

# Chapter Twelve

# ATOMS



## 12.1 INTRODUCTION

By the nineteenth century, enough evidence had accumulated in favour of atomic hypothesis of matter. In 1897, the experiments on electric discharge through gases carried out by the English physicist J. J. Thomson (1856 – 1940) revealed that atoms of different elements contain negatively charged constituents (electrons) that are identical for all atoms. However, atoms on a whole are electrically neutral. Therefore, an atom must also contain some positive charge to neutralise the negative charge of the electrons. But what is the arrangement of the positive charge and the electrons inside the atom? In other words, what is the structure of an atom?

The first model of atom was proposed by J. J. Thomson in 1898. According to this model, the positive charge of the atom is uniformly distributed throughout the volume of the atom and the negatively charged electrons are embedded in it like seeds in a watermelon. This model was picturesquely called *plum pudding model* of the atom. However subsequent studies on atoms, as described in this chapter, showed that the distribution of the electrons and positive charges are very different from that proposed in this model.

We know that condensed matter (solids and liquids) and dense gases at all temperatures emit electromagnetic radiation in which a continuous distribution of several wavelengths is present, though with different intensities. This radiation is considered to be due to oscillations of atoms

and molecules, governed by the interaction of each atom or molecule with its neighbours. *In contrast*, light emitted from rarefied gases heated in a flame, or excited electrically in a glow tube such as the familiar neon sign or mercury vapour light has only certain discrete wavelengths. The spectrum appears as a series of bright lines. In such gases, the average spacing between atoms is large. Hence, the radiation emitted can be considered due to individual atoms rather than because of interactions between atoms or molecules.

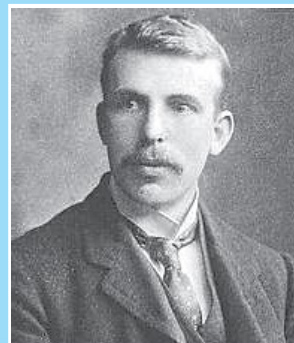
In the early nineteenth century it was also established that each element is associated with a characteristic spectrum of radiation, for example, hydrogen always gives a set of lines with fixed relative position between the lines. This fact suggested an intimate relationship between the internal structure of an atom and the spectrum of radiation emitted by it. In 1885, Johann Jakob Balmer (1825 – 1898) obtained a simple empirical formula which gave the wavelengths of a group of lines emitted by atomic hydrogen. Since hydrogen is simplest of the elements known, we shall consider its spectrum in detail in this chapter.

Ernst Rutherford (1871–1937), a former research student of J. J. Thomson, was engaged in experiments on  $\alpha$ -particles emitted by some radioactive elements. In 1906, he proposed a classic experiment of scattering of these  $\alpha$ -particles by atoms to investigate the atomic structure. This experiment was later performed around 1911 by Hans Geiger (1882–1945) and Ernst Marsden (1889–1970, who was 20 year-old student and had not yet earned his bachelor's degree). The details are discussed in Section 12.2. The explanation of the results led to the birth of Rutherford's planetary model of atom (also called the *nuclear model of the atom*). According to this the entire positive charge and most of the mass of the atom is concentrated in a small volume called the nucleus with electrons revolving around the nucleus just as planets revolve around the sun.

Rutherford's nuclear model was a major step towards how we see the atom today. However, it could not explain why atoms emit light of only discrete wavelengths. How could an atom as simple as hydrogen, consisting of a single electron and a single proton, emit a complex spectrum of specific wavelengths? In the classical picture of an atom, the electron revolves round the nucleus much like the way a planet revolves round the sun. However, we shall see that there are some serious difficulties in accepting such a model.

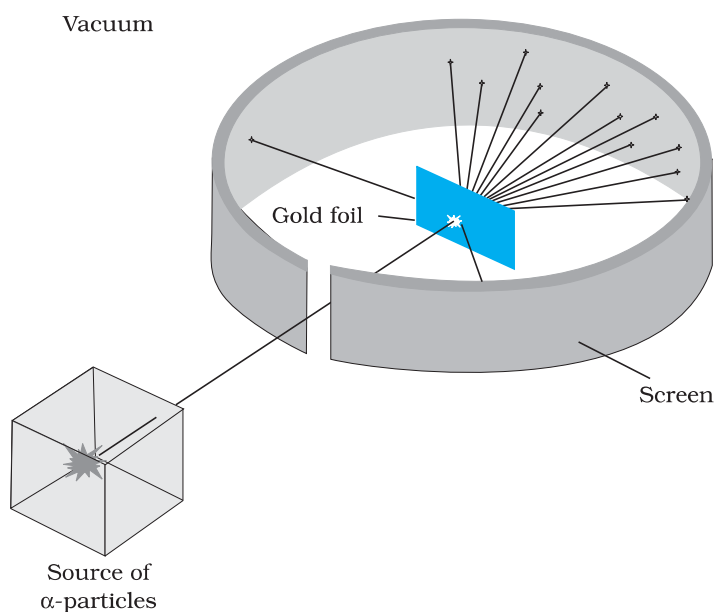
## 12.2 ALPHA-PARTICLE SCATTERING AND RUTHERFORD'S NUCLEAR MODEL OF ATOM

At the suggestion of Ernst Rutherford, in 1911, H. Geiger and E. Marsden performed some experiments. In one of their experiments, as shown in



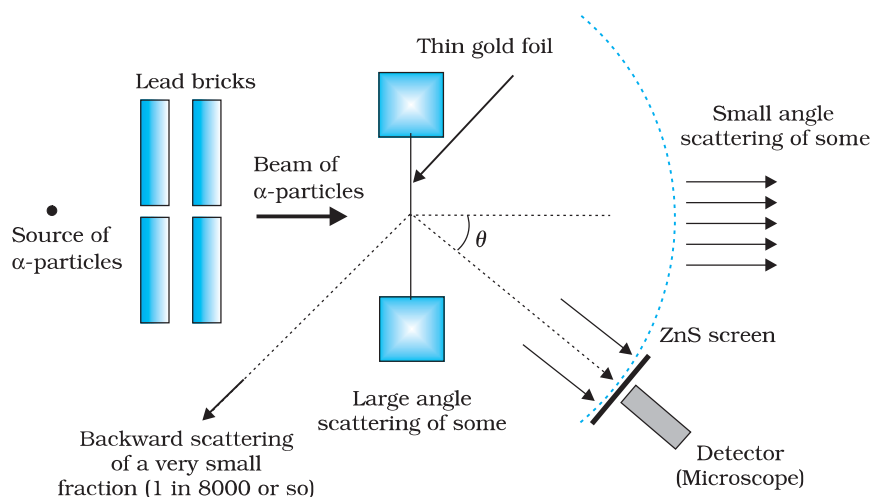
**Ernst Rutherford (1871 – 1937)** British physicist who did pioneering work on radioactive radiation. He discovered alpha-rays and beta-rays. Along with Federick Soddy, he created the modern theory of radioactivity. He studied the 'emanation' of thorium and discovered a new noble gas, an isotope of radon, now known as thoron. By scattering alpha-rays from the metal foils, he discovered the atomic nucleus and proposed the planetary model of the atom. He also estimated the approximate size of the nucleus.

ERNST RUTHERFORD (1871 – 1937)



**FIGURE 12.1** Geiger-Marsden scattering experiment. The entire apparatus is placed in a vacuum chamber (not shown in this figure).

