom, the electron should emit energy and spirally fall on the nucleus.

1.3.3 Bohr's Model of an Atom

Rutherford's model had a major drawback. It could not explain why ultimately electrons did not fall into the nucleus by taking a spiral path. This was in concurrence with the electromagnetic theory that states **'if a charged particle undergoes accelerated motion then it must radiate energy (lose) continuously'.**

In order to explain the stability of an atom Neils Bohr in 1913 gave a new arrangement of electrons in the atom. According to Neils Bohr, **the electrons could revolve around the nucleus in only 'certain orbits' (energy levels), each orbit having a different radius**. When an electron is revolving in a particular orbit or particular energy level around the nucleus, the electron does not radiate energy (lose energy) even though it has accelerated motion around the nucleus.

Arrangement of energy levels around the nucleus



Arrangement of energy levels around the nucleus

1.3.3.1 Concept involved

An atom is made up of three particles, electrons, protons and neutrons. Electrons have a negative charge and protons have a positive charge whereas neutrons have no charge. They are neutral. Due to the presence of equal number of negative electrons and positive protons the atom as a whole is electrically neutral.

- The protons and neutrons are located in a small nucleus at the centre of the atom. Due to the presence of protons the nucleus is positively charged.
- The electrons revolve around the nucleus in fixed circular paths called energy levels or shells. The 'energy levels' or 'shells' or 'orbits' are represented in two ways : either by the numbers 1, 2, 3, 4, 5 and 6 or by letters K, L, M, N, O and P. The energy levels are counted from centre outwards.
- Each energy level is associated with a fixed amount of energy. The shell nearest to the nucleus having minimum energy and the shell farthest from the nucleus having maximum energy.
- There is no change in the energy of electrons s long as they keep revolving in the same energy level. But when an electron jumps from a lower level to a higher one, some energy is absorbed while some energy is emitted. When an electron jumps from a higher energy level to a lower one, the amount of energy absorbed or emitted is given by the difference of energies associated with the two levels. Thus if an electron jumps from orbit 1 (energy E_1) to orbit 2 (energy E_2) the change in energy is given by $E_2 - E_1$. The energy change is accompanied by absorption of radiation energy of $E = E_2 - E_1 = h\nu$ where h is a constant called 'Planck's constant' and ν

is the frequency of radiation absorbed or emitted. The value of h is 6.626 10^{-34} J^{-s}. The absorption and emission of light due to electron jumps are measured by use of spectrometers.

This model of the atom was able to explain the stability of the atom. It also explained the phenomenon of atomic spectra and ionization of gases.

Combining of energy of the classical electron orbit with the quantization of angular momentum, the Bohr approach yields expressions for the electrons orbit radii and energies.

$$\frac{mv^2}{2} = \frac{(mv)^2}{2mr^2} = \frac{n^2h^2}{8\pi^2mr^2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

kinetic energy of electron	expressed in terms of angular momentum	Use quantization of angular momentum	Set equal to total energy of classical orbit

This is for hydrogenic atoms; the use of the atomic number Z is appropriate only if there is only one electron.

Substitution for r gives the Bohr energies and radii :

$$\boxed{E = -\frac{Z^2me^4}{8n^2h^2\varepsilon_0^2} = \frac{-13.6Z^2}{n^2}eV} \quad \& \quad \boxed{r_n = \frac{n^2h^2\varepsilon_0}{zxme^2} = \frac{n^2a_0}{z}}$$

a_0 = 0.0529 nm = Bohr radius

1.3.3.3 Angular Momentum Quantization

In the Bohr model, the wavelength associated with the electron is given by the DeBroglie relationship.

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

and the standing wave condition that circumference = whole number of wavelengths. In the hydrogenic case, the number n is the principal quantum number.

$$2\pi r = n\lambda_n$$

These can be combined to get an expression for the angular momentum of the electron in orbit. (Note that this assumes a circular orbit, a generally unwarranted assumption.)

$$L = mvr = \frac{hr}{\lambda} = \frac{hr}{\left[\frac{2\pi r}{n}\right]} = \frac{nh}{2\pi} \text{ (used in Bohr orbit)}$$

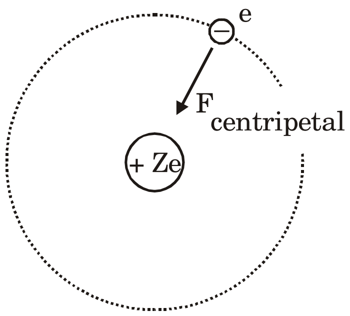
Thus L is not only conserved, but constrained to discrete values by the quantum number n. This quantization of angular momentum is a crucial result and can be used in determining the Bohr orbit radii and Bohr energies.

The velocity of an electron in the nth state V_n is :

$$\boxed{V_n = \frac{2\pi KZe^2}{nh} = 2.165\times10^6\frac{z}{n}m/s}$$

1.3.3.3 Energy Considerations

Classical Electron Orbit



Newton's Second Law	Kinetic Energy T
$= \frac{mv^2}{r} = \frac{Ze^2}{4\pi \in_0 r^2}$	So $T = \frac{mv^2}{2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$
Potential Energy	Total Energy
$U = \frac{-Ze^2}{4\pi\varepsilon_0 r}$	$T + U = \frac{-Ze^2}{8\pi\varepsilon_0 r}$
The orbit energy is negative because this is a bound state.	This is the energy of a single electron in orbit around a bare nucleus.

Note : The total energy of the electron is negative because of attraction of electron by the nucleus.

In the Bohr theory, this classical result was combined with the quantization of angular momentum to get an expression for quantized energy levels.

Substituting the value of r and x, we get the following reaction.

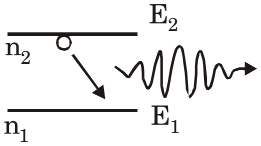
$$\boxed{E_n = \frac{-2\pi^2 K^2 e^4 m Z^2}{n^2 h^2} = -2.178 \times 10^{-18} \frac{Z^2}{n^2}\,\text{J/atom}}$$

Also $$\boxed{E_n = 13.6 \frac{Z^2}{n^2}\,\text{eV}\left(1\text{eV} = 1.6 \times 10^{-19}\,\text{J}\right)}$$

Note : The value of E_n in terms of eV is more important.

1.3.3.4 Electron Transitions

The Bohr model for an electron transition in hydrogen between quantized energy levels with different quantum numbers n yields a photon by emission with quantum energy.



$E_{photon} = h\nu = E_2 - E_1$

A downward transition involves emission of a photon of energy

Given the expression for the energies of the hydrogen electron states :

$$h\nu = \frac{2\pi^2 me^2 k^2}{h^2} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = -13.6 Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{eV}$$

This is often expressed in terms of the inverse wavelength or **"wave number"** as follows :

$\boxed{\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]}$ where $R_H = \frac{2\pi^2 me^4 k^2}{Ch^3}$ is called the Rydberg constant.

$R_H = 1.0973731 \quad 10^7\ m^{-1}$.

Example 1

Determine the frequency of revolution of the electron in 2nd Bohr's orbit in hydrogen atom.

Solution :

The frequency of revolution of electron is given by : frequency = $\dfrac{1}{\text{time period}}$

Time period = $\dfrac{\text{total distance covered in 1 revolution}}{\text{velocity}} = \dfrac{2\pi r}{v}$

Hence frequency = $\dfrac{v}{2\pi r}$

First we will have to calculate velocity (v) and radius (r) of electron in second Bohr's orbit by using the standard relations for v and r. (Z = 1 for H-atom)

$$r_n = \frac{n^2h^2}{4\pi^2me^2K} = (0.53\times10^{-10}n^2)\text{m}$$

Now, n = 2

$$r_2 = 0.53 \quad 10^{-10}\ (2)^2\text{m} = 2.12 \quad 10^{-10}\ \text{m}$$

$$v_n = \frac{2\pi Ke^2}{nh} = \frac{2.165\times10^6}{n}\text{m/s}$$

$$v_2 = \frac{2.165\times10^6}{n} = 1.082 \quad 10^6$$

$$\text{Hence frequency} = \frac{v_2}{2\pi r_2} = \frac{1.082\times10^6}{2(\pi)(2.12\times10^{-10})}$$

$$\nu = 8.13 \quad 10^{14}\ \text{Hz.}$$

Example 2

The Velocity of electron in a certain Bohr's orbit of H atom bears the ratio 1:275 to the Velocity of Light :

- **(a) What is the quantum number (n) of the orbit ?**
- **(b) Calculate the wave number of radiations emitted when electron jumps from (n + 1) state to ground state.**

Solution :

$$\text{Velocity of electron} = \frac{1}{275}\times \text{ velocity of light}$$

$$= \frac{1}{275}\times\ 3 \quad 10^{10} = 1.09 \quad 10^8\ \text{cm sec}^{-1}$$

Since, $$u_n = \frac{2\pi e^2}{nh}$$

$$\therefore \qquad 1.09 \quad 10^8 = \frac{2\times3.14\times(4.803\times10^{-10})^2}{6.625\times10^{-27}\times n}$$

$$n = 20.06 \quad 10^{-1} \approx 2$$

Also when electron jumps from (n + 1) i.e. 3, to ground state

$$\underset{\text{(wave number)}}{\bar{v}} = \frac{1}{\lambda} = R_H\left[\frac{1}{1^2}-\frac{1}{3^2}\right]$$

$$= 109678\left[\frac{1}{1}-\frac{1}{9}\right]$$

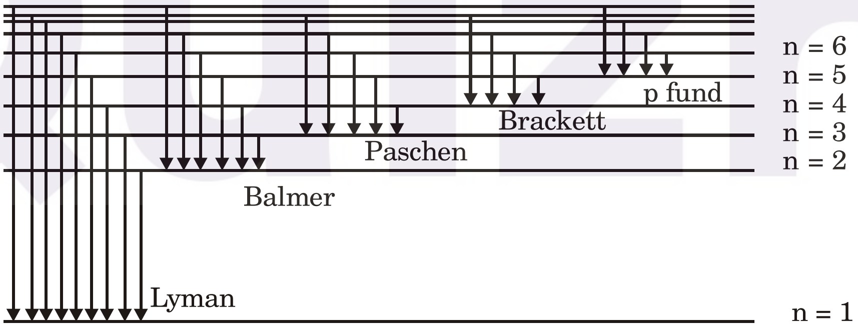
$$= 9.75 \quad 10^4 \text{ cm}^{-1}$$

1.3.3.5 Energy Levels of Hydrogen Atom

The spectrum of H-atom studied by Lyman, Balmer, Paschen, Brackett and Pfund can now be explained on the basis of Bohr's Model.

