14

ATOMIC STRUCTURE

14.1. INTRODUCTION

According to ancient philosophers, an atom was indivisible. However, later experiments have shown that atoms are made up of electrons, protons and neutrons. Protons and neutrons are present in the nucleus and electrons are outside the nucleus. Electrons are in a state of continuous motion and possess both particle and wave characteristics. You will learn that according to this modern concept of an atom, it has been possible to explain the behaviour of atoms by assigning, a particle wave nature to electrons You may be curious to know where exactly is the electron located around the nucleus and what is the energy associated with it ? Can we label these energy levels and distribute the electrons in them ? What is the energy absorbed or given out when an electron jumps from one level to the other ? Let us read about these concepts in this lesson and try to get answers to all these questions.

14.2. OBJECTIVES

After reading this lesson you will be able to :

- recognise the existence of fundamental particles in an atom, i.e , eletrons, protons, neutrons.
- describe the experiment of scattering of alpha-particles.
- explain the discovery of neutron.
- discuss about the passage of electricity through gases.

- describe the existence of cathode rays, anode rays etc.
- corelate the existence of proton and neutron inside the nucleus and electrons in motion, outside the nucleus.
- describe the salient features of Rutherfords, nuclear model.
- recognise that radiant energy is transmitted by electromagnetic waves.
- illustrate that a wave is dependent upon frequency wavelength.
- explain the visible spectra.
- explain the line spectra of H-atom and Balmer equation.
- explain Bohr model and energy level of an atom.
- recognise the particle and wave nature of electron in an atom.
- state the Heisenberg's uncertainity principle.
- state and explain De-Broglie's equation.
- solve simple numericals,
- state the quantum mechanical model, existence of orbitals emphasising the probability picture.
- state Paulis' exclusion principle and Hund's Rule.
- state Aufbau principle and write the electronic configuration of atoms when atomic number is given.
- represent 1s, and 2s orbitals.
- know the shapes of s, p and d orbitals.
- identify the existence of quantum numbers to describe an electron completely.

14.3. DISCHARGE OF ELECTRICITY THROUGH GASES

During the end of 19th century, various scientists such as Crookes, Perrin and Thompson carried out experiments by passing electricity through gases at low pressure. It was concluded, that atoms can be further divided into some fundamental particles. Atom has a definite structure also. However, atom is still considered to be the smallest particle of matter which takes part in a chemical reaction. Some of the discoveries on which modern theory of atomic structure is based are given below:

(a) Cathode Rays

In 1897 J.J. Thompson carried out an experiment to pass electricity through gases. At a very low pressure, i.e., between 0.01 to 0.001 mm of Hg and high potential difference it is observed that a luminous stream of rays comes out from the cathode as given in figure (14.1). These rays are called cathode rays.

The properties of cathode rays suggest that these rays consist of negatively charged particles of finite mass. (see figures 14.2, 14.3, 14.4, 14.5). Later it was found that each electron has a unit negative charge and has a mass equal to 1/ 1840 of that of Hydrogen atom.

Can you suggest what will happen if the gas in the discharge tube is changed. It is interesting to note that each time the same type of particles are produced which are called electrons.

Electrons are fundamental particles carrying a unit negative charge and are a common constituent of all atoms.

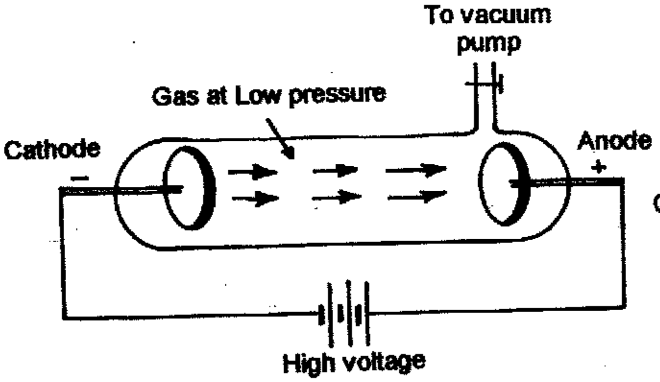

Fig.14.1 Cathode Rays.

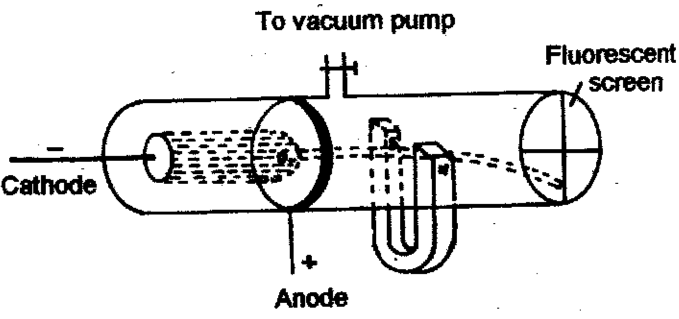

Fig.14.2 Effect of magnetic field on cathode rays.

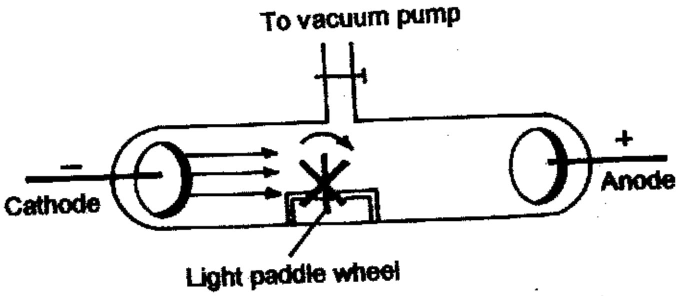

Fig. 14.3 Movement of light paddle wheel.

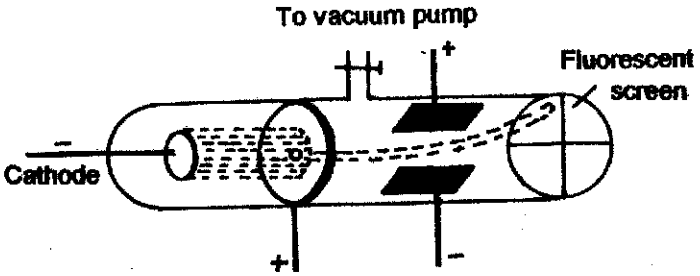

Fig. 14.4 Effect of electric field on cathode rays.

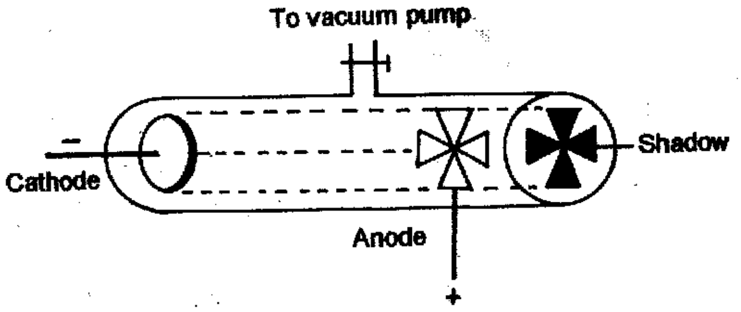

Fig.14.5 An object placed in the path of cathode rays casts a sharp shadow

(b) Anode Rays

You have learnt that an electron is a negatively charged particle of finite mass and is a common constituent of all atoms. You also know that an atom as a whole is electrically neutral. So it must have some positively charged particle also. In 1886 Goldstein observed that if a perforated cathode is used in the discharge tube experiment (described in the previous section) a glow is seen on the wall behind the cathode. This glow is seen when rays pass through the holes (canals) of the cathode. (see fig. 14.6)

Do you realise that these must be positively charged as they move from the anode towards the cathode and are also called canal rays and are made up of positively charged ions. As the electrons in the discharge tube move towards the cathode, they hit some neutral atoms of the gas and cause its ionization. The nature of positive ions varies with the gas filled in the discharge tube. Note that the positive particles obtained from hydrogen gas are the lightest. They carry a unit positive charge. Rutherford gave the name proton to this particle which has a mass nearly equal to that of a Hydrogen atom.