Fig. 12.1, they directed a beam of 5.5 MeV  $\alpha$ -particles emitted from a  $^{214}_{83}\text{Bi}$  radioactive source at a thin metal foil made of gold. Figure 12.2 shows a schematic diagram of this experiment. Alpha-particles emitted by a  $^{214}_{83}\text{Bi}$  radioactive source were collimated into a narrow beam by their passage through lead bricks. The beam was allowed to fall on a thin foil of gold of thickness  $2.1 \times 10^{-7}$  m. The scattered alpha-particles were observed through a rotatable detector consisting of zinc sulphide screen and a microscope. The scattered alpha-particles on striking the screen produced brief light flashes or scintillations. These flashes may be viewed through a microscope and the distribution of the number of scattered particles may be studied as a function of angle of scattering.



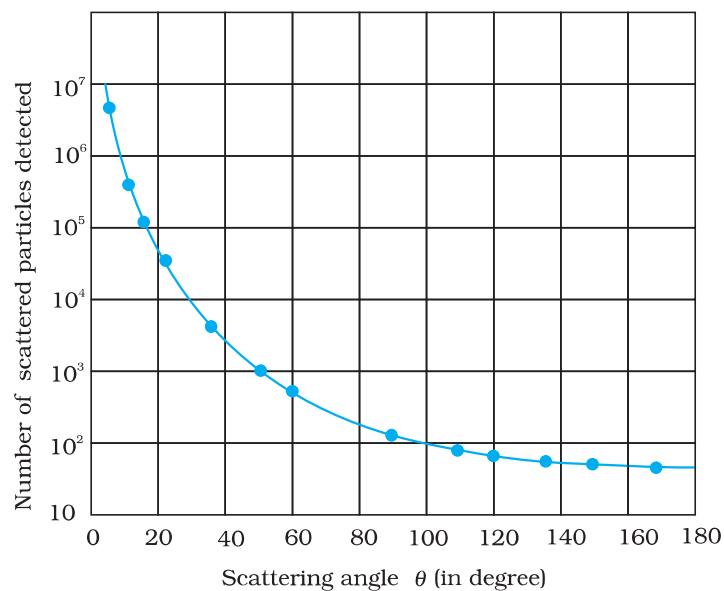
**FIGURE 12.2** Schematic arrangement of the Geiger-Marsden experiment.

A typical graph of the total number of  $\alpha$ -particles scattered at different angles, in a given interval of time, is shown in Fig. 12.3. The dots in this figure represent the data points and the solid curve is the theoretical prediction based on the assumption that the target atom has a small, dense, positively charged nucleus. Many of the  $\alpha$ -particles pass through the foil. It means that they do not suffer any collisions. Only about 0.14% of the incident  $\alpha$ -particles scatter by more than  $1^\circ$ ; and about 1 in 8000 deflect by more than  $90^\circ$ . Rutherford argued that, to deflect the  $\alpha$ -particle backwards, it must experience a large repulsive force. This force could

be provided if the greater part of the mass of the atom and its positive charge were concentrated tightly at its centre. Then the incoming  $\alpha$ -particle could get very close to the positive charge without penetrating it, and such a close encounter would result in a large deflection. This agreement supported the hypothesis of the nuclear atom. This is why Rutherford is credited with the *discovery* of the nucleus.

In Rutherford's nuclear model of the atom, the entire positive charge and most of the mass of the atom are concentrated in the nucleus with the electrons some distance away. The electrons would be moving in orbits about the nucleus just as the planets do around the sun. Rutherford's experiments suggested the size of the nucleus to be about  $10^{-15}$  m to  $10^{-14}$  m. From kinetic theory, the size of an atom was known to be  $10^{-10}$  m, about 10,000 to 100,000 times larger than the size of the nucleus (see Chapter 11, Section 11.6 in Class XI Physics textbook). Thus, the electrons would seem to be at a distance from the nucleus of about 10,000 to 100,000 times the size of the nucleus itself. Thus, most of an atom is empty space. With the atom being largely empty space, it is easy to see why most  $\alpha$ -particles go right through a thin metal foil. However, when  $\alpha$ -particle happens to come near a nucleus, the intense electric field there scatters it through a large angle. The atomic electrons, being so light, do not appreciably affect the  $\alpha$ -particles.

The scattering data shown in Fig. 12.3 can be analysed by employing Rutherford's nuclear model of the atom. As the gold foil is very thin, it can be assumed that  $\alpha$ -particles will suffer not more than one scattering during their passage through it. Therefore, computation of the trajectory of an alpha-particle scattered by a single nucleus is enough. Alpha-particles are nuclei of helium atoms and, therefore, carry two units,  $2e$ , of positive charge and have the mass of the helium atom. The charge of the gold nucleus is  $Ze$ , where  $Z$  is the atomic number of the atom; for gold  $Z = 79$ . Since the nucleus of gold is about 50 times heavier than an  $\alpha$ -particle, it is reasonable to assume that it remains stationary throughout the scattering process. Under these assumptions, the trajectory of an alpha-particle can be computed employing Newton's second law of motion and the Coulomb's law for electrostatic force of repulsion between the alpha-particle and the positively charged nucleus.



**FIGURE 12.3** Experimental data points (shown by dots) on scattering of  $\alpha$ -particles by a thin foil at different angles obtained by Geiger and Marsden using the setup shown in Figs. 12.1 and 12.2. Rutherford's nuclear model predicts the solid curve which is seen to be in good agreement with experiment.

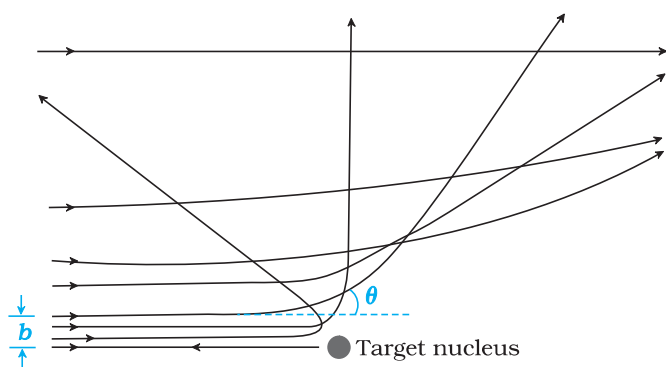
The magnitude of this force is

$$F = \frac{1}{4\pi\epsilon_0} \frac{(2e)(Ze)}{r^2} \quad (12.1)$$

where  $r$  is the distance between the  $\alpha$ -particle and the nucleus. The force is directed along the line joining the  $\alpha$ -particle and the nucleus. The magnitude and direction of the force on an  $\alpha$ -particle continuously changes as it approaches the nucleus and recedes away from it.

### 12.2.1 Alpha-particle trajectory

The trajectory traced by an  $\alpha$ -particle depends on the impact parameter,  $b$  of collision. The *impact parameter* is the perpendicular distance of the initial velocity vector of the  $\alpha$ -particle from the centre of the nucleus (Fig. 12.4).



**FIGURE 12.4** Trajectory of  $\alpha$ -particles in the coulomb field of a target nucleus. The impact parameter,  $b$  and scattering angle  $\theta$  are also depicted.

12.4). A given beam of  $\alpha$ -particles has a distribution of impact parameters  $b$ , so that the beam is scattered in various directions with different probabilities (Fig. 12.4). (In a beam, all particles have nearly same kinetic energy.) It is seen that an  $\alpha$ -particle close to the nucleus (small impact parameter) suffers large scattering. In case of head-on collision, the impact parameter is minimum and the  $\alpha$ -particle rebounds back ( $\theta \cong \pi$ ). For a large impact parameter, the  $\alpha$ -particle goes nearly undeviated and has a small deflection ( $\theta \cong 0$ ).