It is now clear that when an electron jumps from a higher energy state to a lower energy state, the radiation is emitted in form of photons. The radiation emitted in such a transition corresponds to the spectral line in the atomic spectra of H-atom.

Spectral Lines & Energy Levels of H-atom



Lyman Series

When an electron jumps from any of the higher state to the ground state or **Ist state** (n = 1), the series of **spectral lines emitted lies in ultra-violet region** and are called as Lyman Series. The wavelength (or wave number) of any line of the series can be given by using the relation :

$$\boxed{\bar{v} = RZ^2\left(\frac{1}{1^2}-\frac{1}{n_2^2}\right)} \qquad n_2 = 2, 3, 4, 5, \ldots$$

Note : For H-atom, Z = 1, He^+ ion, Z = 2 & Li^{2+}, Z = 3

Balmer Series

When an electron jumps from any of the higher states to the state with n **= 2** (IInd state), the series of **spectral lines emitted lies in visible** region and are called as Balmer Series. The wave number of any spectral line can be given by using the relation :

$$\boxed{\bar{v} = RZ^2\left(\frac{1}{2^2}-\frac{1}{n_2^2}\right)} \qquad n_2 = 3, 4, 5, ...$$

Paschen Series

When an electron jumps from any of the higher states to the state with n **= 3** (IIIrd state), the series of **spectral lines emitted lies in near infra-red region** and are called as Paschen Series. The wave number of any spectral line can be given by using the relation :

$$\boxed{\bar{v} = RZ^2\left(\frac{1}{3^2}-\frac{1}{n_2^2}\right)} \qquad n_2 = 4, 5, 6 ...$$

Brackett Series

When an electron jumps from any of the higher states to the state with n **= 4** (IVth state), the series of **spectral lines emitted lies in near in far infra-red region** and are called as Brackett Series. The wave number of any spectral line can be given by using the relation :

$$\boxed{\bar{v} = RZ^2\left(\frac{1}{4^2}-\frac{1}{n_2^2}\right)} \qquad n_2 = 5, 6, 7 ...$$

Pfund Series

When an elelctron jumps from any of the higher states to the state with **n = 5** (Vth state), the series of **spectral lines emitted lies in far infra-red region** and are called as P fund Series. The wave number of any spectral line can be given by using the relation :

$$\boxed{\bar{v} = RZ^2\left(\frac{1}{5^2}-\frac{1}{n_2^2}\right)} \qquad n_2 = 6, 7 ...$$

Example 3

Estimate the wavelength of second line in Balmer series.

Solution :

The transition responsible for second Balmer line is

$$4 \rightarrow 2, \quad \text{so} \quad n_1 = 2, n_2 = 4$$

$$\Delta E = 13.6\ Z^2\left(\frac{1}{n_1^2}-\frac{1}{(n_2)^2}\right) = 2.55\,\text{eV}$$

Now $$\lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{2.55 \times 1.6 \times 10^{-19}}$$

$$\Rightarrow \quad \lambda = 4.862 \quad 10^{-7}\ \text{m} = 4862\ \text{Å}$$

Important Note : In any series,
first line = transition from $(n_1 + 1) \rightarrow n_1$; also called as α-line & so on.
For example : In Lyman series α-line = $2 \rightarrow 1$; β-line = $3 \rightarrow 1$; γ-line = $4 \rightarrow 1$

Example 4

Calculate the shortest and longest warelength in H speetrum of lyman series R_H = 109678 cm^{-1}

Solution :

For lyman series $n_1 = 1$

For shortest λ of lyman series; energy difference in two levels showing transition should be maximum,

i.e., $$n_z = \propto$$

$$\frac{1}{\lambda} = R_H \left\{\frac{1}{\lambda} - \frac{1}{\infty^2}\right\}$$

$$\frac{1}{\lambda} = 109678$$

$$\Rightarrow \quad \lambda = 911.7 \quad 10^{-8}\ \text{cm} = 911.7\text{A}$$

For longest λ of lyman series; energy difference in two levels showing transition should be minimum,

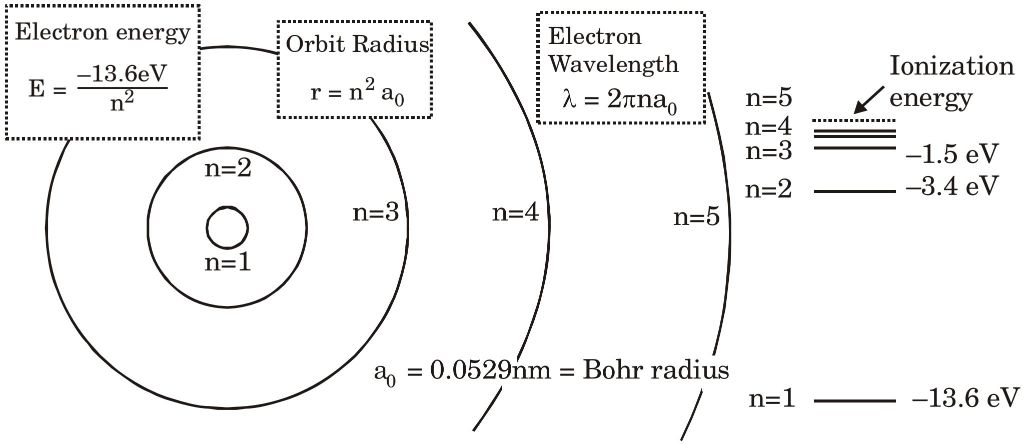
i.e., $$n_2 = 2$$

$$\frac{1}{\lambda} = R_H \left\{\frac{1}{1^2} - \frac{1}{2^2}\right\} = 109678 \times \frac{3}{4}$$

$$\Rightarrow \quad \lambda = 1215.67 \quad 10^{-8}\ \text{cm} = 1215.67\ \text{A}$$

1.3.3.6 Hydrogen Energy Levels

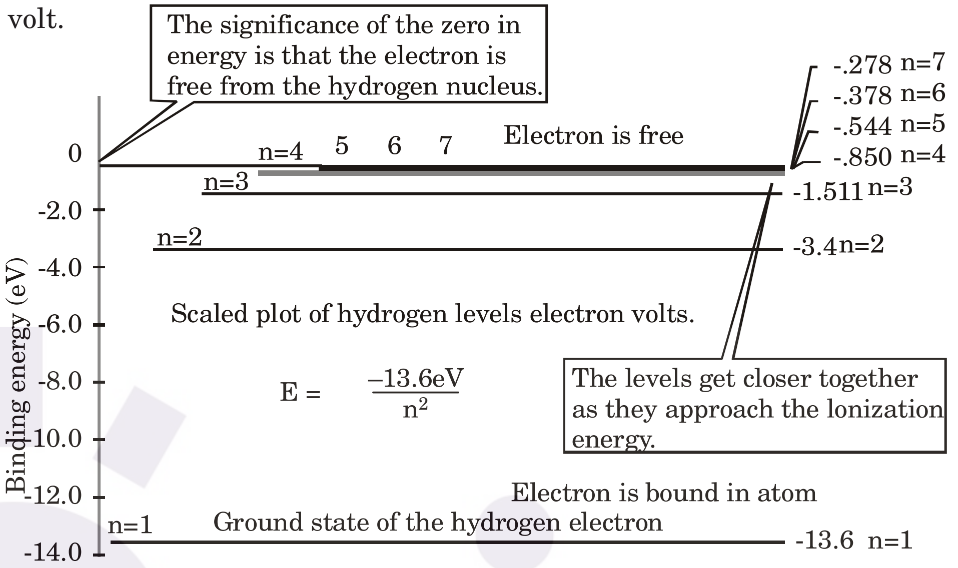
The basic hydrogen energy level structure is in agreement with the Bohr model. Common pictures are those of a shell structure with each main shell associated with a value of the principal quantum number n.