A proton is defined as that fundamental particle which carries one unit of positive charge and has a mass nearly equal to that of H-atom. Mass of a proton = 1.6726×10^{-24}g

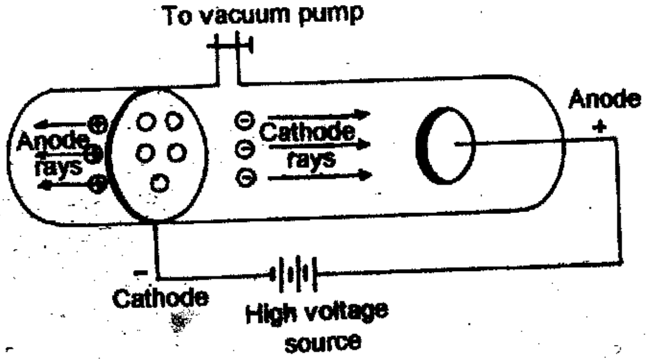

Fig. 14.6 Canal rays

14.4. RUTHERFORD'S EXPERIMENT

In 1911, Rutherford performed an experiment in which he bombarded thin foils (4×10^{-5} cm) of metals like gold, silver or copper with a beam of fast moving alpha (α)particles.*

The source of alpha(α) particles was radium (a radioactive substance), placed in a block of lead.

Slits were used to get a fine beam (see figure 14.7). The presence of α particles was detected with the help of a zinc sulphide screen. Whenever a particle strikes this screen, a flash of light is given out. From this experiment, Rutherford made the following observations :

(i) Most of the particles passed through the foil without undergoing any deflection.

(ii) Few of the particles were deflected slightly.

(iii) Very few particles were deflected back with an angle of more than 90° (Fig 14.8)

From these observations of the experiment, we can draw the following conclusions.

(i) Since most of the α particles pass through the foil without undergoing any deflection, there must be sufficiently empty space in the atom.

(ii) Since few of the α particles are deflected through a small angle and α particles being positively charged particles, they can be deflected only by a positively charged body present within the atom.

(iii) Since very few α particles are deflected back completely they must have struck against a heavy positive body inside the atom.

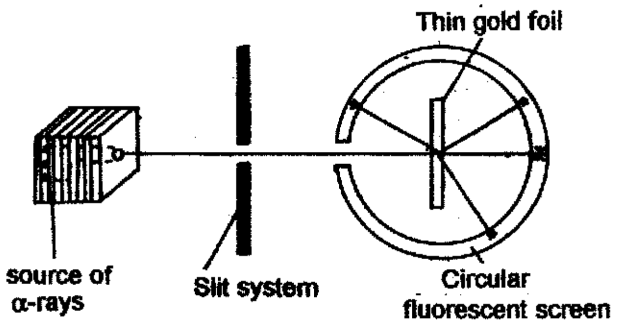

Fig.14.7 Rutherford's scattering experiment.

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* An α-particle is a particle which carries two unit positive charge and has a mass equal to that of a helium atom.

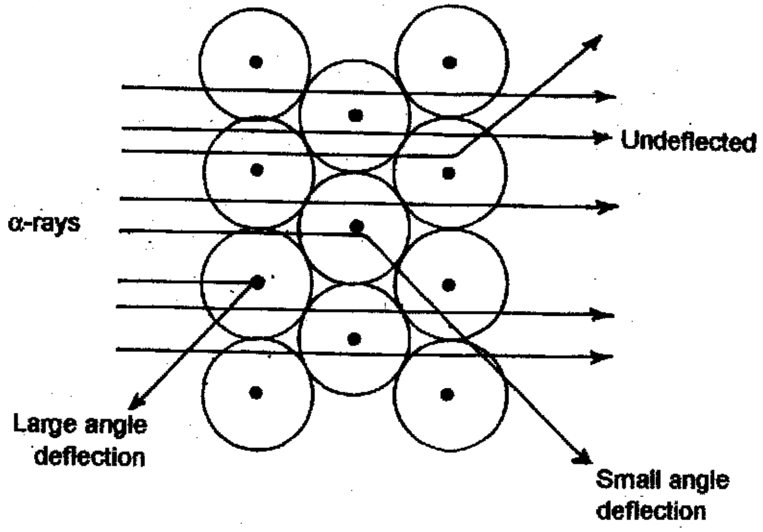

Fig. 14.8 Behaviour of the particles when passed through a metal foil.

(iv) Since number of α particles striking back is very very small, this positive body inside the atom must be occupying a very small volume.

The small heavy positively charged body in the atom was called nucleus.

Thus according to Rutherford's model of the atom, the atom consists of two parts.

1. **Nucleus** : Nucleus which is very small in size and carries positive charge and in which the entire mass of the atom is concentrated.
2. **Extra Nuclear part** : The space around the nucleus in which the electrons are distributed.

14.5 EXISTENCE OF NEUTRONS

Mosely in 1913 performed experiments to determine the exact quantity of charge present in the nucleus. The number of unit positive charges present in the nucleus was called its atomic number. This value was different for different elements. Since each positive charge corresponds to one proton, the atomic number would be equal to the number of protons present in the nucleus.

Note that each proton has a unit mass on the atomic mass scale and the mass of electron is negligible. It means that the mass of an atom should be equal to the mass of the protons only. But it was found that the mass of the atom was more than the mass of the protons alone.

Does it not mean that there must be some other particle also in the dense nucleus that has mass but is not charged ? Chadwick in 1932 proved the presence of such particles and called them *Neutrons*.

A neutron is defined as that fundamental particle which has a mass nearly equal to that of H atom but has no charge.
Mass of neutron =1.6749 × 10^{-24} g.

You have learnt that atom is made up of electrons, protons and neutrons. Electrons are around the nucleus. To explain why electrons do not fall into the nucleus as a result of attraction, Rutherford suggested that the electrons are not stationary but are in constant motion. This model of an atom is similar to the solar system where the nucleus is the sun and electreons are like planets moving around it. So it was also called the **Planetary Model.**

14.6. INTEXT QUESTIONS 14.1

1. What happens when an electric discharge is passed through a gas in a discharge tube at low pressure and high potential difference?

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2. What will happen if a perforated cathode is used in the experiment stated in question (1) ?

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3. What will happen if a paddle wheel is placed in the path of the rays mentioned in the question (1) ?

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4. Why are anode rays called canal rays ?

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5. What conclusions can you draw from Rutherford's experiment ?

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6. How will you show that electrons are negatively charged ?

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7. The mass of an atom is equal to the sum of masses of : (Tick the correct answer)

   (a) Electrons and Protons

   (b) Neutrons and Protons

   (c) Neutrons and Electrons

14.7. ELECTROMAGNETIC RADIATION

You have heard about x-rays and gamma rays. Both of these are electromagnatic radiation. Light is also an electro magnatic radiation. Experiments have led to the conclusion that electromagnetic radiation behave as if it is composed of waves. Some properties shown by electro magnetic radiation are diffraction and interference which are due to its wave nature.

The properties of electromagnetic radiation is summarised in the Electromagnetic wave theory.

Electromagnetic Wave Theory

This theory was put forward by **Maxwell** in **1864**. The main points of this theory are summed up as follows:

(i) Energy is emitted from any source (like a heated rod or filament of a bulb) continuously in the form of radiation. This is called radiant energy.

(ii) Radiation consists of electric and magnetic fields oscillating perpendicular to each other. Both of these are also perpendicular to the line of propagation of the radiation.

(iii) Radiation has a wave like property and travels with the velocity of light (3×10^8 m/sec).

(iv) These do not require any medium for propagation. For example. rays from the sun reach us through space which is a non-material medium. Various types of electromagnetic radiation have different wavelengths (λ)and frequency (ν). Wavelength of a wave is defined as the distance between any two crests or troughs. It is represented by symbol lamda(λ) and is expressed in m or cm or nm or Å .(Fig. 14.9)

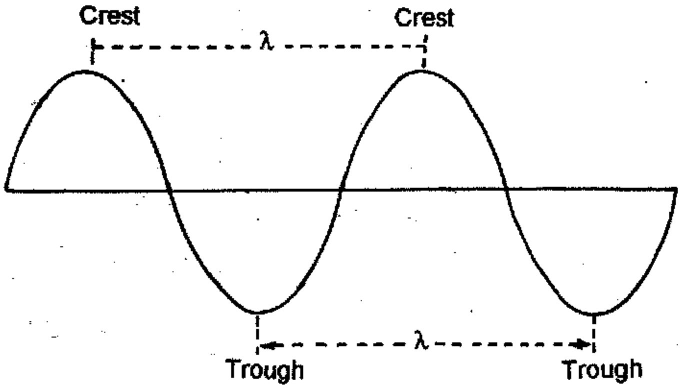


Fig14.9 Propagation of wave motion

Frequency of a wave is defined as the number of waves passing through a point in one second. It is represented by nu(ν) and is expressed in hertz(Hz) or cycles/sec. or simply sec^{-1}

1 Hz = 1 cycle/sec

Velocity of a wave is defined as the linear distance travelled by the wave in one second .It is represented by *c* and is expressed in cm/sec or m/sec.