The fact that only a small fraction of the number of incident particles rebound back indicates that the number of  $\alpha$ -particles undergoing head on collision is small. This,

in turn, implies that the mass of the atom is concentrated in a small volume. Rutherford scattering therefore, is a powerful way to determine an upper limit to the size of the nucleus.

**EXAMPLE 12.1**

**Example 12.1** In the Rutherford's nuclear model of the atom, the nucleus (radius about  $10^{-15}$  m) is analogous to the sun about which the electron move in orbit (radius  $\approx 10^{-10}$  m) like the earth orbits around the sun. If the dimensions of the solar system had the same proportions as those of the atom, would the earth be closer to or farther away from the sun than actually it is? The radius of earth's orbit is about  $1.5 \times 10^{11}$  m. The radius of sun is taken as  $7 \times 10^8$  m.

**Solution** The ratio of the radius of electron's orbit to the radius of nucleus is  $(10^{-10} \text{ m}) / (10^{-15} \text{ m}) = 10^5$ , that is, the radius of the electron's orbit is  $10^5$  times larger than the radius of nucleus. If the radius of the earth's orbit around the sun were  $10^5$  times larger than the radius of the sun, the radius of the earth's orbit would be  $10^5 \times 7 \times 10^8 \text{ m} = 7 \times 10^{13} \text{ m}$ . This is more than 100 times greater than the actual orbital radius of earth. Thus, the earth would be much farther away from the sun.

It implies that an atom contains a much greater fraction of empty space than our solar system does.

**Example 12.2** In a Geiger-Marsden experiment, what is the distance of closest approach to the nucleus of a 7.7 MeV  $\alpha$ -particle before it comes momentarily to rest and reverses its direction?

**Solution** The key idea here is that throughout the scattering process, the total mechanical energy of the system consisting of an  $\alpha$ -particle and a gold nucleus is conserved. The system's initial mechanical energy is  $E_i$ , before the particle and nucleus interact, and it is equal to its mechanical energy  $E_f$  when the  $\alpha$ -particle momentarily stops. The initial energy  $E_i$  is just the kinetic energy  $K$  of the incoming  $\alpha$ -particle. The final energy  $E_f$  is just the electric potential energy  $U$  of the system. The potential energy  $U$  can be calculated from Eq. (12.1).

Let  $d$  be the centre-to-centre distance between the  $\alpha$ -particle and the gold nucleus when the  $\alpha$ -particle is at its stopping point. Then we can write the conservation of energy  $E_i = E_f$  as

$$K = \frac{1}{4\pi\epsilon_0} \frac{(2e)(Ze)}{d} = \frac{2Ze^2}{4\pi\epsilon_0 d}$$

Thus the distance of closest approach  $d$  is given by

$$d = \frac{2Ze^2}{4\pi\epsilon_0 K}$$

The maximum kinetic energy found in  $\alpha$ -particles of natural origin is 7.7 MeV or  $1.2 \times 10^{-12}$  J. Since  $1/4\pi\epsilon_0 = 9.0 \times 10^9$  N m<sup>2</sup>/C<sup>2</sup>. Therefore with  $e = 1.6 \times 10^{-19}$  C, we have,

$$d = \frac{(2)(9.0 \times 10^9 \text{ Nm}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2 Z}{1.2 \times 10^{-12} \text{ J}}$$

$$= 3.84 \times 10^{-16} Z \text{ m}$$

The atomic number of foil material gold is  $Z = 79$ , so that  $d$  (Au) =  $3.0 \times 10^{-14}$  m = 30 fm. (1 fm (i.e. fermi) =  $10^{-15}$  m.)

The radius of gold nucleus is, therefore, less than  $3.0 \times 10^{-14}$  m. This is not in very good agreement with the observed result as the actual radius of gold nucleus is 6 fm. The cause of discrepancy is that the distance of closest approach is considerably larger than the sum of the radii of the gold nucleus and the  $\alpha$ -particle. Thus, the  $\alpha$ -particle reverses its motion without ever actually touching the gold nucleus.



Simulate Rutherford scattering experiment  
[http://www-outreach.phy.cam.ac.uk/camphy/nucleus/nucleus6\\_1.htm](http://www-outreach.phy.cam.ac.uk/camphy/nucleus/nucleus6_1.htm)

EXAMPLE 12.2

### 12.2.2 Electron orbits

The Rutherford nuclear model of the atom which involves classical concepts, pictures the atom as an electrically neutral sphere consisting of a very small, massive and positively charged nucleus at the centre surrounded by the revolving electrons in their respective dynamically stable orbits. The electrostatic force of attraction,  $F_e$  between the revolving electrons and the nucleus provides the requisite centripetal force ( $F_c$ ) to keep them in their orbits. Thus, for a dynamically stable orbit in a hydrogen atom

$$F_e = F_c$$

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \tag{12.2}$$

Thus the relation between the orbit radius and the electron velocity is

$$r = \frac{e^2}{4 \epsilon_0 m v^2} \quad (12.3)$$

The kinetic energy ( $K$ ) and electrostatic potential energy ( $U$ ) of the electron in hydrogen atom are

$$K = \frac{1}{2} m v^2 = \frac{e^2}{8 \epsilon_0 r} \quad \text{and} \quad U = -\frac{e^2}{4 \epsilon_0 r}$$

(The negative sign in  $U$  signifies that the electrostatic force is in the  $-r$  direction.) Thus the total energy  $E$  of the electron in a hydrogen atom is

$$E = K + U = \frac{e^2}{8 \epsilon_0 r} - \frac{e^2}{4 \epsilon_0 r} = -\frac{e^2}{8 \epsilon_0 r} \quad (12.4)$$

The total energy of the electron is negative. This implies the fact that the electron is bound to the nucleus. If  $E$  were positive, an electron will not follow a closed orbit around the nucleus.

**Example 12.3** It is found experimentally that 13.6 eV energy is required to separate a hydrogen atom into a proton and an electron. Compute the orbital radius and the velocity of the electron in a hydrogen atom.

**Solution** Total energy of the electron in hydrogen atom is  $-13.6 \text{ eV} = -13.6 \times 1.6 \times 10^{-19} \text{ J} = -2.2 \times 10^{-18} \text{ J}$ . Thus from Eq. (12.4), we have

$$\frac{e^2}{8 \epsilon_0 r} = 2.2 \times 10^{-18} \text{ J}$$

This gives the orbital radius

$$r = \frac{e^2}{8 \epsilon_0 E} = \frac{(9 \times 10^9 \text{ N m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2}{(2)(-2.2 \times 10^{-18} \text{ J})} = 5.3 \times 10^{-11} \text{ m}.$$

The velocity of the revolving electron can be computed from Eq. (12.3) with  $m = 9.1 \times 10^{-31} \text{ kg}$ ,