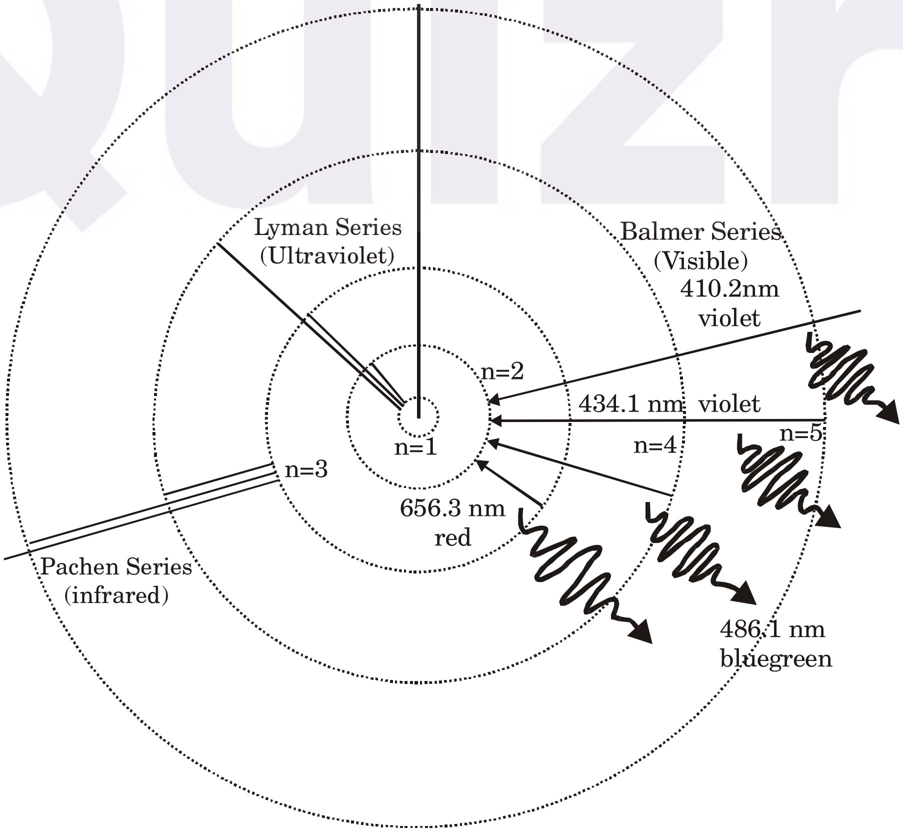
This Bohr model picture of the orbits has some usefulness for visualization so long as it is realized that the “orbits” and the “orbit radius” just represent the most probable values of a considerable range of values. If the radial probabilities for the states are used to make sure you understand the distributions of the probability, then the Bohr picture can be superimposed on that as a kind of conceptual skeleton.

Hydrogen Energy Level Plot

The basic structure of the hydrogen energy levels can be calculated from the Schrodinger equation. The energy levels agree with the earlier Bohr model, and agree with experiment within a small fraction of an electron volt.



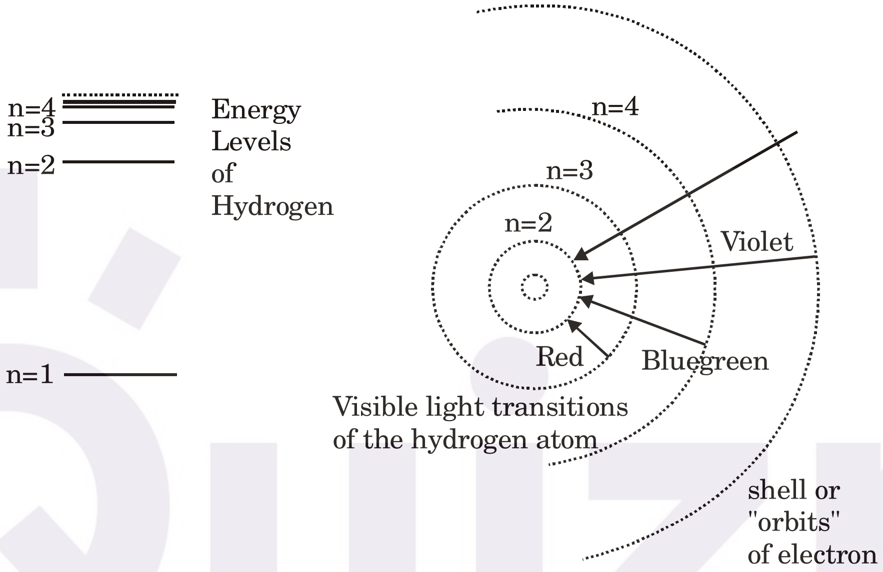
HYDROGEN SPECTRUM



This spectrum was produced by exciting a glass tube of hydrogen gas with about 5000 volts from a transformer. It was viewed through a diffraction grating with 600 lines/mm.

Quantized Energy States

The electrons in free atoms can be found in only certain discrete energy states. These sharp energy states are associated with the orbits or shells of electrons in an atom, e.g., a hydrogen atom. One of the implications of these quantized energy states is that only certain photon energies are allowed when electrons jump down from higher levels to lower levels, producing the hydrogen spectrum. The Bohr model successfully predicted the energies for the hydrogen atom, but had significant failures that were corrected by solving the Schrodinger equation for the hydrogen atom.



1.3.3.7 Failures of the Bohr Model

While the Bohr model was a major step toward understanding the quantum theory of the atom, it is not in fact a correct description of the nature of electron orbits. Some of the shortcomings of the model are :

1. It fails to provide any understanding of why certain spectral lines are brighter than others. There is no mechanism for the calculation of transition probabilities.
2. The Bohr model treats the electron as if it were a miniature planet, with definite radius and momentum. This is an direct violation of the uncertainty principle which dictates that position and momentum cannot be simultaneously determined.

The Bohr model gives us a basic conceptual model of electrons orbits and energies. The precise details of spectra and charge distribution must be left to quantum mechanical calculations, as with the Schrodinger equation.

Example 5

Calculate the energy emitted when electrons of 1.0 gm atom of Hydrogen undergo transition giving the spectral lines of lowest energy in visible region of its atomic spectra. Given that, $R_H = 1.1 \quad 10^7\ m^{-1}$, $c = 3 \quad 10^8$ m/sec, $h = 6.625 \quad 10^{-34}$ J sec.

Solution :

Visible region of H-spectrum correspond to Balmer series $n_1 = 2$, $n_2 = 3$ (for minimum energy transition),

$$1/\lambda = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$\Rightarrow \frac{1}{\lambda} = R_H\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$$

$$\Rightarrow \frac{1}{\lambda} = 1.1\times 10^7\left[\frac{1}{4}-\frac{1}{9}\right] = \frac{1.1\times10^7\times5}{4\times9}$$

$$\lambda = 6.55 \quad 10^{-7}$$

$$E = \frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3\times10^8}{6.55\times10^{-7}}$$

$$= 3.03 \quad 10^{-19} \text{ joule / molecule}$$

$\therefore$ Energy released by 1 gm atom of H (1 mol)

$= E_n = 3.03 \quad 10^{-19} \quad 6.023 \quad 10^{23} = 18.25 \quad 10^4$ J = 182.5 kJ

Example 6

A doubly ionized Lithium atom is hydrogen like with atomic number 3.

(i) Find the wavelength of radiation required to excite the electron in Li^{++} from the first to the third Bohr Orbit. (Ionization energy of the hydrogen atom equal 13.6 eV).

(ii) How many spectral lines are observed in the emission spectrum of the above excited system?

Solution :

(i) $E_n = \dfrac{-13.6Z^2}{n^2}$, $Z = 3$, $n_2 = 3$, $n_1 = 1$

Excitation energy, $\Delta E = E_3 - E_1 = -13.6 \quad 3^2\left[\frac{1}{3^2}-\frac{1}{1^2}\right]$

$= +13.6 \quad 9\ [1 - 1/9]$

$= 13.6 \quad 9 \quad 8/9 = 108.8$ eV

Wavelength, $$\lambda = \frac{hc}{\Delta E} = \frac{6.63\times 10^{-34}\times 3\times 10^{8}}{13.6\times 8\times 1.6\times 10^{-19}}$$

$$= 114.26 \quad 10^{-10}\text{ m} = 114.3\text{ Å}$$

(ii) From the excited state (E_3), coming back to ground state, there can be 3 possible radiations.

Example 7

Wavelength of high energy transition of H-atom is 91.2 nm. Calculate the corresponding wavelength of He^+ ion.

Solution :

For H atom

$$\frac{1}{\lambda_n} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (i)}$$

For He^+ ion $$\frac{1}{\lambda_{He+}} = R_H Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (ii)}$$

By eq. (i) and (ii)

$$\frac{\lambda_{He+}}{\lambda_H} = \frac{1}{Z^2}$$

$$\lambda_{He+} = \lambda_H \quad \frac{1}{Z^2} = 91.2 \quad \frac{1}{2^2}$$

$$= 22.8\text{ nm}$$

Example 8

The electron energy in hydrogen atom is given by $\mathbf{E = \dfrac{-21.7\times 10^{-12}}{n^2}}$ ergs. Calculate the energy required to remove an electron completely from n = 2 orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?

Solution : $$E_n = \frac{-21.7\times 10^{-12}}{n^2}\text{ ergs}$$

$$E_2 = \frac{-21.7\times 10^{-12}}{2^2}$$

Removing the electron completely from the atom implies that the electron has been exited to the level ∞.

$$\therefore \qquad E_\infty = \frac{-21.7\times 10^{-12}}{\infty^2} = 0$$

$$\Delta E = E_\infty - E_2 = \frac{21.7\times 10^{-12}}{4}\text{ ergs}$$

$$\Delta E = \frac{21.7 \times 10^{-12}}{4} \times 10^{-7} \text{ Joule} = 5.425 \quad 10^{-19} \text{ J}$$

$$\Delta E = \frac{hc}{\lambda}$$

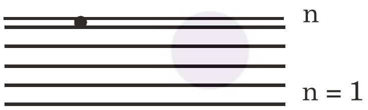
$$\therefore \quad \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{5.425 \times 10^{-19}} = 3.66414 \times 10^{-7}$$

$$\therefore \quad \lambda = 3664.14 \text{ Å}$$

Example 9

There is a hydrogen atom in the ground state. It is exited to a higher energy level n. When the electron comes back to the ground state, it emits radiation. What is the maximum number of unique wavelengths it can emit?

Solution :



Let us imagine the electron to be in the energy level n. When it comes to the ground state it can come in many no. of ways. Either it will directly come to n = 1, in which case it will emit only one wavelength (corresponding to n to 1) or it can fall to n = 2 and then from n = 2 to n = 1, in which case it will emit two unique wavelengths (one corresponding to n to 2 and the other corresponding to n = 2 to n = 1) and so on. We have to find how the electron must come back by emitting maximum number of unique wavelengths. It is very clear that every jump of the electron would radiate a unique wavelength as

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

λ cannot be same for different sets of n_1 and n_2.