Amplitude of a wave is the height of the crest or depth of the trough. It is represented by 'a' and is expressed in units of length.

Wave number is defined as the number of waves present in 1cm length. Naturally it will be reciprocal of wavelength. It is represented by $\bar{v}$ (read as nu bar) and its units are cm^{-1}

14.8. RELATIONSHIP BETWEEN VELOCITY, WAVELENGTH AND FREQUENCY OF A WAVE:

As the frequency (ν) is the number of waves passing thorugh a point per second and the wavelength (λ) is the length of each wave, their product will be the velocity.

Thus $c = \nu \times \lambda$

14.9. ELECTROMAGNETIC SPECTRUM

Different types of electromagnetic radiations differ from each other only in their wavelengths and hence frequencies. When the electro-magnetic radiations are arranged in the order of their increasing wavelength the complete spectrum is obtained. This is called **Electromagnetic spectrum**.

Only a certain portion of the electro-magnetic spectrum is seen by our eyes. It is known as visible spectrum. Do you remember the flash of rainbow colours when you hold a prism in front of the light from sun? Have you seen the rainbow colours on a thin film of a soap bubble? This is called a spectrum. (see fig 14.10)

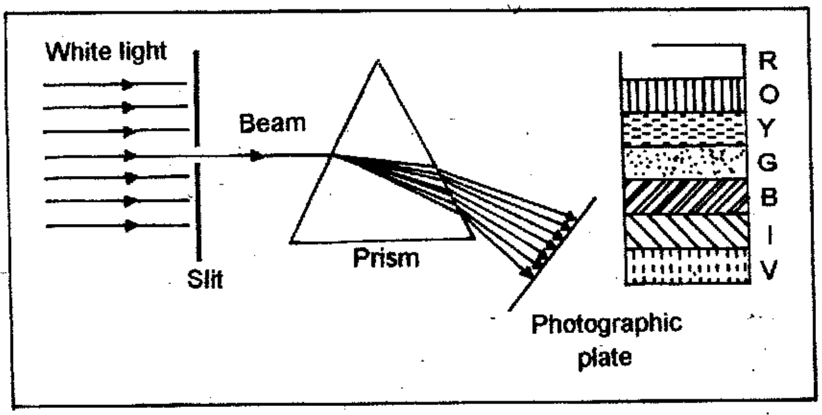


Fig.14.10 Continuous spectrum of white light

14.10 STUDY OF SPECTRA

You just learnt that when radiation from the sun is passed through a prism a continuous band of seven colours (rainbow colours) ranging form violet to red is obtained. Such a spectrum is called **Emission Spectra.**

Continuous spectrum is obtained when the source is sun, a bulb or a hot glowing body.(fig 14.11).

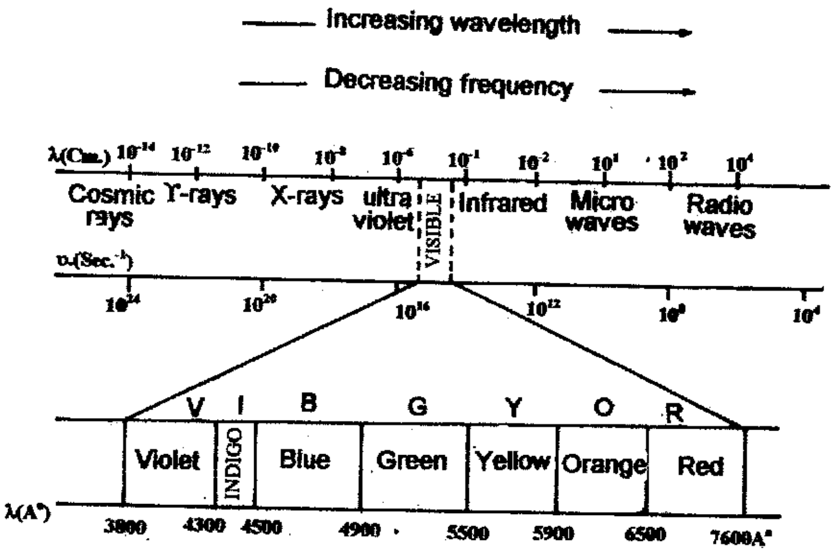


Fig.14.11 Complete electromagnetic spectrum

When the spectra has isolated coloured lines on a photographic plate it is called a **Line Spectra.**(see fig. 14.12 and 14.13).

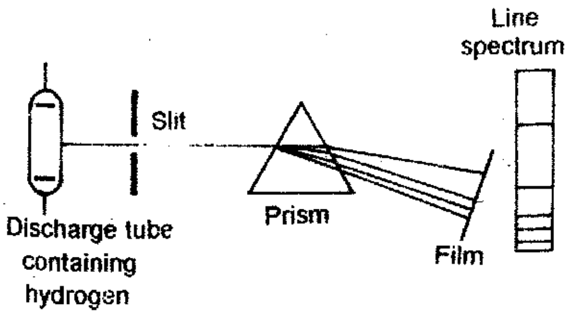


Fig. 14.12 Emission Spectrum of hydrogen.

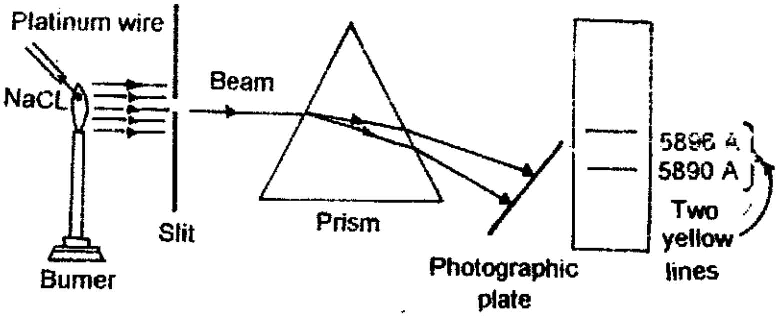


Fig.14.13 Line spectrum produced from a volatile salt placed in a flame.

14.11 ATOMIC SPECTRUM OF HYDROGEN

When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharg is passed through a spectroscope, the spectrum obtained is called *Atomic Spectrum* of hydrogen

We find that it consists of a large number of lines which are grouped together into different regions of the electromagnetic spectra. Each group is named after its discoverer. (see Fig.14.14)

The lines in the spectrum of hydrogen are classified into five series as follows :

(i)	Lyman series	Ultravoilet region
(ii)	Balmer series	Visible region
(iii)	Pashchen Series	Infra-red region
(iv)	Bracket series	
(v)	Pfund series	

The complete spectrum of hydrogen is shown is Fig. 14.14

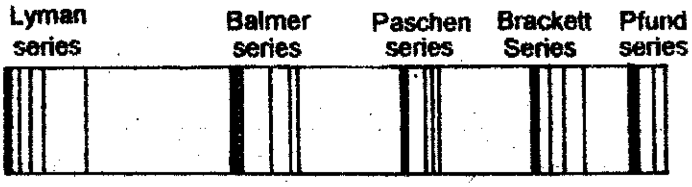


Fig. 14.14 Atomic spectrum of hydrogen

14.12 RYDBERG FORMULA

Although a large number of lines are present in the hydrogen spectrum, Rydberg in 1890 gave a simple equation to calculate the wave lengths of these lines.

$$\bar{v} = \frac{1}{\lambda} = R = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

where R is a constant called Rydberg constant and has a value 109677 cm^{-1}, n_1 and n_2 are positive numbers and for a particular series n_1=constant, n_2 varies.