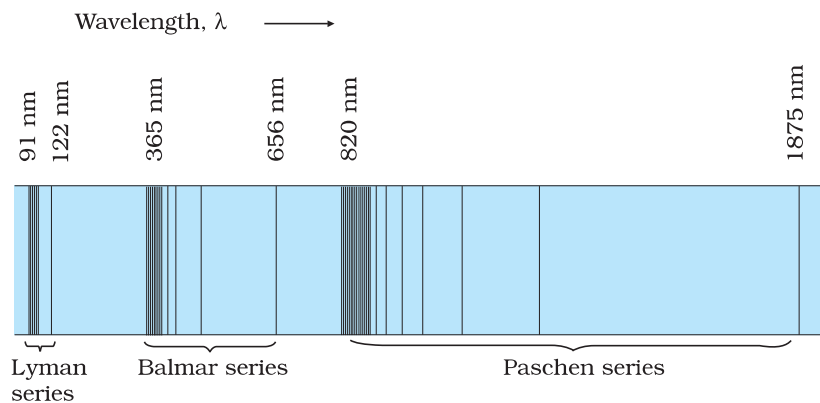
$$v = \frac{e}{\sqrt{4 \epsilon_0 m r}} = 2.2 \times 10^6 \text{ m/s}.$$

## 12.3 ATOMIC SPECTRA

As mentioned in Section 12.1, each element has a characteristic spectrum of radiation, which it emits. When an atomic gas or vapour is excited at low pressure, usually by passing an electric current through it, the emitted radiation has a spectrum which contains certain specific wavelengths only. A spectrum of this kind is termed as emission line spectrum and it

Atoms

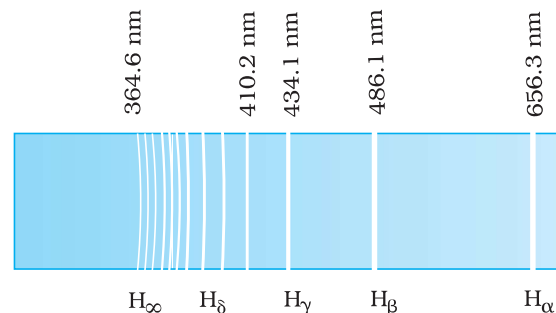
consists of bright lines on a dark background. The spectrum emitted by atomic hydrogen is shown in Fig. 12.5. Study of emission line spectra of a material can therefore serve as a type of “fingerprint” for identification of the gas. When white light passes through a gas and we analyse the transmitted light using a spectrometer we find some dark lines in the spectrum. These dark lines correspond precisely to those wavelengths which were found in the emission line spectrum of the gas. This is called the *absorption spectrum* of the material of the gas.



**FIGURE 12.5** Emission lines in the spectrum of hydrogen.

### 12.3.1 Spectral series

We might expect that the frequencies of the light emitted by a particular element would exhibit some regular pattern. Hydrogen is the simplest atom and therefore, has the simplest spectrum. In the observed spectrum, however, at first sight, there does not seem to be any resemblance of order or regularity in spectral lines. But the spacing between lines within certain sets of the hydrogen spectrum decreases in a regular way (Fig. 12.5). Each of these sets is called a *spectral series*. In 1885, the first such series was observed by a Swedish school teacher Johann Jakob Balmer (1825–1898) in the visible region of the hydrogen spectrum. This series is called *Balmer series* (Fig. 12.6). The line with the longest wavelength, 656.3 nm in the red is called  $H_{\alpha}$ ; the next line with wavelength 486.1 nm in the blue-green is called  $H_{\beta}$ , the third line 434.1 nm in the violet is called  $H_{\gamma}$ ; and so on. As the wavelength decreases, the lines appear closer together and are weaker in intensity. Balmer found a simple empirical formula for the observed wavelengths



**FIGURE 12.6** Balmer series in the emission spectrum of hydrogen.

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (12.5)$$

where  $\lambda$  is the wavelength,  $R$  is a constant called the *Rydberg constant*, and  $n$  may have integral values 3, 4, 5, etc. The value of  $R$  is  $1.097 \times 10^7 \text{ m}^{-1}$ . This equation is also called Balmer formula.

Taking  $n = 3$  in Eq. (12.5), one obtains the wavelength of the  $H_{\alpha}$  line:

$$\begin{aligned} \frac{1}{\lambda} &= 1.097 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \text{ m}^{-1} \\ &= 1.522 \times 10^6 \text{ m}^{-1} \end{aligned}$$

i.e.,  $\lambda = 656.3 \text{ nm}$



For  $n = 4$ , one obtains the wavelength of  $H_{\beta}$  line, etc. For  $n = \infty$ , one obtains the limit of the series, at  $\lambda = 364.6$  nm. This is the shortest wavelength in the Balmer series. Beyond this limit, no further distinct lines appear, instead only a faint continuous spectrum is seen.

Other series of spectra for hydrogen were subsequently discovered. These are known, after their discoverers, as Lyman, Paschen, Brackett, and Pfund series. These are represented by the formulae:

*Lyman series:*

$$\frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots \quad (12.6)$$

*Paschen series:*

$$\frac{1}{\lambda} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots \quad (12.7)$$

*Brackett series:*

$$\frac{1}{\lambda} = R \left( \frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots \quad (12.8)$$

*Pfund series:*

$$\frac{1}{\lambda} = R \left( \frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots \quad (12.9)$$

The Lyman series is in the ultraviolet, and the Paschen and Brackett series are in the infrared region.

The Balmer formula Eq. (12.5) may be written in terms of frequency of the light, recalling that

$$c = v\lambda$$

$$\text{or } \frac{1}{\lambda} = \frac{v}{c}$$

Thus, Eq. (12.5) becomes

$$= R c \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (12.10)$$

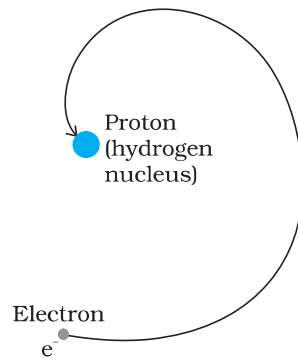
There are only a few elements (hydrogen, singly ionised helium, and doubly ionised lithium) whose spectra can be represented by simple formula like Eqs. (12.5) – (12.9).

Equations (12.5) – (12.9) are useful as they give the wavelengths that hydrogen atoms radiate or absorb. However, these results are empirical and do not give any reasoning why only certain frequencies are observed in the hydrogen spectrum.

## 12.4 BOHR MODEL OF THE HYDROGEN ATOM

The model of the atom proposed by Rutherford assumes that the atom, consisting of a central nucleus and revolving electron is stable much like sun-planet system which the model imitates. However, there are some fundamental differences between the two situations. While the planetary system is held by gravitational force, the nucleus-electron system being charged objects, interact by Coulomb's Law of force. We know that an

object which moves in a circle is being constantly accelerated – the acceleration being centripetal in nature. According to classical electromagnetic theory, an accelerating charged particle emits radiation in the form of electromagnetic waves. The energy of an accelerating electron should therefore, continuously decrease. The electron would spiral inward and eventually fall into the nucleus (Fig. 12.7). Thus, such an atom can not be stable. Further, according to the classical electromagnetic theory, the frequency of the electromagnetic waves emitted by the revolving electrons is equal to the frequency of revolution. As the electrons spiral inwards, their angular velocities and hence their frequencies would change continuously, and so will the frequency of the light emitted. Thus, they would emit a continuous spectrum, in contradiction to the line spectrum actually observed. Clearly Rutherford model tells only a part of the story implying that the classical ideas are not sufficient to explain the atomic structure.



**FIGURE 12.7** An accelerated atomic electron must spiral into the nucleus as it loses energy.



**Niels Henrik David Bohr (1885 – 1962)** Danish physicist who explained the spectrum of hydrogen atom based on quantum ideas. He gave a theory of nuclear fission based on the liquid-drop model of nucleus. Bohr contributed to the clarification of conceptual problems in quantum mechanics, in particular by proposing the complementary principle.