The only way maximum wavelengths can be emitted is when the electron comes back to ground state by maximum jumps. This means the electron must jumps stepwise i.e., n to n – 1 to n – 2 to n – 3 and so on. This means the total jumps would be n – 1 and so would be the number of unique wavelength.

$\therefore$ n – 1

Example 10

Calculate the wavelength and wave number of the spectral line when an electron in H-atom falls from higher energy state n = 3 to a state n = 2. Also determine the energy of a photon that can remove the electron from state n = 2. Compare it with the energy of photon required to remove the electron from ground state.

Solution :

Now there are two ways of solving this problem. One by using the relation for the energy emitted (ΔE) by an electron and then calculating the wavelength and wave number. Other by directly using the expression for wave number and then calculating wavelength. In the second method, the value of Rydberg constant (R) is required. The value of R should be given to you otherwise its value cannot be used and the problem should be done by the former method i.e. by finding ΔE.

$$\Delta E = 2.17 \times 10^{-18} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{(n_2)^2}\right) J$$

$$\Delta E = 2.17 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 3.04 \times 10^{-19} \text{ J}$$

Now $\Delta E = h\nu = hc / \lambda$

$$\Rightarrow \quad \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34})(3 \times 10^8)}{3.04 \times 10^{-19}}$$

$$\lambda = 6.59 \quad 10^{-7} \text{ m} = 6590 \text{ Å}$$

$$\Rightarrow \quad \bar{v} = \frac{1}{\lambda} = \frac{1}{659 \times 10^{-7}} \text{m}^{-1} = 1.517 \quad 10^6 \text{ m}^{-1}$$

Alternative Method :

To be used only when the value of R is given.

Using the relation for wave number $(\bar{v})$:

$$\bar{v} = RZ^2 \left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right)$$

$$= 1.097 \quad 10^7 \quad (1)^2 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{ (R} = 1.097 \quad 10^7 \text{ m}^{-1}\text{)}$$

$$= 1.52 \quad 10^6 \text{ m}^{-1}$$

Hence $\lambda = 1/v = 6.56 \quad 10^{-7}$ m/s $= 6560$ Å

To remove electron from n = 2, the responsible transition will be n = 2 → n = ∞.

$$\Delta E = 2.17 \quad 10^{-18}\left(\frac{1}{2^2}-\frac{1}{\infty^2}\right) = 5.42\times10^{-19}\ \text{J}$$

To remove electron from ground state (n = 1), the transition is n = 1 → n = ∞.

$$\Delta E = 2.17 \quad 10^{-18}\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right) = 2.17\times10^{-18}\ \text{J}$$

Example 11

A hydrogen atom in the ground state is hit by a particle exciting the electron to 4s orbital. The electron then drops to 2s orbital. What is the frequency of radiation emitted and absorbed in the process?

Solution :

Energy is absorbed when electron moves from ground state (n = 1) to 4s orbital (n = 4).

$$\Delta E = 13.6\ Z^2\left(\frac{1}{n_1^2}-\frac{1}{(n_2)^2}\right)\text{eV} \quad (\Delta E : \text{energy absorbed})$$

Putting $n_1 = 1$ & $n_2 = 4$ we get,

$\Delta E = 12.75\ \text{eV} = 12.75\ (1.6 \quad 10^{-19})\ \text{J} = 2.04 \quad 10^{-18}\ \text{J}$

$$\text{frequency } (\nu) = \frac{\Delta E}{h} = \frac{2.04\times10^{-18}}{6.63\times10^{-34}} = 3.07\times10^{15}\ \text{Hz}$$

When electron jump from n = 4 to n = 2 (2s), energy is emitted and is given by the same relation :

Put $n_1 = 2$, $n_2 = 4$ in the expression of ΔE.

$\Delta E = 2.55\ \text{eV} = 4.08 \quad 10^{-19}\ \text{J}$

$\Rightarrow \quad \nu = \Delta E/h = 6.15 \quad 10^{15}\ \text{Hz}$

Example 12

Calculate the wavelength of light radiation that would be emitted, when an electron in the fourth Bohr's orbit of He$^+$ ion falls to the second Bohr's orbit. To what transition does this-light radiation correspond in the H-atom ?

Solution :

Let us calculate ΔE first

$$\Delta E = 21.7 \quad 10^{-19}\ Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

substituting $n_1 = 2$ and $n_2 = 4$, $Z = 2$ we get;

$$\Delta E = 1.632 \quad 10^{-18}\ J$$

Now $\lambda = \frac{hc}{\Delta E} = 1.218 \times 10^{-7}\ m = 1218\ Å$

The value of λ = 1218 Å implies that, in H-atom this transition would lie in Lyman Series.

Hence our aim is now to find the transition : $n_2 \to 1$

$$\Rightarrow \quad \Delta E = 21.7 \quad 10^{-19} \quad 1^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \quad 1.632 \quad 10^{-18} = 21.7 \quad 10^{-19} \left(1 - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \quad n_2 = 2$$

Hence the corresponding transition in H-atom is 2 → 1.

Example 13

1.8 g hydrogen atoms are excited to radiations. The study of spectra indicates that 27% of the atoms are in IIIrd energy level and 15% of atoms in IInd energy level and the rest in ground state. IP of H is 13.6 eV. Calculate

(a) No. of atoms present in III and II energy level.

(b) Total energy evolved when all the atoms return to ground state.

Solution : 1 g H contains = N atoms

∴ 1.8 H contains = N   1.8 atoms

$= 6.023 \quad 10^{23} \quad 1.8$

$= 10.84 \quad 10^{23}$ atoms

(a) ∴ No. of atoms in III shell $= \frac{10.84 \times 10^{23} \times 27}{100}$

$= 292.68 \quad 10^{21}$ atoms

$$\therefore \quad \text{No. of atoms in II shell} = \frac{10.84 \times 10^{23} \times 15}{100}$$

$$= 162.6 \quad 10^{21} \text{ atoms}$$

$$\text{and} \quad \text{No. of atoms in I shell} = \frac{10.84 \times 10^{23} \times 58}{100}$$

$$= 628.72 \quad 10^{21} \text{ atoms}$$

(b) When all the atoms return to I shell, then

$$E' = (E_3 - E_1) \times 292.68 \times 10^{21}$$

$$= \left(-\frac{13.6}{9} + 13.6\right) \times 1.602 \times 10^{-19} \times 292.68 \times 10^{21}$$

$$= 5.668 \quad 10^{5} \text{ Joule}$$

$$E'' = (E_2 - E_1) \quad 162.6 \quad 10^{21}$$

$$= \left(-\frac{13.6}{4} + 13.6\right) \times 1.602 \times 10^{-19} \times 162.6 \times 10^{21}$$

$$= 2.657 \quad 10^{5} \text{ Joule}$$

$$\therefore \quad E = E' + E'' = 5.668 \quad 10^{5} + 2.657 \quad 10^{5} \text{ Joule}$$

$$= 832.50 \text{ kJ}$$

Example 14

Find out the energy of H atom in first excitation state. The value of permittivity factor $4\pi\varepsilon_0$ = 1.11264 10^{-10} C^2 N^{-1} m^{-2}.

Solution :

In M.K.S. system

$$E_n = \frac{2\pi^2 Z^2 m e^4}{(4\pi\varepsilon_0)^2 n^2 h^2} \quad \therefore \quad n = 2$$

$$= \frac{2 \times (3.14)^2 \times (1)^2 \times 9.108 \times 10^{-31} \times \left(1.602 \times 10^{-19}\right)^4}{\left(1.11264 \times 10^{-10}\right)^2 \times (2)^2 \times \left(6.625 \times 10^{-34}\right)^2}$$

$$= 5.443 \quad 10^{-19} \text{ Joule}$$

1.4 DUAL NATURE OF MATTER

Wave-particle duality is the concept that all matter and energy exhibits both wave-like and particle-like properties. A central concept of quantum mechanics, duality addresses the inadqucy of classical concepts like “particle” and “wave” in fully describing the behaviour of small-scale objects. Various interpretations of quantum mechanics attempt to explain this ostensible paradox. Wave-particle duality should be distinguished from wave-particle complementarity, the latter implying that matter can demonstrate both particle and wave characteristics, but not both at the same time (that is, not within one and the same experimental arrangement).

1.4.1 de Broglie Wavelength

The energy of an object (E) in motion is equal to its mass (m) times the square of its speed (s).

$$E = mc^2$$

The energy of a wave (E) is proportional to its frequency (v) which is proportional to its speed (s) and inversely proportional to its wavelength (λ) where h is Planck’s constant.

$$E = hv = \frac{hc}{\lambda}$$

If an object acts as both a particle in motion and a wave, then the two equations can be combined :

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

Cancelling like terms and rearranging the equation to solve for the wavelength results in the following:

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

By definition, momentum (p) of an object is equal to the product of its mass (m) times its speed (c), so p can be substituted for mc to get the de Broglie equation.

- **de Broglie equation –** The wavelength (λ) of an object in motion is inversely proportional to its momentum (p) where h is Planck’s constant (6.626 10^{-34} J-S).

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

With this equation, if the mass of an object is too large (as it is with most objects), the wavelength would be negligible. Very small particles such as electrons, however, are small enough to exhibit the properties of both waves and particles.

1.5 HEISENBERG’S UNCERTAINTY PRINCIPLE

In this work on formulating quantum mechanics, Werner Heisenberg postulated his uncertainty principle, which states :

$$\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$$

where

Δ here indicates standard deviation, a measure of spread or uncertainty;

x and p are a particle's position and linear momentum respectively.

$\hbar$ is the reduced Planck's constant (Planck's constant divided by 2π).

Heisenberg originally explained this as a consequence of the process of measuring : Measuring position accurately would disturb momentum and vice-versa, offering an example (the "gamma-ray microscope") that depended crucially on the de-Broglie hypothesis. It is now thought, however, that this only partly explains the phenomenon, but that the uncertainty also exists in the particle itself, even before the measurement is made.