For Lyman	$n_1 = 1$	$n_2 = 2, 3, 4, \ldots\ldots$
For Balmer	$n_1 = 2$	$n_2 = 3, 4, 5, \ldots\ldots$
For Paschen	$n_1 = 3$	$n_2 = 4, 5, 6, \ldots\ldots$
For Bracket	$n_1 = 4$	$n_2 = 5, 6, 7, \ldots\ldots$
For Pfund	$n_1 = 5$	$n_2 = 6, 7, 8, \ldots\ldots$

The same formula was put forward by Balmer and called Balmer's formula. When n_1 =2, n_2 =3, 4, 5..... etc. The lines are observed in the visible region

Hence the Balmer formula would be

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

where n_2 is 3, 4, 5....... etc. and R is a constant

INTEX QUESTION 14.2

1. Give two examples of electromagnetic radiation.

2. State two properties of electromagnetic radiations.

3. Which two properties of electromagnetic radiations indicate that they behave as wave.

4. Which photons are more energetic, those with higher wavelength or those with lower wavelength.

5. Name the spectral regions present in the spectrum of hydrogen atom.

6. Name the series of spectral lines when an electron jumps to

   (a) $n_1 = 2$ from $n_2 = 3, 4.$

   (b) $n_1 = 1$ from $n_2 = 2, 3, 4.$

7. Calculate and compare the energies of two radiations having wavelengths $\lambda_1 = 4000Å$ and $\lambda_2 = 8000Å$

14.14 BOHR'S THEORY FOR STRUCTURE OF HYDROGEN ATOM

You will recall that an atom is composed of a heavy positively charged nucleus and electrons are revolving around it. However, if this were true then :

(i) the electron, being negatively charged would be attracted by the positively charged heavy nucleus and

(ii) the electrons being a charged body, would emit energy in the form of radiation, while revolving in orbit. It will eventually use all its energy and finally fall into the nucleus (see Fig. 14.15). The emmitted radiation is likely to form all types of spectral lines instead of specific spectral lines characteristic to only hudrogen atom.

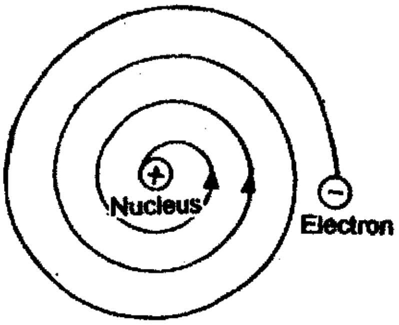


Fig. 14.15

This difficulty was overcome by Niels Bohr by postulating that electron in an atom is allowed to revolve only in certain fixed **stationary orbits** or **states**, having certain specific discrete amount of energy. While revolving in a particular stationary state, an electron does no emit any radiation. It is associated with a fixed amount of energy of that state.

> **The energy of an electron in an atom is quantized i.e. electron energy is packaged in little bundles called quanta.**

Hence each atom of an element has a set of energy levels for its electrons. The different energy levels possess different amount of energy. Normally the atom is in the ground state i.e. all the electrons are in the lowest available energy levels. So under certain conditions each electron drops down from the higher energy state to a lower energy state. According to Niel Bohr, the difference of energy for the two levels concerned, is emitted in the form of radiation. Thus, if an electron drops down or in other words the transition takes place, from a higher energy state (E_2) to a lower energy state (E_1), then the difference between these energies is the amount of energy lost by the electron and equals the energy of radiation which is emitted (see Fig. 14.16).

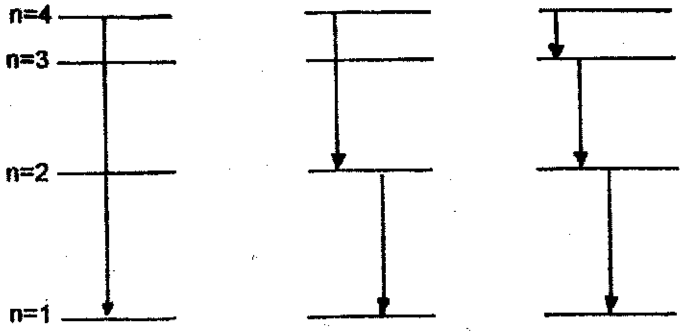


Fig 14.16 Different routes to the ground state from fourth energy level

thus, $E_2 - E_1 = h\nu = hc/\lambda$

where h is the Planck's constant and has a value equal to 6.62×10^{-34}Js.

Thus a discrete spectral line of wavelength λ is accounted for the quantized electronic energies E_2 and E_1. In a given atom many such transitions from higher to lower level are possible. Each transition contributes towards a single discrete line in the spectrum of that element.

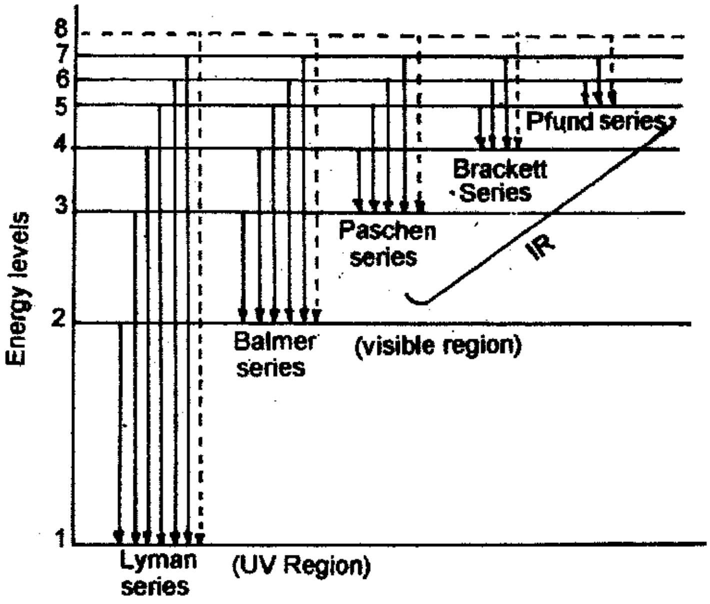
It is possible to calculate the amount of energy associated with each stationary state by making suitable measurements in the spectrum obtained from hydrogen atom.

Coming back to the Rydberg equation,

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

the notations, n_1 and n_2 are known as stationary states.

Larger the value of n_1, n_2, n_3, of an electron in an atom, higher the amount of energy associated with it. Thus, in the ground state, which is the normal state of an atom, the electron will be in a stationary state (orbit) as close to the nucleus as possible (n=1). The energy associated with the electron in this stationary state is minimum. On giving energy to the atom, e.g. by heating it or by putting it in an electric discharge tube across the electrodes of which a high voltage is passed, the electron will be raised to high stationary states, corresponding to n=2, 3, 4, etc. for which the energy will be less negative (excited state). The electron ultimately returns to a less excited state. Energy is radiated in this process. It is this radiation which gives rise to the formation of spectral lines. A pictoral representation of this type of change is shown in Fig. 14.17.



Layman series	From n = 2, 3, 4, 5 .... to n = 1
Balmer series	From n = 3, 4, 5, 6 .... to n = 2

Fig. 14.17 Generation of various spectral series in hydrogen spectrum

Thus we see that the existence of line spectra provides support to the Bohr model of the hydrogen atom.

Weakness of the Bohr Model

The Bohr model of the atom had several weaknesses. The theory is found to work well only for the atom, like hydrogen, i.e., species containing only one electron. It proved inadequate in accounting for the observed atomic spectra other than that of hydrogen. The series of spectral lines for other atoms predicted by the theory simply do not correspond to what is actually observed. However it served as the stepping stone to the quantum mechanical model.

14.14 DUAL NATURE OF ELECTRON : DE BROGLIE WAVES

You know by now that electrons behave as particles. However, in 1924, a French scientist, L. de Broglie, suggested that electrons also possess wave character like the one shown in Fig. 14.18. The wave length associated with the electron is given by expression $\lambda = \frac{h}{p}$ where h is the Planck's constant (= $6{\cdot}62 \times 10^{-34}$ joules sec) and p is the momentum (mv, where m is the mass and v is the velocity of the electron):

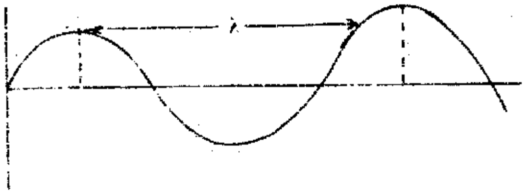


Fig. 14.18 Representation of a wave

This equation is called the De Broglie equation. This relationship has been verified by performing a large number of experiments using electron beams which leads to the conclusion that streams of particles such as electrons exhibit wave properties. Thus, electrons behave as particles as well as waves, i.e. they exhibit wave-particle dualism.