NIELS HENRIK DAVID BOHR (1885 – 1962)

**Example 12.4** According to the classical electromagnetic theory, calculate the initial frequency of the light emitted by the electron revolving around a proton in hydrogen atom.

**Solution** From Example 12.3 we know that velocity of electron moving around a proton in hydrogen atom in an orbit of radius  $5.3 \times 10^{-11}$  m is  $2.2 \times 10^6$  m/s. Thus, the frequency of the electron moving around the proton is

$$\frac{v}{2\pi r} = \frac{2.2 \times 10^6 \text{ m s}^{-1}}{2 \times 5.3 \times 10^{-11} \text{ m}}$$

$$\approx 6.6 \times 10^{15} \text{ Hz.}$$

According to the classical electromagnetic theory we know that the frequency of the electromagnetic waves emitted by the revolving electrons is equal to the frequency of its revolution around the nucleus. Thus the initial frequency of the light emitted is  $6.6 \times 10^{15}$  Hz.

EXAMPLE 12.4

It was Niels Bohr (1885 – 1962) who made certain modifications in this model by adding the ideas of the newly developing quantum hypothesis. Niels Bohr studied in Rutherford’s laboratory for several months in 1912 and he was convinced about the validity of Rutherford nuclear model. Faced with the dilemma as discussed above, Bohr, in 1913, concluded that in spite of the success of electromagnetic theory in explaining large-scale phenomena, it could not be applied to the processes at the atomic scale. It became clear that a fairly radical departure from the established principles of classical mechanics and electromagnetism would be needed to understand the structure of atoms and the relation of atomic structure to atomic spectra. Bohr combined classical and early quantum concepts and gave his theory in the form of three postulates. These are :

(i) Bohr’s first postulate was that *an electron in an atom could revolve in certain stable orbits without the emission of radiant energy*, contrary to the predictions of electromagnetic theory. According to this postulate, each atom has certain definite stable states in which it can exist, and each possible state has definite total energy. These are called the stationary states of the atom.

(ii) Bohr’s second postulate defines these stable orbits. This postulate states that the *electron* revolves around the nucleus *only in those orbits for which the angular momentum is some integral multiple of  $h/2\pi$*  where  $h$  is the Planck’s constant ( $= 6.6 \times 10^{-34}$  J s). Thus the angular momentum ( $L$ ) of the orbiting electron is quantised. That is

$$L = nh/2\pi \tag{12.11}$$

(iii) Bohr’s third postulate incorporated into atomic theory the early quantum concepts that had been developed by Planck and Einstein. It states that *an electron might make a transition from one of its specified non-radiating orbits to another of lower energy. When it does so, a photon is emitted having energy equal to the energy difference between the initial and final states. The frequency of the emitted photon is then given by*

$$h\nu = E_i - E_f \tag{12.12}$$

where  $E_i$  and  $E_f$  are the energies of the initial and final states and  $E_i > E_f$ .

For a hydrogen atom, Eq. (12.4) gives the expression to determine the energies of different energy states. But then this equation requires the radius  $r$  of the electron orbit. To calculate  $r$ , Bohr’s second postulate about the angular momentum of the electron—the quantisation condition – is used. The angular momentum  $L$  is given by

$$L = mvr$$

Bohr’s second postulate of quantisation [Eq. (12.11)] says that the allowed values of angular momentum are integral multiples of  $h/2\pi$ .

$$L_n = mv_n r_n = \frac{nh}{2} \tag{12.13}$$

where  $n$  is an integer,  $r_n$  is the radius of  $n^{\text{th}}$  possible orbit and  $v_n$  is the speed of moving electron in the  $n^{\text{th}}$  orbit. The allowed orbits are numbered

1, 2, 3 ..., according to the values of  $n$ , which is called the *principal quantum number* of the orbit.

From Eq. (12.3), the relation between  $v_n$  and  $r_n$  is

$$v_n = \frac{e}{\sqrt{4\pi m r_n}}$$

Combining it with Eq. (12.13), we get the following expressions for  $v_n$  and  $r_n$ ,

$$v_n = \frac{1}{n} \frac{e^2}{4\pi \epsilon_0 h/2} \quad (12.14)$$

and

$$r_n = \frac{n^2}{m} \frac{h^2}{2} \frac{4\pi \epsilon_0}{e^2} \quad (12.15)$$

Eq. (12.14) depicts that the orbital speed in the  $n^{\text{th}}$  orbit falls by a factor of  $n$ . Using Eq. (12.15), the size of the innermost orbit ( $n = 1$ ) can be obtained as

$$r_1 = \frac{h^2 \epsilon_0}{m e^2}$$

This is called the *Bohr radius*, represented by the symbol  $a_0$ . Thus,

$$a_0 = \frac{h^2 \epsilon_0}{m e^2} \quad (12.16)$$

Substitution of values of  $h$ ,  $m$ ,  $\epsilon_0$  and  $e$  gives  $a_0 = 5.29 \times 10^{-11}$  m. From Eq. (12.15), it can also be seen that the radii of the orbits increase as  $n^2$ .

The total energy of the electron in the stationary states of the hydrogen atom can be obtained by substituting the value of orbital radius in Eq. (12.4) as

$$E_n = \frac{e^2}{8\pi \epsilon_0} \frac{m}{n^2} \frac{2}{h} \frac{e^2}{4\pi \epsilon_0}$$

or 
$$E_n = \frac{m e^4}{8 n^2 \epsilon_0^2 h^2} \quad (12.17)$$

Substituting values, Eq. (12.17) yields

$$E_n = \frac{2.18 \times 10^{-18}}{n^2} \text{ J} \quad (12.18)$$

Atomic energies are often expressed in electron volts (eV) rather than joules. Since  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ , Eq. (12.18) can be rewritten as

$$E_n = \frac{13.6}{n^2} \text{ eV} \quad (12.19)$$

The negative sign of the total energy of an electron moving in an orbit means that the electron is bound with the nucleus. Energy will thus be required to remove the electron from the hydrogen atom to a distance infinitely far away from its nucleus (or proton in hydrogen atom).

The derivation of Eqs. (12.17) – (12.19) involves the assumption that the electronic orbits are circular, though orbits under inverse square force are, in general elliptical. (Planets move in elliptical orbits under the inverse square gravitational force of the sun.) However, it was shown by the German physicist Arnold Sommerfeld (1868 – 1951) that, when the restriction of circular orbit is relaxed, these equations continue to hold even for elliptic orbits.

### ORBIT VS STATE (ORBITAL PICTURE) OF ELECTRON IN ATOM

We are introduced to the Bohr Model of atom one time or the other in the course of physics. This model has its place in the history of quantum mechanics and particularly in explaining the structure of an atom. It has become a milestone since Bohr introduced the revolutionary idea of definite energy orbits for the electrons, contrary to the classical picture requiring an accelerating particle to radiate. Bohr also introduced the idea of quantisation of angular momentum of electrons moving in definite orbits. Thus it was a semi-classical picture of the structure of atom.

Now with the development of quantum mechanics, we have a better understanding of the structure of atom. Solutions of the Schrödinger wave equation assign a wave-like description to the electrons bound in an atom due to attractive forces of the protons.