Example 15

An electron is accelerated through a potential difference of V volts. Find the debroglie wavelength associated with the e**.**

Solution :

When the electron is accelerated through a potential difference of V volts, it acquires a kinetic energy given by E = eV, where e is the charge on the electron. Also, if m be its mass and v be the velocity then,

$$E = \frac{1}{2}mv^2 \qquad \Rightarrow \qquad v = \sqrt{\frac{2E}{m}}$$

deBroglie wavelength $\lambda = \dfrac{h}{mv}$

$$\Rightarrow \qquad \boxed{\lambda = \frac{h}{\sqrt{2Em}}}$$

Note : The above result can be used directly, whenever required.

In the given case E = eV

$$\Rightarrow \qquad \lambda = \frac{h}{\sqrt{2(eV)m}}$$

Example 16

Calculate the uncertainty in position assuming uncertainty in momentum within 0.1% for :

(a) a tennis ball weighing 0.2 kg and moving with a velocity of 10 m/s

(b) a electron moving in an atom with a velocity of 2 $\quad 10^6$ m/s

Solution : Using Uncertainty Principle,

$$\Delta x \, \Delta p = \frac{h}{4\pi}$$

(a)

$$p = mv = 0.2 \quad 10 = 2.0 \text{ Kgm/s}$$

$$\Delta p = 0.1\% \text{ of } p = 2 \quad 10^{-3}$$

$$\Rightarrow \qquad \Delta x = \frac{h}{4\pi\Delta p} = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 2 \times 10^{-3}}$$

$$= 2.135 \quad 10^{-32} \text{ m}$$

(b) For an electron,

$$p = m \; v$$

$$= 9.1 \quad 10^{-31} \quad 2 \quad 10^{6}$$

$$= 1.82 \quad 10^{-24} \text{ Kgm/s}$$

$$\Delta p = 0.1\% \text{ of } p = 1.82 \quad 10^{-27} \text{ Kgm/s}$$

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.63 \times 10 - 34}{2 \times 3.14 \times 1.82 \times 10^{-21}}$$

$$\Rightarrow \qquad \Delta x = 2.89 \quad 10^{-8} \text{ m}$$

Example 17

Show that the circumferenceof an orbit of Bohr hydrogen atom is an integral multiple the de Broglie wavelength associates with the electron revolving round the nucleus.

Solution :

According to Bohr's postulates,

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

$\therefore$ the circumference, $$2\pi r = \frac{nh}{mv}$$

From de Broglie's equation $$\lambda = \frac{h}{mv}$$

$$\therefore \qquad 2\pi r = n\lambda$$

Example 18

(a) If a 1 g body is travelling along the x-axis with an uncertainity in veocityof 1 cm/s, what is theoretical uncertainty in its position ? (b) If an electron is traveling with uncertainity in velocity of 1 m/s, what is the theoretical uncertainity in its position ?

Solution :

(a) According the uncertainity

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

$$\Delta x = \frac{\lambda}{4\pi m \Delta v}$$

$$= \frac{6.626\times 10^{-27}\ \text{ergs sec}}{4\times 3.14\times 1\text{g}\times 1\text{cms}^{-1}}$$

$$= 5.275 \quad 10^{-28}\ \text{cm} = 5.275 \quad 10^{-30}\ \text{m}$$

(b) $$\Delta x = \frac{6.626\times 10^{-34}\ \text{Js}}{4\times 3.14\times 9.1\times 10^{-31}\ \text{kg}\times 1\,\text{ms}^{-1}}$$

$$= 5.797 \quad 10^{-5}\ \text{m}$$

1.6 PHOTOELECTRIC EFFECT

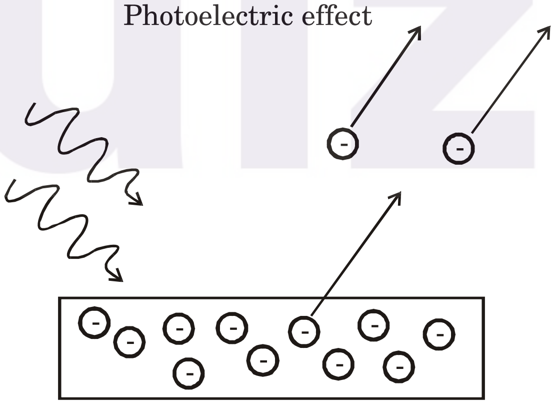
1.6.1 Introduction

The photoelectric effect is a phenomenon in which electrons are emitted from matter after the absorption of energy from electromagnetic radiation such as X-rays or visible light. The emitted electrons can be referred to as photoelectrons in this context. The effect is also termed the **Hertz Effect,** due to its discovery by Heinrich Rudolf Hertz, although the term has generally fallen out of use.

Photoelectric effect takes place with photons with energies of about a few electronvolts. If the photon has sufficiently high energy, Compton scattering (– keV) or pair production (– MeV) may take place.

Study of the photoelectric effect led to important steps in understanding the quantum nature of light and electrons and influenced the formation of the concept of wave-particle duality.

Photoelectric effect



The term may also refer to the photoconductive effect (also known as photoconductivity or photoresistivity), the photovoltaic effect, or the photoelectrochemical effect.

1.6.2 Concept

When a metallic surface is exposed to electromagnetic radiation above a certain threshold frequency (typically visible light), the light is absorbed and electrons are emitted. In 1902, Philipp Eduard Anton von Lenard observed that the energy of individual emitted electrons increased with the frequency, or color of the light. This was at odds with James Clerkk Maxwell's wave theory of light, which predicted that the electron energy would be proportional to the intensity of the radiation. In 1905, Einstein solved this paradox by describing light as composed of discrete quanta, now called **photons**, rather than continuous waves. Based upon Max Planck's theory of black-body radiation, Einstein theorized that the energy in each quantum of light was equal to the frequency multiplied by a constant, later called **Planck's constant**. A photon above a threshold frequency has the required energy to eject a single electron, creating the observed effect. This discovery led to the quantum revolution in physics and **earned Einstein the Nobel Prize in 1921.**

The photons of a light beam have a characteristic energy determined by the frequency of the light. In the photoemission process, if an electron within some material absorbs the energy of one photon and thus has more energy than the work function (the electron binding energy) of the material, it is ejected. If the photon energy is too low, the electron is unable to escape the material. Increasing the intensity of the light beam increases the number of photons in the light beam, and thus increases the number of electrons emitted, but does not increase the energy that each electron possesses. Thus the energy of the emitted electrons does not depend on the intensity of the incoming light, but only on the energy of the individual photons.

Electrons can absorb energy from photons when irradiated, but they follow an "all or nothing" principle. All of the energy from one photon must be absorbed and used to liberate one electron from atomic binding, or the energy is re-emitted. If the photon energy is absorbed, some of the energy liberates the electron from the atom, and the rest contributes to the electron's kinetic energy as a free particle.

1.6.3 Experimental results

1. For a given metal and frequency of incident radiation, the rate at which photoelectrons are ejected is directly proportional to the intensity of the incident light.
2. For a given metal, there exists a certain minimum frequency of incident radiation below which no photoelectrons can be emitted. This frequency is called the threshold frequency.
3. Above the threshold frequency, the maximum kinetic energy of the emitted photoelectron is independent of the intensity of the incident light but depends on the frequency of the incident light.
4. The time lag between the incidence of radiation and the emission of photoelectron is very small, less than 10^{-9} second.

In effect quantitatively using Einstein's method, the following equivalent equations are used :

Energy of photons = Energy needed to remove an electron + Kinetic energy of the emitted electron

Algebraically :

$$\boxed{hf = \phi + E_{kmax}}$$

where

- h is Planck's constant
- f is the frequency of the incident photon

- $\phi = hf_0$ is the work function (sometimes denoted W instead), the minimum energy required to remove a delocalised electron from the surface of any given metal.

  $E_{kmax} = \frac{1}{2}mv_m^2$ is the maximum kinetic energy of ejected electrons.

- f_0 is the threshold frequency for the photoelectric effect to occur.
- m is the rest mass of the ejected electron, and
- v_m is the speed of the ejected electron.

Since an emitted electron cannot have negative kinetic energy, the equation implies that if the photon's energy (hf) is less than the work function (φ), no electron will be emitted.

Example 19

Find the ratio of frequencies of violet light ($\lambda = 4.10 \quad 10^{-5}$ cm) to that of red light ($\lambda = 6.56 \quad 10^{-5}$ cm). Also determine the ratio of energies carried by them.

Solution :

Using c = v λ;

c : speed of light; v = frequency & λ : wavelength

$$\frac{v_1}{v_2} = \frac{\lambda_2}{\lambda_1} \qquad 1 : \text{red} \qquad \& \qquad 2 : \text{violet}$$

$$\Rightarrow \quad \frac{v_1}{v_2} = \frac{6.56 \times 10^{-5}}{4.10 \times 10^{-5}} = 1.6$$

Now the energy associated with electromagnetic radiation is given by E = hv.

$$\Rightarrow \quad \frac{E_1}{E_2} = \frac{v_1}{v_2} = \frac{\lambda_2}{\lambda_1} = 1.6$$

Hence the ratio of energies is same as that of frequencies.

Example 20

A bulb exits light of λ = 4500 A . The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second ?