Davisson and Germer and G.P.Thomson independently showed that stream of fast moving electrons is diffracted by crystals. Diffraction is a phenomenon which is characteristic of waves. Hence we can say electrons behave like waves.

It has been observed that the values of the wavelengths (λ) determined experimentally are in agreement with the calculations of λ made by using de-Broglie equation, $\lambda = h/mv$. Actually, the value of λ for electrons is of the order of internuclear distances in molecules. For particles of large mass (m) the wavelength will be insignificantly small.

Louis de Broglie's wave concept was experimentally proved by Davisson and Germer.They subjected a stream of electrons from a tungsten filament to strike against a *nickel* crystal. Concentric dark lines were formed on the screen. Such diffraction patterns are actually seen when X-rays are used and we know X-rays have wave character. Hence it was concluded that electrons also have a wave character

14.15 HEISENBERG'S UNCERTAINTY PRINCIPLE

Werner Heisenberg, a German physicist developed an important relationship known as the uncertainty principle. It states that :

Simultaneous and precise determination of position and momentum of any electron is not possible.

The above stated Heisenberg's uncertainty principle is expressed mathematically as :

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

where Δx denotes the uncertainity in determining the position and Δp denotes the uncertainty in determining the momentum of any electron at a particular time.

The value of h, the Planck's constant (6.62×10^{-34} J s) is numerically very small. Therefore, the importance of this principle is practically restricted to the measurement of momentum of the electron. Thus, if Δp is very small, the uncertainity in determining the position of the electron would be very large, and vice versa.

Therefore, on the basis of Heisenberg's uncertainty principle, it can be said that it is not possible to determine the exact position and momentum of an electron at a given time. However, the probability of the electron being in a given position at a particular time or the probablity of the electron possessing a particular velocity (or momentum) at a particular instant can be found out.

INTEXT QUESTIONS 14.3

1. State an experiment that proves wave nature of an electron.

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2. Write the de Broglie expression.

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3. Using de Broglie expression, calculate the momentum of a moving particle whose wavelength (λ) is 200 pm. (pm=picometers)

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4. What is the uncertainty in the velocity of a moving cricket ball having mass 150 g if its uncertainity in position is $1\overset{\circ}{A}$.

14.17 QUANTUM MECHANICAL MODEL OF AN ATOM

On the basis of de Broglie's hypothesis and Heisenberg's uncertainity principle a new model of an atom was developed. This was called the Quantum Mechanical model and to describe the wave property of electron a mathematical equation was given.

Solution of this equation gave the definite energy values. Each permitted energy state is called an orbital. But how is it different from an orbit ? Moreover, according to uncertainity principle we have just learnt that it is not possible to determine the position of a moving electron with 100% accuracy. Then how do we define an orbital. We have to use a term called probability.

To understand this word, let us take a small example. Take a coin and toss it. The probability of head or tail would be 50% each. Applying this word to electron probability. You can understand that the probability of finding an electron in the nucleus is zero but there is some value of probability of finding the electron around the nucleus.

This region in space around the nucleus where there is greatest chance of finding the electron i.e. region of maximum probability is called the orbital.

Let us view it in another way. If we could photograph the position of a moving electron in a particular instant and plot these points on a three dimentional scale (we would have to take several millions of photographs). We will find that a dotted figure would emerge (see Fig. 14.19).

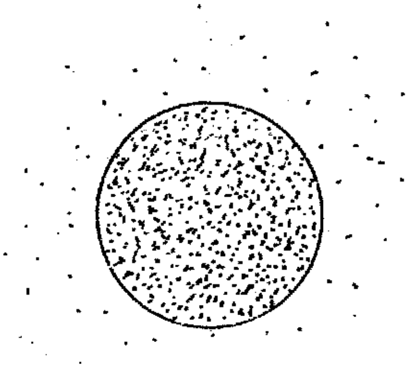

Fig. 14.19 Position of a moving electron

The dense region would be of high probability where an electron could be located. That region would be called orbital.

14.18 QUANTUM NUMBERS

Bohr's theory and wave mechanical model describe an electron around the nucleus differently. According to Bohrs theory the electron is found around the nucleus in well-defined orbits but in wave theory the probability of finding the electron around the nucleus is in a three dimensional region around the nucleus called '*Orbitals*'. The description of an electron in a given atomic orbital is expressed in terms of three numbers called Quantum Numbers.

(i) Principal Quantum Number(n)

(ii) Azimuthal Quantum Number(l)

(iii) Magnetic Quantum Number(m)

A fourth number called Spin Quantum Number (s) was introduced later. It was necessary because an electron is capable of spinning about its own axis. It could be clockwise or anticlockwise. What do these numbers signify ? Let us read about each one of them in the following text.

(i) Principle Quantum number (n)

It determines roughly to a large extent the energy of an electron. It also determines the average distance of an electron from the nucleus i.e., it determines the size of an atom.

The allowed values for n are the positive integers 1, 2, 3........

The principal quantum number tells us the shell in which the electron is found.

Thus, n = 1 corresponds to the first or K-shell.

n = 2 corresponds to the second or L-shell and so on.

The quantum number is the same as the n in the Bohr theory which you have already learnt. We called it stationary state earlier.

The energy of an electron in H atom of H like species with one electron in the extranuclear part is given by.

$$E_n = \; = -\frac{2\pi^2 e^4 m}{n^2 h^2}$$

where, e = electronic charge

m = mass of electron (9.1×10^{-31}kg)

h = Planck's constant (6.627×10^{-34}J s)

n = principal quantum number

E_n = energy

It can be solved and simplified as

$$E_n = \frac{-2.173 \times 10^{-18}}{n^2} \text{ J/atom}$$

On multiplying the above expression by Avogadro's number (N = $6{\cdot}022 \times 10^{23}$)

we get $E_n = \dfrac{-1.312 \times 10^6}{n^2}$ J/mol.

It means the energy of an electron in first shell of H atom is

$$E_1 = -1{\cdot}312 \times 10^6/1^2 = 1{\cdot}321 \times 10^6 \text{ J/mol}$$

The energy of the electron in the second principal quantum state will be

$$E_2 = -1{\cdot}312 \times 10^6/2^2 = -0{\cdot}328 \times 10^6 \text{J/mol}$$

The energy if the electron in the first principal quantum state is highest negative value meaning it is the lowest energy state. This is called *Ground State.* This electron when in higher energy states is said to be in excited states.

ii) Azimuthal Quantum Number or Orbital Quantum Number (*l*)

This quantum number specifies the subshell. It determines the shape of the orbital in which an electron is located.

This quantum number *l*, can have all integral values from 0, 1,2,...... to (*n* – 1). Thus for

K shell	when $n = 1$,	$l = 0$
L shell	when $n = 2$,	$l = 0, 1$
M shell	when $n = 3$,	$l = 0, 1, 2$
N shell	when $n = 4$,	$l = 0, 1, 2, 3$

Depending on the value of l, sub–levels or orbitals are designated as shown in table. 14.1

Table: 14.1

Designations of sub-levels corresponding to various values of the azimuthal quantum numbers

S. No.	Value of l	Designation of sub-level	Shape
1	0	s	spherical
2	1	p	dumb-bell
3	2	d	
4	3	f	

Thus, when principal quantum number $n = 1$, then $l = 0$, and only one sub-level, i.e., s, exists. This means that an electron with n = 1 can only be located in a sub-shell of the first principal energy level (K-shell).

When $n = 2$, then $l = 0$ or 1. It can have two sub-levels i.e., *s* and *p*, which implies that an electron with n = 2 may be located in either s or p subshell of the second principal energy level (L - shell). If $l = 0$, it will be located in the s subshell and if $l = 1$ it will be located in the *p* subshell of the second principal energy level. (L-shell).

When $n = 3$, $l = 0, 1, 2$, it can have three subshells, i.e., *s*, *p* and *d* which implies that an electron with $n = 3$, may be located in any of the three subshells *s*, *p* or *d* of the third principal energy level (M-shell). If $l = 0$, the electron will be located in the *s* subshell ; if $l = 1$, the electron will be located in the p subshell, $l = 2$ the electron will be located in the *d* subshell of the third principal energy level (M-shell).

When $n = 4$, $l = 0, 1, 2, 3$ the electrons will be located in the s, *p*, *d* and *f* subshells or orbitals, and so on. (see Fig. 14.20 and Fig. 14.21).