An orbit of the electron in the Bohr model is the circular path of motion of an electron around the nucleus. But according to quantum mechanics, we cannot associate a definite path with the motion of the electrons in an atom. We can only talk about the probability of finding an electron in a certain region of space around the nucleus. This probability can be inferred from the one-electron wave function called the *orbital*. This function depends only on the coordinates of the electron.

It is therefore essential that we understand the subtle differences that exist in the two models:

- Bohr model is valid for only one-electron atoms/ions; an energy value, assigned to each orbit, depends on the principal quantum number  $n$  in this model. We know that energy associated with a stationary state of an electron depends on  $n$  only, for one-electron atoms/ions. For a multi-electron atom/ion, this is not true.
- The solution of the Schrödinger wave equation, obtained for hydrogen-like atoms/ions, called the wave function, gives information about the probability of finding an electron in various regions around the nucleus. This *orbital* has no resemblance whatsoever with the *orbit* defined for an electron in the Bohr model.

#### EXAMPLE 12.5

**Example 12.5** A 10 kg satellite circles earth once every 2 h in an orbit having a radius of 8000 km. Assuming that Bohr's angular momentum postulate applies to satellites just as it does to an electron in the hydrogen atom, find the quantum number of the orbit of the satellite.

**Solution**

From Eq. (12.13), we have

$$m v_n r_n = nh/2\pi$$

Here  $m = 10^4 \text{ kg}$  and  $r_n = 8 \times 10^6 \text{ m}$ . We have the time period  $T$  of the circling satellite as 2 h. That is  $T = 7200 \text{ s}$ .

Thus the velocity  $v_n = 2\pi r_n/T$ .

The quantum number of the orbit of satellite

$$n = (2\pi r_n)^2 \times m / (T \times h).$$

Substituting the values,

$$n = (2\pi \times 8 \times 10^6 \text{ m})^2 \times 10^4 / (7200 \text{ s} \times 6.64 \times 10^{-34} \text{ J s}) \\ = 5.3 \times 10^{45}$$

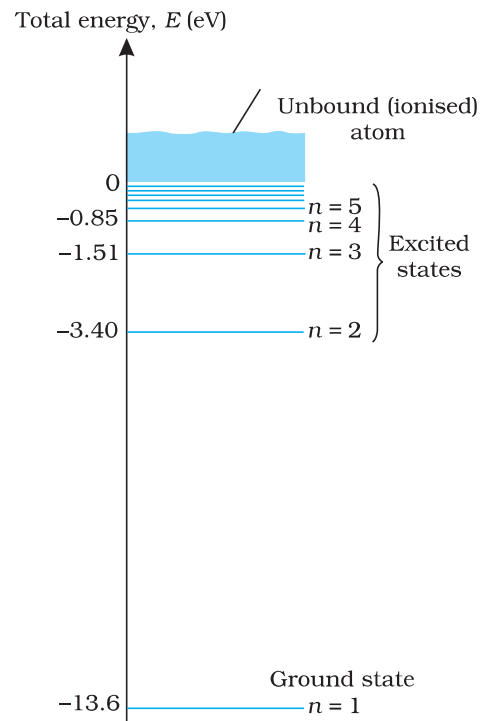
Note that the quantum number for the satellite motion is extremely large! In fact for such large quantum numbers the results of quantisation conditions tend to those of classical physics.

### 12.4.1 Energy levels

The energy of an atom is the *least* (largest negative value) when its electron is revolving in an orbit closest to the nucleus i.e., the one for which  $n = 1$ . For  $n = 2, 3, \dots$  the absolute value of the energy  $E$  is smaller, hence the energy is progressively larger in the outer orbits. The *lowest* state of the atom, called the *ground state*, is that of the lowest energy, with the electron revolving in the orbit of smallest radius, the Bohr radius,  $a_0$ . The energy of this state ( $n = 1$ ),  $E_1$  is  $-13.6 \text{ eV}$ . Therefore, the minimum energy required to free the electron from the ground state of the hydrogen atom is  $13.6 \text{ eV}$ . It is called the *ionisation energy* of the hydrogen atom. This prediction of the Bohr's model is in excellent agreement with the experimental value of ionisation energy.

At room temperature, most of the hydrogen atoms are in *ground state*. When a hydrogen atom receives energy by processes such as electron collisions, the atom may acquire sufficient energy to raise the electron to higher energy states. The atom is then said to be in an *excited state*. From Eq. (12.19), for  $n = 2$ ; the energy  $E_2$  is  $-3.40 \text{ eV}$ . It means that the energy required to excite an electron in hydrogen atom to its first excited state, is an energy equal to  $E_2 - E_1 = -3.40 \text{ eV} - (-13.6 \text{ eV}) = 10.2 \text{ eV}$ . Similarly,  $E_3 = -1.51 \text{ eV}$  and  $E_3 - E_1 = 12.09 \text{ eV}$ , or to excite the hydrogen atom from its ground state ( $n = 1$ ) to second excited state ( $n = 3$ ),  $12.09 \text{ eV}$  energy is required, and so on. From these excited states the electron can then fall back to a state of lower energy, emitting a photon in the process. Thus, as the excitation of hydrogen atom increases (that is as  $n$  increases) the value of minimum energy required to free the electron from the excited atom decreases.

The energy level diagram\* for the stationary states of a hydrogen atom, computed from Eq. (12.19), is given in



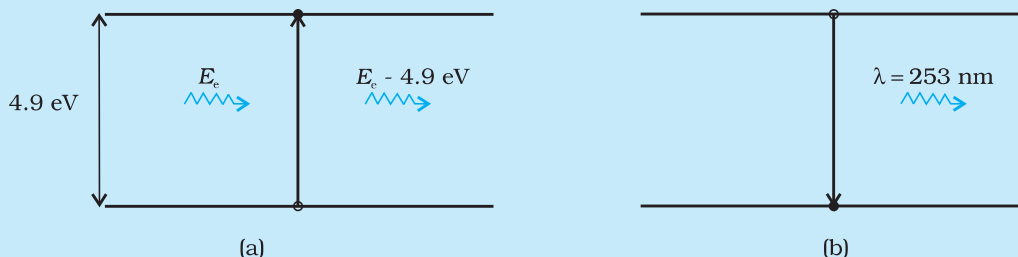
**FIGURE 12.8** The energy level diagram for the hydrogen atom. The electron in a hydrogen atom at room temperature spends most of its time in the ground state. To ionise a hydrogen atom an electron from the ground state,  $13.6 \text{ eV}$  of energy must be supplied. (The horizontal lines specify the presence of allowed energy states.)

\* An electron can have any total energy above  $E = 0 \text{ eV}$ . In such situations the electron is free. Thus there is a continuum of energy states above  $E = 0 \text{ eV}$ , as shown in Fig. 12.8.

Fig. 12.8. The principal quantum number  $n$  labels the stationary states in the ascending order of energy. In this diagram, the highest energy state corresponds to  $n = \infty$  in Eq. (12.19) and has an energy of 0 eV. This is the energy of the atom when the electron is completely removed ( $r = \infty$ ) from the nucleus and is at rest. Observe how the energies of the excited states come closer and closer together as  $n$  increases.