Solution :

$$\text{Energy of one photon} = \frac{hc}{\lambda}$$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}}$$

$$= 4.42 \quad 10^{-19} \text{ J}$$

$$\text{Energy emitted by bulb} = 150 \quad \frac{8}{100}\,\text{J}$$

$$= 12\ \text{J}$$

$$\therefore \qquad n \quad 4.42 \quad 10^{-19} = 12 \qquad (n = \text{no. of photons})$$

$$n = \frac{12}{4.42 \times 10^{-19}}$$

$$= 2.72 \quad 10^{19}$$

Example 21

An electronic beam can under go diffraction by crystals. Through what potential should a beams of electrons be accelerated so that its wave length becomes equal to 1.54 A

Solution :

We know that

$$\frac{1}{2}\,mv^2 = eV$$

and
$$\lambda = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\lambda}$$

$$\text{or} \quad v^2 = \frac{h^2}{m^2\lambda^2}$$

or
$$\frac{1}{2}m \times \frac{h^2}{m^2\lambda^2} = eV$$

or
$$V = \frac{1}{2}m \times \frac{h^2}{m^2\lambda^2 \times e}$$

$$= \frac{1}{2} \times \frac{h^2}{m\lambda^2 e}$$

Substituting the values, we get
$$V = \frac{1}{2} \times \frac{(6.62 \times 10^{-34})^2}{9.108 \times 10^{-31} \times (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}}$$

$$= 63.3 \text{ volt.}$$

Example 22

A photon of light with λ = 470 nm falls on a metal surface. As a result, photoelectrons are ejected with a velocity of 6.4 $\quad 10^4$ m/s. Find :

(a) the kinetic energy of emitted photoelectrons;

(b) the work function (in eV) of the metal surface.

Solution :

(a) Kinetic energy of electron $= \frac{1}{2} mv^2$

$$KE = \tfrac{1}{2}(9.1 \quad 10^{-31})(6.4 \quad 10^4)^2 = 7.45 \quad 10^{-22}\ J$$

(b) From Einstein's photoelectric equation, we have,

Kinetic energy = incident energy – work function

$KE = E_{incident} - \Phi$ (Φ = work function)

$\Phi = E_{incident} - KE$

$$\Phi = \frac{hc}{\lambda} - KE = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{470 \times 10^{-9}} - 7.45 \times 10^{-22}$$

$$= 4.224 \quad 10^{-19}\ J$$

$$\Rightarrow \qquad \phi = 4.224 \quad 10^{-19}\ J$$

$$= 2.64\ eV$$

Note : More tough problems on photoeletric effect will be dealt with in Modern Physics.

Example 23

The dissociation energy of H_2 is 430.53 KJ mol^{-1}. If H_2 is exposed to radiation energy of wave length 253.7 nm. What % of radiant energy will be converted into kinetic energy ?

Solution :

Energy required to break H–H bond $= \dfrac{430.53 \times 10^3}{6.023 \times 10^{23}}$ J/molecule

$= 7.15 \quad 10^{-19}$ J

Energy of photon used for this purpose $= \dfrac{hc}{\lambda}$

$$= \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{253.7 \times 10^{-9}}$$

$= 7.83 \quad 10^{-19}$ J

$\therefore$ Energy left after dissociation of bond

$= (7.83 - 7.15) \quad 10^{-19}$

or Energy converted into K.E. $= 0.68 \quad 10^{-19}$ J

$\therefore$ % of energy used in kinetic energy $= \dfrac{0.68 \times 10^{-19}}{7.83 \times 10^{-19}} \times 100$

$= 8.68\%$

Example 24

Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

Solution :

For an electron to be in a particular energy level of radius r, with de Broglie wavelength λ :

$$\boxed{2\pi r = n\lambda}$$

(where n = number of waves in one revolution)

$$\lambda = \frac{h}{mv} \quad \Rightarrow \quad n = \frac{2\pi r\, mv}{h}$$

for third orbit;

$r = 0.53 \quad 10^{-10}(3)^2$ m; $\quad v = 2.165 \quad 10^6\,(1/3)$

substituting the value of r, v, m and h, we get,

$n = 3$

Example 25

An electron in the first excited state of H-atom absorbs a photon and is further excited. The debroglie wavelength of the electronic this state is found to 13.4 A^0. Find the wavelength of photon absorbed by the electron in A^0. Also find the longest wavelength emitted when this electron de-excites back to ground state.

Solution :

First excited state refers to the energy level n = 2

The electron from n = 2 absorbs a photon and is further excited to an higher energy level (let us say n)

The electron in this energy level (n) has de Broglie wavelength (λ) = 13.4 Å.

$$\lambda = \frac{h}{mv} \;\; \& \;\; v_n = 2.165 \quad 10^6 \; \frac{Z}{n}$$

$$\Rightarrow \quad \frac{h}{\lambda m} = 2.165 \times 10^6 \times \frac{1}{n} \qquad \Rightarrow \qquad \frac{6.63 \times 10^{-34}}{\left(13.4 \times 10^{-10}\right) \times \left(9.1 \times 10^{-31}\right)} = 2.165 \times 10^6 \times \frac{1}{n}$$

$\Rightarrow \quad n = 4$

First find the wavelength of the photon responsible for the excitation from n = 2 to n = 4

Using the relation :

$$\Delta E = \frac{hc}{\lambda} = 2.17 \times 10^{-18} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$\Rightarrow \quad \lambda = 4861.33$ Å

The longest wavelength emitted when this electron (from n = 4) falls back to the ground state will corresponds to the minimum energy transition.

The transition corresponding to minimum energy will be 4 → 3

Note : The transition corresponding to maximum energy will be 4 → 1

Using the same relation :

$$\Delta E = \frac{hc}{\lambda} = 2.17 \times 10^{-18}\ Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

⇒ λ = 18750.85 Å

Note : If the value of R is given then use :

$$\bar{v} = \frac{1}{\lambda} = R Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad R = 1.097 \quad 10^7\ m^{-1}.$$

Example 26

The IP, of H is 13.6 eV. It is exposed to electromagnetic waves of 1028A and gives out induced radiations. Find the wave length of these induced radiations.

Solution :

E_1 of H atom = –13.6 eV

Energy given to H atom $= \dfrac{6.625 \times 10^{-34} \times 3 \times 10^8}{1028 \times 10^{-10}}$

= 1.933 10^{-18} J

= 12.07 eV

∴ Energy of H atom after exitation = –13.6 + 12.07

= – 1.53 eV

$$E_n = \frac{E_1}{n^2}$$

$$n^2 = \frac{-13.6}{-1.53} \simeq 9$$

n = 3

Thus, electron in H atom is excited to 3rd shell

∴ induced $\lambda_1 = \dfrac{hc}{(E_3 - E_1)}$

E1 = – 13.6 eV

E3 = –1.53 eV

$$\lambda_1 = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{(-1.53 + 13.6) \times 1.602 \times 10^{-19}}$$

= 1028 10^{-10}m.

λ = 1028 A

1.7.1 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, ... corresponding to 1, 2, 3, 4, ... 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 with-in 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 on sub-shell designed as 1s, the second energy level (L or 2) has two sub-shells as 2s & 2p, the third energy level (M or 3) has three sub-shells as 3s, 3p & 3d, and the fourth energy level (N or 4) has four sub-shells s 4s, 4p, 4d & 4f. The energy sub-shells 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. Sub-shell s has one orbital, p has three orbitals, d has five orbitals and f has seven orbitals.

To describe or to characterise 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 number represents the main energy levels (principal energy levels) designated as n = 1, 2, 3, ... 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, ... 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 (Zeeman Lines).

- It can assume all integral values from 0 to n-1. The possible values of l are :
  1, 2, 3, ..., n - 1.

- Each value of l describes a particular sub-shell with 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 sub-shell. So for l = 0, the corresponding sub-shell is s sub-shell. Similarly when l = 1, 2, 3, the sub-shells are called as 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-shells 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 = $\boxed{\sqrt{l(l+1)}\,\frac{h}{2\pi}}$

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

Magnetic Quantum Number : (m)

An electron with angular quantum number 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 (this 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, -l + 1, ..., 0, 1, 2, 3, ..., l - 1, + l. We can say that a total of (2l + 1) values of m are there for a given value of l.
- In s sub-shell, there is only one orbital [l = 0, ⇒ m = (2l + 1) = 1].
- I p sub-shell, there are three orbitals corresponding to three values of m : - 1, 0, + 1. [l = 1 ⇒ 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 ⇒ m = (2l + 1) = 5]. These five orbitals are represented as d_{xy}, d_{yz}, 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 ⇒ m = (2l + 1) = 7].

Spin Quantum Number : (s)

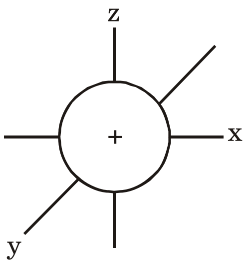
When an electron rotates around a nucleus it also spins about its axis. If the spin is clockwise, its spin quantum number is (+ ½) and is represented as ↑ or 1. If the spin is anti-clockwise, its value is

– ½ and is represented as ↓ or 1. If the value of s is (+ ½) then by convention, we take that electron as the first electron in that orbital and if the value of s is (– ½) it is taken as second electron.

1.7.2 Shapes of Atomic Orbitals

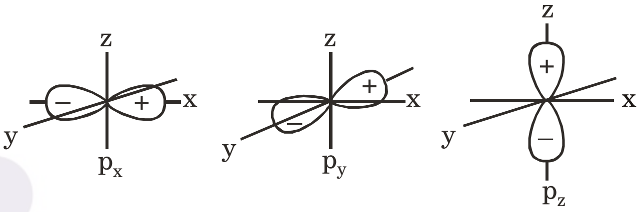
(i) **s-orbital :** An electron is considered to be smeared out in the form of a cloud. The shape of the cloud is the shape of the orbital. The cloud is not uniform but denser in the region where the probability of finding the electron in maximum.

The orbital with the lowest energy is the 1s orbital. It is a sphere with its centre at the nucleus of the atom. The s-orbital is said to 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 orbital.



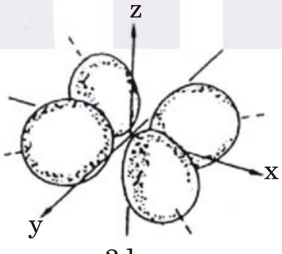
Shape of s-orbital

(ii) **p-orbitals :** There are three p-orbitals : p_x, p_y and p_z. They are dumb-bell shaped, the two levels being separated by a nodal plane, i.e., a plane where there is no likely hood of finding the electron. The p-orbitals have a marked directional character, depending on 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 degenerate.