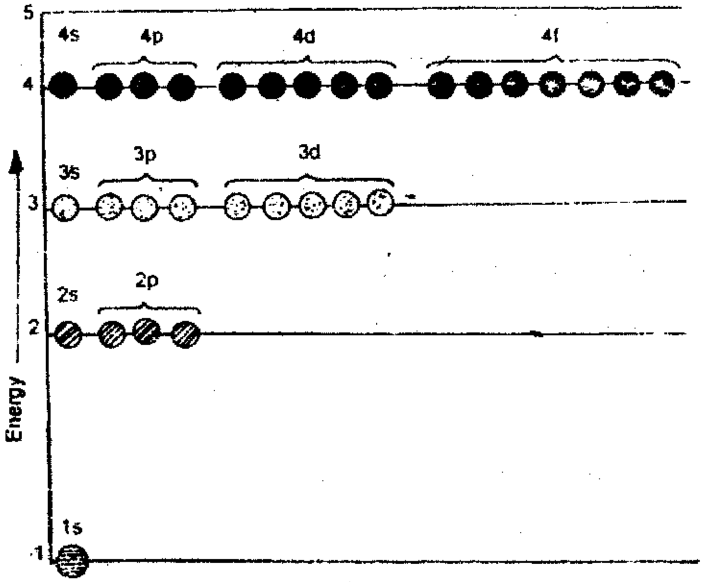

Fig. 14.20 Energy level diagram of hydrogen atom

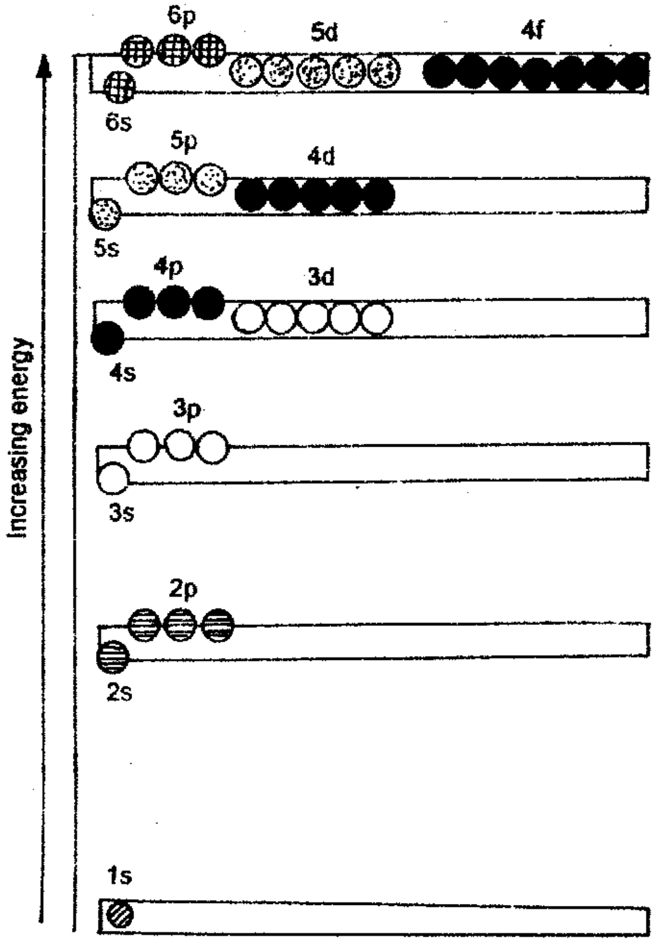

Fig. 14.21 Energy level diagram of multi-electron atoms

(iii) Magnetic Quantum Number (m_l) or Simply m

The magnetic quantum number gives the orientation of the electron in space. It gives information about the orientation of an orbital in space. m can have all values from $-l$ to $+l$ through zero ($-l$…… -3, -2, -1, 0, $+1$, $+2$, $+3$ ……… $+ l$) where l is the azimuthal quantum number, i.e. m can have $2l+1$ values.

When $l = 0$ (s subshell), m can have only one value (0). For example, for s orbital there can be no possible orientation of electrons in space and hence a spherical shape. (Fig. 14.22).

When $l = 1$ (p subshell), m can have three values, viz., -1, 0, $+1$, i.e. p subshell can have three **orbitals**. Therefore, there can be three possible oreintations of electrons in space. They are denoted by p_x (along X-axis), p_y (along Y-axis) and p_z (along Z-axis) (Fig. 14.23)

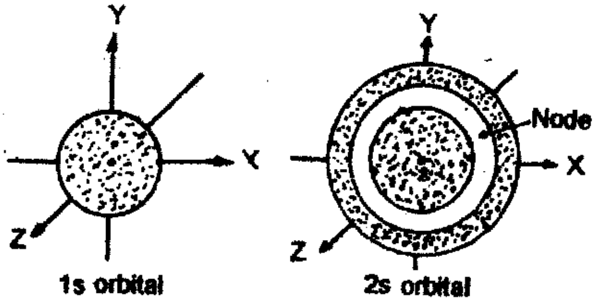

Fig. 14.22 Shapes of 1s and 2s - orbitals

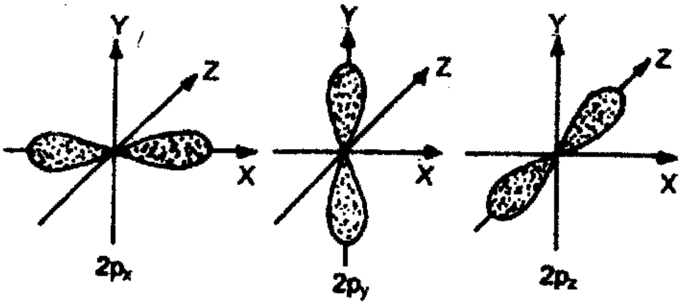

Fig. 14.23 2p-orbitals

When $l = 2$ (d subshell)m can have five values, viz., −2, −1, 0, +1 and +2. Therefore, d subshell an **have five** orbitals so that there can be five possible orientation of electrons in space. They are denoted by

d_{xy}, d_{yz}, d_{zx} and d_z2

(iv) Spin quantum number(s)

It has been found by spectral evidence that an electron rotates about its own axis (like earth which rotates about its own axis). The spin quantum number may be regarded as the direction of spin of an electron on its own axis. It has a value of either +1/2 or −1/2 corresponding to clockwise or anti-clockwise spins.

The information that the four quantum numbers provide, and their possible values are summarized in table 14.2

Table 14.2 : Information about the four quantum numbers

Name of the Quantum number	Symbol	Information provided about	Possible values
Principal	n	shell	1, 2, 3, 4, ...
Azimuthal	l	subshell	0, 1, 2, ... (n−1)
Magnetic	m	orbital	$-l$, ... 0 .... + l
Spin	s	spin	+1/2, −1/2

14.19 PAULI'S EXCLUSION PRINCIPLE

The four quantum numbers described above define completely the position of an electron in a given atom. These numbers give its position in the principal energy level (n), the sub-level (l), the orientation of the sub-level (m) and the direction of spin(s). It is thus possible to identify an electron by giving its four quantum numbers.

> **Pauli's exclusion principle states that it is impossible for any two electrons in the same atom to have all four identical quantum numbers.**

This principle is useful in determining the maximum number of electrons that can exist in an orbital and subsequently in a shell. Thus for K-shell, $n = 1$, $l = 0$, $m = 0$, s can be either +1/2 or −1/2.

These two possibilities can be written as $n = 1\ l = 0,\ m = 0,\ s = +\frac{1}{2}, -\frac{1}{2}$.

This shows that in *K*-shell, there is only one subshell ($l=0$) and in this subshell only two electrons having opposite spins can be accommodated. This can be represented as (↑↓).

For *L*-shell, $n=2$, l can have two values, viz., 0 and 1. The value of m corresponding to $l=0$ is 0; the values of m corresponding to $l=1$ will be equal to −1, 0 and +1 respectively. The values of spin quantum number s, will be equal to +1/2 and −1/2 corresponding to each value of m.