### FRANCK – HERTZ EXPERIMENT

The existence of discrete energy levels in an atom was directly verified in 1914 by James Franck and Gustav Hertz. They studied the spectrum of mercury vapour when electrons having different kinetic energies passed through the vapour. The electron energy was varied by subjecting the electrons to electric fields of varying strength. The electrons collide with the mercury atoms and can transfer energy to the mercury atoms. This can only happen when the energy of the electron is higher than the energy difference between an energy level of Hg occupied by an electron and a higher unoccupied level (see Figure). For instance, the difference between an occupied energy level of Hg and a higher unoccupied level is 4.9 eV. If an electron of having an energy of 4.9 eV or more passes through mercury, an electron in mercury atom can absorb energy from the bombarding electron and get excited to the higher level [Fig (a)]. The colliding electron's kinetic energy would reduce by this amount.



The excited electron would subsequently fall back to the ground state by emission of radiation [Fig. (b)]. The wavelength of emitted radiation is:

$$\frac{hc}{E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4.9 \times 1.6 \times 10^{-19}} = 253 \text{ nm}$$

By direct measurement, Franck and Hertz found that the emission spectrum of mercury has a line corresponding to this wavelength. For this experimental verification of Bohr's basic ideas of discrete energy levels in atoms and the process of photon emission, Frank and Hertz were awarded the Nobel prize in 1925.

## 12.5 THE LINE SPECTRA OF THE HYDROGEN ATOM

According to the third postulate of Bohr's model, when an atom makes a transition from the higher energy state with quantum number  $n_i$  to the lower energy state with quantum number  $n_f$  ( $n_f < n_i$ ), the difference of energy is carried away by a photon of frequency  $\nu_{if}$  such that

$$h\nu_{if} = E_{n_i} - E_{n_f} \quad (12.20)$$

Using Eq. (12.16), for  $E_{n_f}$  and  $E_{n_i}$ , we get

$$h\nu_{if} = \frac{me^4}{8 \cdot 0^2 h^2} \frac{1}{n_f^2} - \frac{1}{n_i^2} \quad (12.21)$$

$$\text{or } \nu_{if} = \frac{me^4}{8 \cdot 0^2 h^3} \frac{1}{n_f^2} - \frac{1}{n_i^2} \quad (12.22)$$

Equation (12.21) is the Rydberg formula, for the spectrum of the hydrogen atom. In this relation, if we take  $n_f = 2$  and  $n_i = 3, 4, 5, \dots$ , it reduces to a form similar to Eq. (12.10) for the Balmer series. The Rydberg constant  $R$  is readily identified to be

$$R = \frac{me^4}{8 \cdot 0^2 h^3 c} \quad (12.23)$$

If we insert the values of various constants in Eq. (12.23), we get

$$R = 1.03 \times 10^7 \text{ m}^{-1}$$

This is a value very close to the value ( $1.097 \times 10^7 \text{ m}^{-1}$ ) obtained from the empirical Balmer formula. This agreement between the theoretical and experimental values of the Rydberg constant provided a direct and striking confirmation of the Bohr's model.

Since both  $n_f$  and  $n_i$  are integers, this immediately shows that in transitions between different atomic levels, light is radiated in various discrete frequencies. For hydrogen spectrum, the Balmer formula corresponds to  $n_f = 2$  and  $n_i = 3, 4, 5, \dots$ , etc. The results of the Bohr's model suggested the presence of other series spectra for hydrogen atom—those corresponding to transitions resulting from  $n_f = 1$  and  $n_i = 2, 3, \dots$ ;  $n_f = 3$  and  $n_i = 4, 5, \dots$ , and so on. Such series were identified in the course of spectroscopic investigations and are known as the Lyman, Balmer, Paschen, Brackett, and Pfund series. The electronic transitions corresponding to these series are shown in Fig. 12.9.

The various lines in the atomic spectra are produced when electrons jump from higher energy state to a lower energy state and photons are emitted. These spectral lines are called emission lines. But when an atom absorbs a photon that has precisely

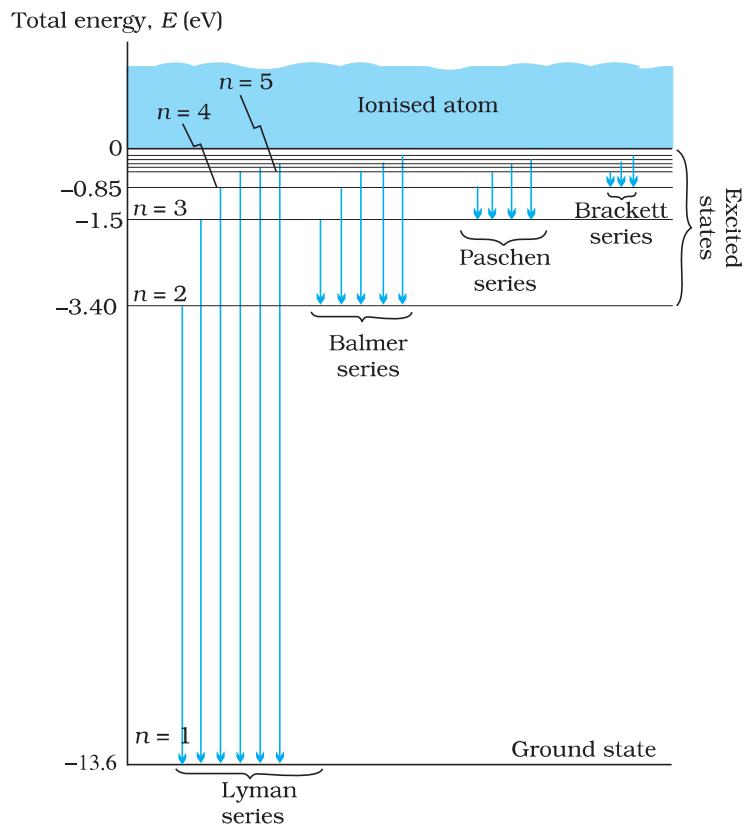


FIGURE 12.9 Line spectra originate in transitions between energy levels.



the same energy needed by the electron in a lower energy state to make transitions to a higher energy state, the process is called absorption. Thus if photons with a continuous range of frequencies pass through a rarefied gas and then are analysed with a spectrometer, a series of dark spectral absorption lines appear in the continuous spectrum. The dark lines indicate the frequencies that have been absorbed by the atoms of the gas.

The explanation of the hydrogen atom spectrum provided by Bohr's model was a brilliant achievement, which greatly stimulated progress towards the modern quantum theory. In 1922, Bohr was awarded Nobel Prize in Physics.

**Example 12.6** Using the Rydberg formula, calculate the wavelengths of the first four spectral lines in the Lyman series of the hydrogen spectrum.

**Solution** The Rydberg formula is

$$hc/\lambda_{if} = \frac{me^4}{8^2 h^2} \frac{1}{n_f^2} - \frac{1}{n_i^2}$$

The wavelengths of the first four lines in the Lyman series correspond to transitions from  $n_i = 2, 3, 4, 5$  to  $n_f = 1$ . We know that

$$\frac{me^4}{8^2 h^2} = 13.6 \text{ eV} = 21.76 \times 10^{-19} \text{ J}$$

Therefore,

$$\begin{aligned} \lambda &= \frac{hc}{21.76 \times 10^{-19} \left( \frac{1}{1} - \frac{1}{n_i^2} \right)} \text{ m} \\ &= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times n_i^2}{21.76 \times 10^{-19} (n_i^2 - 1)} \text{ m} = \frac{0.9134 \times n_i^2}{(n_i^2 - 1)} \times 10^{-7} \text{ m} \\ &= 913.4 \times n_i^2 / (n_i^2 - 1) \text{ \AA} \end{aligned}$$

Substituting  $n_i = 2, 3, 4, 5$ , we get  $\lambda_{21} = 1218 \text{ \AA}$ ,  $\lambda_{31} = 1028 \text{ \AA}$ ,  $\lambda_{41} = 974.3 \text{ \AA}$ , and  $\lambda_{51} = 951.4 \text{ \AA}$ .