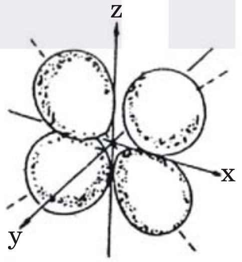


Shapes of p-orbital

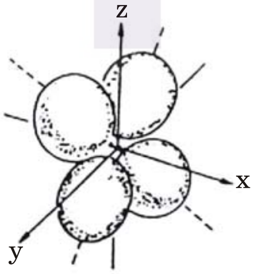
(iii) **d-orbitals :** There are five d-orbitals. The shapes of four d-orbitals resemble four leaf cloves. The fifth d-orbital loops differently. The shapes of these orbitals are given below.



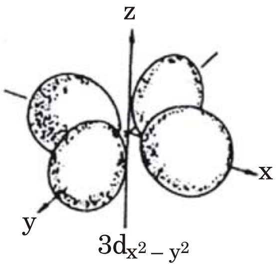
$3d_{xy}$



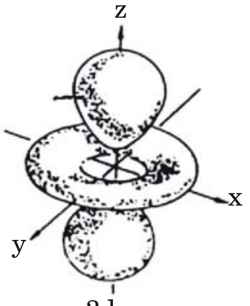
$3d_{xz}$



$3d_{yx}$



$3d_{x^2-y^2}$



$3d_{z^2}$

Quantum Mechanical Model

In the quantum mechanical model of an atom, there is only a “chance” or probability of finding an electron in space. Where this probability is maximum (over 95%), that region of space is called ‘an orbital’.

The concept of orbital comes from the **Schrodinger wave equation.**

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

The symbols have the following meanings :

m → Mass of an electron

h → Planck’s constant

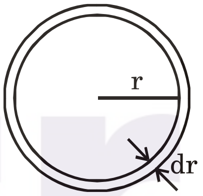
E → Total energy of electron

V → Potential energy of electron

Ψ → Wave function

Electrons have associated wave functions denoted by Ψ

Ψ itself has no physical significance. Its square, however, gives the probability of finding an electron at a given point. More often, we are interested in finding the probability of finding an electron in a region. For this, consider a sphere of radius r and thickness dr.



The volume of the shell of thickness dr is $4\pi r^2 dr$.

This volume multiplied by the probability (Ψ^2) gives the probability of finding an electron in the shell of thickness dr.

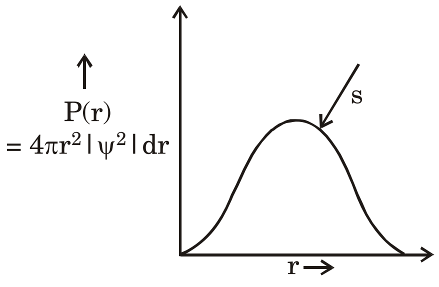
Thus, $p(r) = 4\pi r^2 dr\ |\Psi^2|$

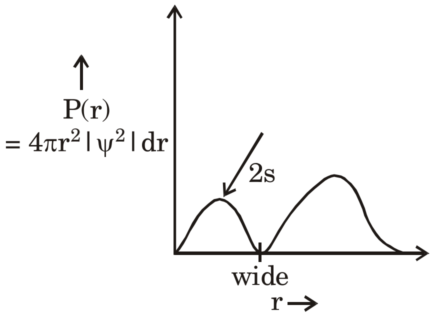
Since this function depends only on the value of radial distance from the centre, it is called radial probability function.

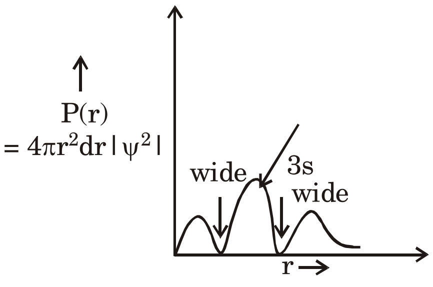
Radial node or Spherical nodes : Now, in any atom, the quantum number n gives the distance between the nucleus & the outermost shell. So, it is a measure of the radial distance of an electron. It so happens that for certain orbitals, the probability of finding an electron drops to zero at certain distances from the nucleus. Such points are called radial nodes. (A node is a region where the probability of finding an electron is zero).

Following graphs will further illustrate this point

The number of radical nodes increased with the increase in distance between nucleus and the outermost shell.



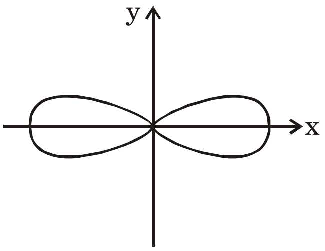




Angular or Planar node : This type of node corresponds to the quantum number l. In s orbitals, due to their spherical symmetry, there are no nodal plane. Consider p_x orbital.

In the y-z plane, the probability of finding an electron is O. So, y-z is a nodal plane.

Similarly, for d-orbitals there are 2 nodal planes.



Formulae :

No of radial nodes = n – l – 1

No. of angular nodes = l

Total no. of nodes = n – 1

1.8 ELECTRONIC CONFIGURATION OF ELEMENTS :

Quantum numbers can now characterise the electrons in an atom. To describe the arrangements and distribution of electrons for different elements, following rules and selective principles are used. The distribution 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 state 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, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,.....

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

Pauli 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 Ist energy level (n = 1). For n = 1, l = 0, & m = 0. Now s can have two values corresponding to each value of m i.e. s = + ½, – ½. Hence, the possible designation of an electron in a state with n = 1 is 1, 0, 0, + ½ and 1, 0, 0, – ½ (n, l, m, s) i.e., two quantised states. This implies that an orbital can accommodate (for n = 1, m = 0, ⇒ one orbital) maximum of two electrons having opposite spins.

The maximum number of electrons in the different subshells are :

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 them."

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 s 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 numbers 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

Ground-State Electronic Configuration of the Elements

Atomic Number	Symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
1	H										
2	He	1									
		2									
3	Li	2	1								
4	Be	2	2								
5	B	2	2	1							
6	C	2	2	2							
7	N	2	2	3							
8	O	2	2	4							
9	F	2	2	5							
10	Ne	2	2	6							
11	Na	2	2	6	1						
12	Mg	2	2	6	2						
13	Al	2	2	6	2	1					
14	Si	2	2	6	2	2					
15	P	2	2	6	2	3					
16	S	2	2	6	2	4					
17	Cl	2	2	6	2	5					
18	Ar	2	2	6	2	6					
19	K	2	2	6	2	6	1				
20	Ca	2	2	6	2	6	2				
21	Sc	2	2	6	2	6	1	2			
22	Ti	2	2	6	2	6	2	2			
23	V	2	2	6	2	6	3	2			
24	Cr	2	2	6	2	6	5	1			
25	Mn	2	2	6	2	6	5	2			
26	Fe	2	2	6	2	6	6	2			
27	Co	2	2	6	2	6	7	2			
28	Ni	2	2	6	2	6	8	2			
29	Cu	2	2	6	2	6	10	1			
30	Zn	2	2	6	2	6	10	2			
31	Ga	2	2	6	2	6	10	2	1		
32	Ge	2	2	6	2	6	10	2	2		
33	As	2	2	6	2	6	10	2	3		
34	Se	2	2	6	2	6	10	2	4		
35	Br	2	2	6	2	6	10	2	5		
36	Kr	2	2	6	2	6	10	2	6		

Note : In atomic numbers, 24 and 29, observe the rule of extra-stability of half filled and fully filled orbitals.

Example 27

(a) Find the orbital angular momentum of an electron in the following orbital

(i) 3p (ii) 3d (iii) 3s

(b) Arrange the electrons represented by the following sets of quantum numbers in decreasing order of energy

(i) n = 4, l = 0, m = 0, s = ±½ **(ii)** n = 3, l = 2, m = 0, s = ±½

(iii) n = 3, l = 1, m = 1, s = – ½ **(iv)** n = 3, l = 0, m = 0, s = – ½

Solution :

(a) $\mu = \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$

(i) For 3p, l = 1, $\mu_l = \sqrt{1(1+1)}\,\hbar = \sqrt{2}\,\hbar$

(ii) For 3d, l = 2, $\mu_l = \sqrt{2(2+1)}\,\frac{h}{2\pi} = \sqrt{6}\,\hbar$

(iii) For 3s, l = 0, $\mu_l = 0$

(b) Higher the value of (n + l) higher will be the energy of orbital. If the two values are same then one having higher value of n the energy will be higher

For (i) (n + l) = 4 4s orbital

For (ii), (n + l) = 5, 3d orbital

For (iii) (n + l) = 4 3p orbital

For (iv), (n + l) = 3 3s orbital

Decreasing order of energy : (ii) > (i) > (iii) > (iv)

Example 28

Consider the following electronic configuration of the element

(i) $1s^2 2s^1$ (ii) $1s^2 3s^1$

(a) Name the element corresponding to (i)

(b) Does (ii) correspond to the same or different element

(c) How can (ii) be obtained from (i)

(d) Is it easier to remove one electron from (ii) or (i) ? Explain.

Solution :

(a) The element corresponding to (i) is lithium (Li).

(b) This electronic configuration represents the same element in the excited state.

(c) By supplying energy to the element when the electron jumps from the lower energy 2s orbital to the higher energy 3s orbital.

(d) It is easier to remove an electron from (ii) than from (i) since in the former case the electron is present in a 3s orbital and hence is less strongly attached by the nucleus than a 2s orbital.