The values of all the four different quantum numbers for three different shells are summarised in table 14.3

Table : 14.3 Electrons in different atoms and their quantum numbers

Shell	n	l	m	s	total number of electrons
K	1	0	0	−1/2, +1/2	2 (1s=2)
L	2	0	0	−1/2, +1/2	8 (2s=2, 2p = 6)
		1	−1	−1/2, +1/2	
			0	−1/2, +1/2	
			+1	−1/2, +1/2	
M	3	0	0	−1/2, +1/2	
		1	−1	−1/2, +1/2	
			0	−1/2, +1/2	
			+1	−1/2, +1/2	
		2	−2	−1/2, +1/2	
			−1	−1/2, +1/2	
			0	−1/2, +1/2	
			+1	−1/2, +1/2	18(3s=2, 3p=6, 3d =10)
			+2	−1/2, +1/2	

Maximum number of electrons in a particular shell or energy level is given by $2n^2$ where n is the principal quantum number. The distribution of the electrons in various shells and the orbitals there in is shown in Fig. 14.24.

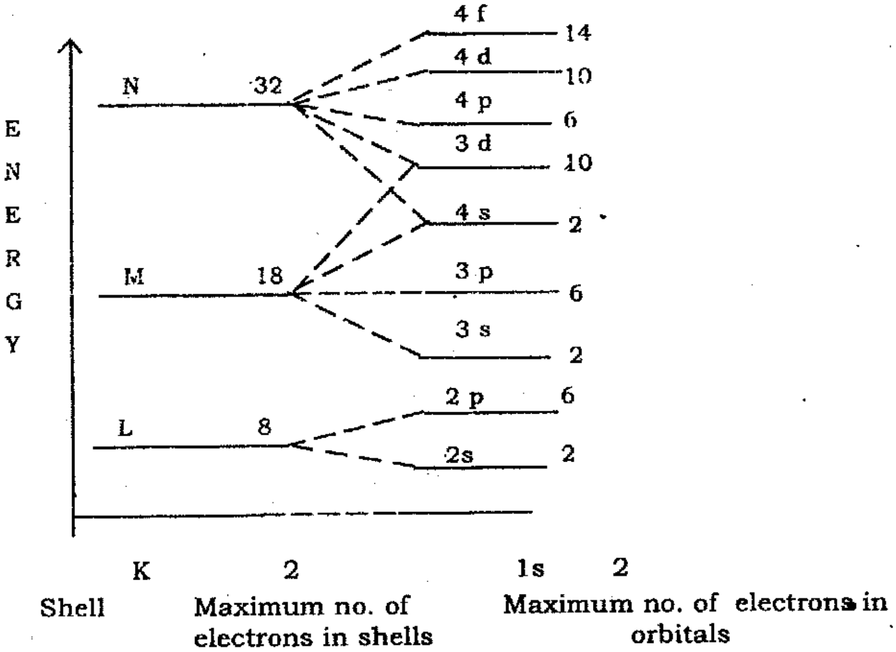

Fig 14.24 Distribution of electrons in shells and orbitals

14.20 METHOD OF REPRESENTING THE POSITION OF ELECTRONS

In representing the position of electrons in various shells and subshells, the following rules are observed.

1. The principal energy shell, viz, 1, 2, 3, 4 etc. is written first.
2. The subshell, viz, s, p, d, ... is written next.
3. The number of electrons in a particular subshell is shown by a superscript placed to the right of the symbol for that subshell, for example, $1s^2$ indicates the location of 2 electron in s-subshell of first energy shell (n=1). Similarly, $2p^6$ denotes the location of 6 electrons in p-subshell of the second principal energy level (n=2).

14.21 FILLING OF VARIOUS ORBITALS IN ATOMS

An atom in its lowest energy state is said to be in the normal state or the ground state. The ground state of an atom is the most stable state. The filling of orbitals in the ground state is determined by the following rules:

(i) The electrons are added one after the other to various orbitals.

(ii) The orbitals with a lower energy is filled up first before the filling of an orbital with higher energy commences.

(iii) Lower the value of (n+l) for an orbital, the lower is its energy. If two orbitals have the same (n+l) value, the orbital with lower value of n has lower energy.

The following table illustrates the (n+l) rule:

Orbital	value of *n*	value of *l*	value of (*n*+l)
1*s*	1	0	1 + 0 = 1
2*s*	2	0	2 + 0 = 2
2*p*	2	1	2 + 1 = 3

(iv) No two electrons in one atom can have all four identical quantum numbers(Pauli's exclusion principle).

(v) Electron pairing in any orbital is not possible until all the orbitals of a given subshell contain one electron each. This is known as Hund's Rule of maximum multiplicity or simply **Hund's Rule.**Hydrogen (H) atom has only one electron. This electron occupies the lowest energy level, 1s, i.e., the electronic configuration of hydrogen is $1s^1$.

Helium (He) atom contains two electrons. Second electron also occupies 1s orbital (since there is no other subshell in the first energy level). The electronic configuration of helium is $1s^2$ Lithium (Li) has three electrons. Two electrons occupy $1s^2$ orbital. The third electron in lithium goes to 2s orbital since that is the first orbital of second energy level. Therefore, the electronic configuration of lithium is $1s^2$ $2s^1$. It is possible to determine with the help of energy level diagram the sequence in which the orbitals are filled up (Fig. 14.25).

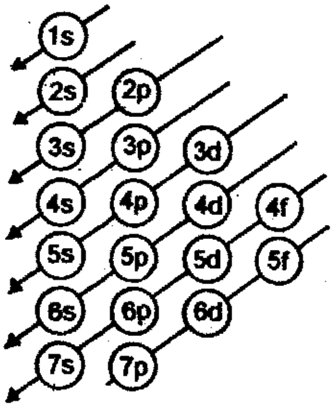

Fig. 14.25 Order of filling of orbitals

The filling of electrons in different energy levels is known as Aufbau principle. (In German Aufbau means building up).

As is shown in Fig.14.25, filling of 4s orbital takes place before 3d orbital. Filling of 3d orbital starts after the orbital 4s has acquired its share of two electrons.

The specific way in which the orbitals of an atom are occupied by electrons is called electronic configuration of that atom.

Electronic configuration of the atoms of some elements are given in the Table 14.4.

Table 14.4 Electronic Configuration of some elements

Element (Symbol)	Atomic No.	Electronic configuration
Hydrogen (H)	1	$1s^1$
Helium (He)	2	$1s^2$
Lithium (Li)	3	$[He]2s^1$ [He] represents electronic configuration of helium.
Beryllium (Be)	4	$[He]\ 2s^2$
Boron (B)	5	$[He]\ 2s^2\ 2p^1$
Carbon (C)	6	$[He]\ 2s^2\ 2p^2$
Nitrogen (N)	7	$[He]\ 2s^2\ 2p^3$
Oxygen (O)	8	$[He]\ 2s^2\ 2p^4$
Fluorine (F)	9	$[He]\ 2s^2\ 2p^5$
Neon (Ne)	10	$[He]\ 2s^2\ 2p^6$
Sodium (Na)	11	$[Ne]3s^1$ [Ne] represents electronic configuration of neon.
Magnesium (Mg)	12	$[Ne]\ 3s^2$
Aluminium (Al)	13	$[Ne]\ 3s^2\ 3p^1$
Silicon (Si)	14	$[Ne]\ 3s^2\ 3p^2$
Phosphorus (P)	15	$[Ne]\ 3s^2\ 3p^3$
Sulphur (S)	16	$[Ne]\ 3s^2\ 3p^4$
Chlorine (Cl)	17	$[Ne]\ 3s^2\ 3p^5$
Argon (Ar)	18	$[Ne]\ 3s^2\ 3p^6$
Potassium (K)	19	$[Ar]\ 4s^1$ [Ar] represents electronic configuration of argon
Calcium (Ca)	20	$[Ar]\ 4s^2$
Scandium (Sc)	21	$[Ar]\ 3d^1\ 4s^2$
Titanium (Ti)	22	$[Ar]\ 3d^2\ 4s^2$
Vanadium (V)	23	$[Ar]\ 3d^3\ 4s^2$
Chromium (Cr)	24	$[Ar]\ 3d^5\ 4s^1$

INTEXT QUESTION 14.4

1. **State the total number of electrons that a shell will have when n=2.**

----

2. Write the quantum numbers of all the electrons of the atom of an element having atomic number 3.

----

3. What are the azimuthal quantum numbers for an electron in principal shell n=4.

----

4. Which of the following orbitals are spherically symmetrical. $2p_x$, 1s, 2s.

----

5. Write the electronic configuration of the element having atomic no. 19.

----

6. Which orbitals will be filled first

   (a) 3p or 3s.

   (b) 3d or 4s.