EXAMPLE 12.6

## 12.6 DE BROGLIE'S EXPLANATION OF BOHR'S SECOND POSTULATE OF QUANTISATION

Of all the postulates, Bohr made in his model of the atom, perhaps the most puzzling is his second postulate. It states that the angular momentum of the electron orbiting around the nucleus is quantised (that is,  $L_n = nh/2\pi$ ;  $n = 1, 2, 3 \dots$ ). Why should the angular momentum have only those values that are integral multiples of  $h/2\pi$ ? The French physicist Louis de Broglie explained this puzzle in 1923, ten years after Bohr proposed his model.

We studied, in Chapter 11, about the de Broglie's hypothesis that material particles, such as electrons, also have a wave nature. C. J. Davisson and L. H. Germer later experimentally verified the wave nature of electrons

in 1927. Louis de Broglie argued that the electron in its circular orbit, as proposed by Bohr, must be seen as a particle wave. In analogy to waves travelling on a string, particle waves too can lead to standing waves under resonant conditions. From Chapter 15 of Class XI Physics textbook, we know that when a string is plucked, a vast number of wavelengths are excited. However only those wavelengths survive which have nodes at the ends and form the standing wave in the string. It means that in a string, standing waves are formed when the total distance travelled by a wave down the string and back is one wavelength, two wavelengths, or any integral number of wavelengths. Waves with other wavelengths interfere with themselves upon reflection and their amplitudes quickly drop to zero. For an electron moving in  $n^{\text{th}}$  circular orbit of radius  $r_n$ , the total distance is the circumference of the orbit,  $2\pi r_n$ . Thus

$$2\pi r_n = n\lambda, \quad n = 1, 2, 3... \quad (12.24)$$

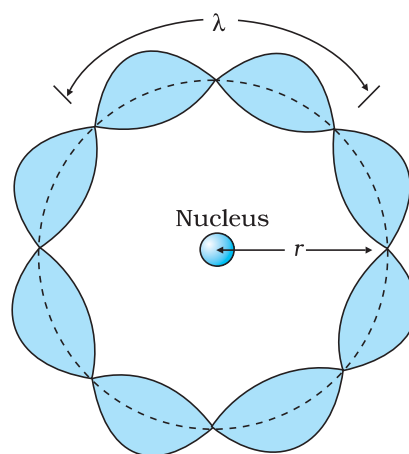
Figure 12.10 illustrates a standing particle wave on a circular orbit for  $n = 4$ , i.e.,  $2\pi r_n = 4\lambda$ , where  $\lambda$  is the de Broglie wavelength of the electron moving in  $n^{\text{th}}$  orbit. From Chapter 11, we have  $\lambda = h/p$ , where  $p$  is the magnitude of the electron's momentum. If the speed of the electron is much less than the speed of light, the momentum is  $mv_n$ . Thus,  $\lambda = h/mv_n$ . From Eq. (12.24), we have

$$2\pi r_n = n h/mv_n \quad \text{or} \quad m v_n r_n = nh/2\pi$$

This is the quantum condition proposed by Bohr for the angular momentum of the electron [Eq. (12.13)]. In Section 12.5, we saw that this equation is the basis of explaining the discrete orbits and energy levels in hydrogen atom. Thus de Broglie hypothesis provided an explanation for Bohr's second postulate for the quantisation of angular momentum of the orbiting electron. The quantised electron orbits and energy states are due to the wave nature of the electron and only resonant standing waves can persist.

Bohr's model, involving classical trajectory picture (planet-like electron orbiting the nucleus), correctly predicts the gross features of the hydrogenic atoms\*, in particular, the frequencies of the radiation emitted or selectively absorbed. This model however has many limitations. Some are:

- (i) The Bohr model is applicable to hydrogenic atoms. It cannot be extended even to mere two electron atoms such as helium. The analysis of atoms with more than one electron was attempted on the lines of Bohr's model for hydrogenic atoms but did not meet with any success. Difficulty lies in the fact that each electron interacts not only with the positively charged nucleus but also with all other electrons.



**FIGURE 12.10** A standing wave is shown on a circular orbit where four de Broglie wavelengths fit into the circumference of the orbit.

\* Hydrogenic atoms are the atoms consisting of a nucleus with positive charge  $+Ze$  and a single electron, where  $Z$  is the proton number. Examples are hydrogen atom, singly ionised helium, doubly ionised lithium, and so forth. In these atoms more complex electron-electron interactions are nonexistent.

The formulation of Bohr model involves electrical force between positively charged nucleus and electron. It does not include the electrical forces between electrons which necessarily appear in multi-electron atoms.

- (ii) While the Bohr's model correctly predicts the frequencies of the light emitted by hydrogenic atoms, the model is unable to explain the relative intensities of the frequencies in the spectrum. In emission spectrum of hydrogen, some of the visible frequencies have weak intensity, others strong. Why? Experimental observations depict that some transitions are more favoured than others. Bohr's model is unable to account for the intensity variations.

Bohr's model presents an elegant picture of an atom and cannot be generalised to complex atoms. For complex atoms we have to use a new and radical theory based on Quantum Mechanics, which provides a more complete picture of the atomic structure.

## LASER LIGHT

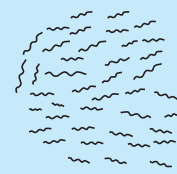
Imagine a crowded market place or a railway platform with people entering a gate and going towards all directions. Their footsteps are random and there is no phase correlation between them. On the other hand, think of a large number of soldiers in a regulated march. Their footsteps are very well correlated. See figure here.

This is similar to the difference between light emitted by an ordinary source like a candle or a bulb and that emitted by a laser. The acronym LASER stands for Light Amplification by Stimulated Emission of Radiation. Since its development in 1960, it has entered into all areas of science and technology. It has found applications in physics, chemistry, biology, medicine, surgery, engineering, etc. There are low power lasers, with a power of 0.5 mW, called pencil lasers, which serve as pointers. There are also lasers of different power, suitable for delicate surgery of eye or glands in the stomach. Finally, there are lasers which can cut or weld steel.

Light is emitted from a source in the form of packets of waves. Light coming out from an ordinary source contains a mixture of many wavelengths. There is also no phase relation between the various waves. Therefore, such light, even if it is passed through an aperture, spreads very fast and the beam size increases rapidly with distance. In the case of laser light, the wavelength of each packet is almost the same. Also the average length of the packet of waves is much larger. This means that there is better phase correlation over a longer duration of time. This results in reducing the divergence of a laser beam substantially.

If there are  $N$  atoms in a source, each emitting light with intensity  $I$ , then the total intensity produced by an ordinary source is proportional to  $NI$ , whereas in a laser source, it is proportional to  $N^2I$ . Considering that  $N$  is very large, we see that the light from a laser can be much stronger than that from an ordinary source.

When astronauts of the Apollo missions visited the moon, they placed a mirror on its surface, facing the earth. Then scientists on the earth sent a strong laser beam, which was reflected by the mirror on the moon and received back on the earth. The size of the reflected laser beam and the time taken for the round trip were measured. This allowed a very accurate determination of (a) the extremely small divergence of a laser beam and (b) the distance of the moon from the earth.



(a) Light from a bulb



(b) Laser light