Example 29

A neutral atom of an element has 2K, 8 L, 5M electrons. Find out the following :

- **(a) Atomic Number**
- **(b) Total number selectrons**
- **(c) Total number of p electrons**
- **(d) Number of protons**
- **(e) Valency**

Solution : Electronic configuration of tievtral atom :

$$\frac{1s^2}{K}, \frac{2s^2 2P^6}{L}, \frac{3s^2 3P^3}{M}$$

(a) Atomic number = Total number of electrons in neutral atom = 15

(b) Total number of s electrons = 6

(c) Total number of p electrons = 9

(d) Number of protons = 15

(e) Valency = 3

Example 30

An electron in a Bohr orbit of hydrogen atom in quantum level n_2 has an angular momentum of 4.276 10^{-34} kgm^2 sec^{-1}. If this electron drops from this level to the next lower level, find the wavelength of this spectral line. (given R_H = 109679 cm^{-1})

Solution : According to Bohr's theory

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

$$mvr = 4.2176 \quad 10^{-34} \text{ kg m}^2\text{s}^{-1}$$

$$n = \frac{2 \times 3.14 \times \left(4.2176 \times 10^{-34} \text{kg m}^2 \text{s}^{-1}\right)}{\left(6.626 \times 10^{-34} \text{ Js}\right)}$$

$$= 3.99$$

$$\approx 4$$

when an electron falls from n = 4 to n = 3 in a hydrogen atom, the wavelength emitted is calculated as,

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

$$= 109679 \left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$$\begin{aligned}\lambda &= 1.8756 \quad 10^{-4}\ \text{cm}\\ &= 1.8756 \quad 10^{-6}\ \text{m}\\ &= 18756 \quad 10^{-10}\ \text{m}\\ &= 18756\ \text{Å}\end{aligned}$$

Example 31

Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra.

$R_H = 1.1 \quad 10^7\ m^{-1}$, $c = 3 \quad 10^8\ m\ sec^{-1}$ and $h = 6.62 \quad 10^{-34}$ J sec

Solution :

For visible line spectrum, i.e., Balmer series $n_1 = 2$. Also for minimum energy transition $n_2 = 3$.

$$\therefore \qquad \frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ for H-atom}$$

$$\therefore \qquad \frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

$$= 1.1 \times 10^7\left[\frac{1}{4} - \frac{1}{9}\right] = 1.1 \times 10^7 \times \frac{5}{36}\text{m}^{-1}$$

$$\therefore \qquad \lambda = 6.55 \quad 10^{-7}\ \text{m}$$

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{6.55 \times 10^{-7}}$$

$$= 3.037 \quad 10^{-19}\ \text{Joule}$$

If N electrons show this transition in 1 g atom of H then

$$\begin{aligned}\text{Energy released } &= E \quad N\\ &= 3.03 \quad 10^{-19} \quad 6.023 \quad 10^{23}\\ &= 18.29 \quad 10^4\ \text{J}\\ &= 182.9\ \text{kJ}\end{aligned}$$

Example 32

Consider the hydrogen atom to be a proton embedded in a cavity of radius (Bohr radius) whose charge is neutralized by the addition of an electron to the cavity in a vacuum, infinity slowly. Estimate the average total energy of an electron of an electron in its ground state as the work done in the above neutralization process. Also, if the magnitude of the average kinetic energy is half of the magnitude of the average potential energy, find the average potential energy.

Solution :

The work done in the neutralization process is the energy due to the electrostatic force of attraction between the electron and the proton.

$$\therefore \quad \text{Potential energy} = \frac{kZe \times (-e)}{a_0}$$

$$= \frac{-kZe^2}{a_0} = \frac{-ke^2}{a_0}$$

where e is the charge on the electron/proton, a_0 is the Bohr radius, k is the coulombic law constant and Z is the atomic number = 1 ($\therefore$ one proton)

Kinetic energy of the electron moving in the orbit = ½ mv^2 (m is the mass of electron and v is the velocity).

$\therefore$ Total energy of the electron

$$E = \frac{-ke^2}{a_0} + \frac{1}{2}mv^2 \qquad \text{... (i)}$$

For the electron to stable in the orbit, the electrostatic force of attraction should be equal to the centripetal force.

$$\therefore \quad \frac{ke^2}{a_0^2} = \frac{mv^2}{a_0}$$

$$\frac{ke^2}{a_0} = mv^2$$

Substituting in (i)

$$E = \frac{-ke^2}{a_0} + \frac{1}{2}\frac{ke^2}{a_0} = \frac{-ke^2}{2a_0}$$

Example 33

Positronium consists of an electron and a positron (same mass, opposite change) orbiting around their common centre of mass. The spectrum is therefore expected to be hydrogen like, the difference arising from the mass differences. Calculate the wave number of the first three lines of Balmer series of positronium.

Solution : The mass of the nucleus and the electron are comparable and in such systems the mass of the nucleus is also to be taken into account. In the energy equation, instead of the mass of the electron, the reduced mass is to be taken.

By definition, reduced mass μ is

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

m is the mass of the electron and M is the mass of the nucleus

$$\mu = \frac{m \times M}{m + M}$$

Since the mass of positron = mass of electron,

$$\mu = \frac{m \times m}{2m} = \frac{m}{2}$$

Therefore with equation for Rydberg constant, for positronium is

$$R_{pos} = \frac{2\pi^2 \mu e^4 k^2}{h^3 c} = \frac{2\pi^2 (m/2) e^4 k^2}{h^3 c}$$

$$= \frac{R_H}{2}$$

$$= \frac{109737}{2} = 54868.5 \text{ cm}^{-1}$$

First line of Balmer series :

$$\bar{v}_1 = 54868.5 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 7620.6 \text{ cm}^{-1}$$

Second line :

$$\bar{v}_2 = 54868.5 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = 10288 \text{ cm}^{-1}$$

Third line :

$$\bar{v}_3 = 54868.5 \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 11522 \text{ cm}^{-1}$$

Example 34

The de Broglie wavelength of electron of He^+ ion is 3.329 Å. If the photon emitted upon de-exiciation of this He^+ ion is made to hit H atom in its ground so as to liberate electron from it, what will be the de Broglie's wavelength of photoelectron?

Solution :

$$\lambda = \frac{h}{\sqrt{2mE}}$$

⇒

$$E = \frac{h^2}{2m\lambda^2} = \frac{\left(6.625 \times 10^{-34}\right)^2}{2 \times 9.11 \times 10^{-31} \times \left(3.329 \times 10^{-10}\right)^2}$$

$$= 21.73 \quad 10^{-19} \text{ J} = 13.58 \text{ eV}$$

this is the K.E. of electron

$$\text{Therefore, total energy} = -\ 13.58 \text{ eV}$$

$$E_n = -\,13.6 \times \frac{Z^2}{n^2} \text{eV}$$

For $\quad H^+$ ion, Z = 2 and $E_n = -13.58$ eV

$$\text{So, } n^2 = \frac{-\,13.6 \times 4}{-\,13.58} \Rightarrow n = 2$$

Thus, He^+ ion is in the 1st excited state.

$$\text{Energy of photon emitted} = 13.6\ Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{eV}$$

$$= 1.36 \quad 4 \left(1 - \frac{1}{4}\right) = 40.8\,\text{eV}$$

Energy of photon = I.P. of H + K.E. of photoelectron

Thus, K.E. of photoelectron = 40.8 – 13.6 = 27.2 eV

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{6.625 \times 10^{-34}}{\sqrt{2\times 9.11\times 10^{-31} \times 27.2\times 1.602\times 10^{-19}}} = 2.351 \quad 10^{-10} \text{ m} = 2.351\ \text{Å}$$

Example 35

The wavelength of the photoelectric threshold of a metal is 230 nm. Determine the K.E. of photoelectron ejected from the surface by UV radiation emitted from the second longest wavelength transition (downward) of electron in Lyman series of the atomic spectrum of hydrogen. (R = 1.9677 $\quad 10^7$ m^{-1})

Solution :

The minimum energy (E) required to eject an electron per atom from metal surface is given by Planck's quantum theory as adopted by Einstein to explain photoelectric effect.

$$E_0 = h\nu_0 = \frac{hc}{\lambda_0} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{230 \times 10^{-9}}$$

$$= 8.63 \quad 10^{-19}$$

For spectral line in Lyman series of H atom

$$\frac{1}{\lambda} = R\left(1 - \frac{1}{n^2}\right)$$

For the 2nd longest wavelength transition, n = 3, so

$$\frac{1}{\lambda} = \frac{8}{9}R = \frac{8}{9} \times 1.09677 \times 10^7\ \text{m}^{-1}$$

or

$$\lambda = \frac{9}{8 \times 1.09677 \times 10^7}$$

$$= 1.025 \quad 10^{-7}\ \text{m} = 102.5\ \text{nm}$$

Energy of photon corresponding to this wavelength is as given below

$$E = h\frac{c}{\lambda} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{1.025 \times 10^{-7}}$$

$$= 1.937 \quad 10^{-18}\ \text{J}$$

$$\therefore \quad \text{K.E. of photoelectron} = E - E_0$$

$$= 19.37 \quad 10^{-19} - 8.63 \quad 10^{-19} = 1.074 \quad 10^{-18}\ \text{J}$$

Example 36

The second ionization potential of Be is 17.98 eV. If the electron in Be^{3+} is assumed to move in a spherical orbit with a central field of effective nuclear charge (Z_{eff}) consisting of the nucleus and other electrons, by how many units of charge is the nucleus shielded by other electrons? (The energy of electron in first Bohr orbit of H is – 13.6 eV). If the extent of shielding by the K electrons of Li atom is the same as you have calculated above, find the ionization potential of Li.

Solution :

$$\text{I.E.} = \frac{13.6 Z_{eff}^2}{n^2} = 17.98$$

$$\therefore \quad Z_{eff} = 2.3$$

$$\text{Shielding extent} = Z - Z_{eff} = 4 - 2.3 = 1.7$$

$$Z_{eff} \text{ for lithium} = 3 - 1.7 = 1.3$$

$$\therefore \quad \text{I.E. of lithium} = 13.6 \quad (1.3)^2 = 22.984\ \text{eV}$$