14.22 WHAT YOU HAVE LEARNT

- Matter is made up of atoms.
- Atom contains a central heavy nucleus and extra nuclear part.
- Protons and neutrons are present in the nucleus and electrons are situated around the nucleus in space and are in constant motion.
- Cathode rays consist of negatively charged particles (electrons) that have a mass equal to 1/1840 of that of hydrogen atom.
- Anode rays consist of positively charged particles. They are called protons if the gas in the discharge tube is hydrogen gas.
- An atom as a whole is electrically neutral and its mass is equal to the mass of neutrons and protons.
- Light is a form of electromagnetic radiation and has both particle and wave nature.
- Emission spectrum is composed of various types of electromagnetic radiation. e.g. visible, ultra violet, infrared etc.
- Light carries energy in the form of packets (called photon) and the energy of each packet is given by the expression $E = h\nu$. This is called a quanta.
- All samples of hydrogen exhibit the same kind of spectra.
- In an atom, the electrons revolve around the nucleus in fixed stationary states called orbits.
- Each stationary state has different energy.
- Energy is emitted when an electron jumps from a higher energy state to lower and vice versa.

- The expression $\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ cm^{-1} helps in explaining the
- Energy contained by the electron is quantized.
- Electrons exhibit dual nature.
- It is not possible to determine the position and velocity of a moving electron simultaneousaly with great accuracy.
- An orbital is the region in space where there is maximum probability of finding the electron.
- A complete description of the electron is given by three quantum numbers the principle quantum number (n), the azimuthal number (*l*) and the maganetic number (m).
- Spin quantum number (s) can have values +1/2 or -1/2. It determines the direction of revolution of the electron about its own axis.
- No electron pairing is possible in any orbital until all the orbitals of a given subshell contain one electron each.
- Pauli's exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers.
- The various subshells are denoted as *s, p, d, f.*
- The principle quantum number determines the energy of an electron.
- The azimuthal quantum number determines the shape of the orbital.
- The magnetic quantum number gives the orientation of an orbital in space.
- Filling up of electrons in various orbitals is governed by Aufbau principle.

14.23TERMINAL EXERCISE

1. The positive rays produced when hydrogen gas is filled in a discharge tube are streams of

   (a) protons.

   (b) neutrons.

   (c) electrons.

   (d) alpha particles.

   ----

2. When atoms are bombarded with α particles, only few of them are deflected and the other pass through. This is because

   (a) The nucleus occupies a very small volume as compared to the volume of the atoms.

   (b) Electrons are not able to attract the particle (which are positively charged He^{2+} ions) with sufficient force of attraction.

   (c) Force of repulsion of α particles between themselves is small.

   ----

3. What is the difference between proton and neutron.

----

4. Describe Rutherford's experiment.

----

5. Write the Balmer formula and explain the terms involved.

----

6. How are spectral lines formed.

----

7. What is the wavelength of the light emitted when the electron in a hydrogen atom jumps from $n_2 = 4$ to $n_1=1$ levels.

----

8. Which of the following sets of quantum numbers is not possible.

   (a) $n=3$, $1 = +2$, $m = 0$, $s = +1/2$

   (b) $n=3$, $1 = 0$, $m = -1$, $s = +1/2$

   (c) $n=3$, $1 = 0$, $m = 0$, $s = -1/2$

   (d) $n=3$, $1 = 1$, $m = 0$, $s = -1/2$

----

9. Assign quantum number to all electrons in Be (atomic number =4) atom.

----

10. Write the electronic configuration of the elements with atomic number: 7, 15, 18, 24, 27, 30.

----

11. What is wrong with the following configuration.

    (a) B : $1s^2\ 2s^2\ 3s^1$

    (b) C : $1s^2\ 2s^2\ 2p_x^2$

CHECK YOUR ANSWERS.

INTEXT QUESTIONS 14.1

1. The walls of the dischargae tube opposite the cathode begins to glow with a brilliant colour. A luminous stream of rays called cathode rays are emitted from the cathode.
2. Anode rays will appear as a glow on the tube wall after passing through the perforation (holes) of the cathode.
3. The paddle will begin to move (rotatory motion).
4. Anode rays are called canal rays as they pass through holes regarded as canals of the perforated cathode.
5. (i) Most of the space inside the atom is empty.

   (ii) The whole mass of the atom is concentrated at its centre which is positively charged.
6. When an electric field is applied across the path of cathode rays, they are deflected towards the positive electron.
7. Neutrons and protons.

INTEXT QUESTIONS 14.2

1. Any two from the following is correct,

   (i) Gamma rays (ii) Radio waves

   (iii) X-Rays (iv) Visible Rays

   (v) IR Rays
2. Interference, diffraction
3. Interference, diffraction
4. $E = h\nu = \frac{hc}{\lambda}$, so the one with lower wavelength is more energetic.
5. Visible region, ultra violet region and infrared region.
6. (i) Balmer (ii) Lymen
7. $E = h\nu = \frac{hc}{\lambda}$

$$E_1 = \frac{6.6 \times 10^{-34}\ \text{Jsec.} \times 3 \times 10^8\ \text{m sec}^{-1}}{4000 \times 10^{-10}\ \text{m}}$$

$$= 4.95 \times 10^{-19}\ \text{J}$$

$$E_2 = \frac{6.6 \times 10^{-34}\ \text{J sec.} \times 3 \times 10^8\ \text{m sec}^{-1}}{8000 \times 10^{-10}\ \text{m}}$$

$$= 2.48 \times 10^{-19}\ \text{J}$$

$$\frac{E_1}{E_2} = \frac{4.95 \times 10^{19}}{2.48 \times 10^{-19}} = 2$$

INTEXT QUESTIONS 14.3

1. Davission and Germer's experiment of diffraction of an electron beam using a nickel crystal as grating. The diffraction pattern is the same as that obtained by X-ray diffraction.

2. $\lambda = h/mv = h/p$

3. $\lambda = h/p$

   $h = 6.62 \times 10^{-34}$ J sec = 6.62×10^{-34} kg m^2 sec^{-1}.

   $\lambda = 200$pm $= 2 \times 10^{-10}$ m.

   $$\text{momentum} = mv = \frac{6\cdot62\times10^{-34}}{2\times10^{-10}\ \text{m}}\ \text{kg m}^2\text{sec}^{-1}$$

   $= 3.31 \times 110^{-24}$ kg m sec^{-1}

4. Mass of the ball = m = 150 g = 0.15kg

   Uncertainty in position $= \Delta x = 1$Å $= 10^{-10}$m.

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

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

   $$\Delta v = \frac{6\cdot6\times10^{-34}\text{kg m}^2\ \text{sec}^{-1}}{4\times3\cdot14\times10^{-10}\text{m}\ \times0.15\ \text{kg}}$$

   $= 3\cdot5 \times 10^{-24}$ m sec^{-1}

INTEXT QUESTIONS 14.4

1. 8 electrons.

2. n = 1 l = 0 m = 0 s = +1/2

   n = 1 l = 0 m = 0 s = -1/2

   n = 2 l = 0 m = 0 s = +1/2

3. n = 4 l = 0, 1, 2, 3.

4. 1s, 2s.

5. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

6. (i) 3s. (ii) 4s.

TERMINAL EXERCISE

1. Protons.

2. (a)

3. Proton is positively charged whereas a neutron is electrically neutral.

4. See section 14.4

5. $$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

where $n_1 = 2 \quad n_2 = 3, 4...$

6. Spectral lines are formed when electrons from an excited state (high energy) return to a less excited state (less energy).

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

$$= 109677\left(\frac{1}{(1)^2} - \frac{1}{(4)^2}\right)$$

$$= 109677 \times \frac{15}{16} = 102822 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{v}} = \frac{1}{102822} = 9 \cdot 7 \times 10^{-6} \text{cm} = 97 \text{ nm}$$

8. (b)

9. n =1 l = 0 m = 0 s = +1/2

n = 1 l = 0 m = 0 s = - 1/2

n = 2 l = 0 m = 0 s = +1/2

n = 2 l = 0 m = 0 s = - 1/2

10. $1s^2 \ 2s^2 \ 2p^3$

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^3$

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6$

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^5 \ 4s^1 \rightarrow$ due to extra stability of d^5 (half filled orbitals).

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^7 \ 4s^2$

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10} \ 4s^2$

11.(a) It should be $1s^2 \ 2s^2 \ 2p^1$ (According to Aufbau principle)

(b) It should be $1s^2 \ 2s^2 \ 2p_x^1 \ 2p_y^1$, (According to Hund's Rule)